

Removal of lead from aqueous solution using *Syzygium cumini* L.: Equilibrium and kinetic studies

P. King*, N. Rakesh, S. Beenalahari, Y. Prasanna Kumar, V.S.R.K. Prasad

Environmental Pollution Control Engineering Laboratory, Department of Chemical Engineering, A.U. College of Engineering,
Andhra University, Visakhapatnam 530 003, India

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Abstract

The biosorption of lead ions from aqueous solution by *Syzygium cumini* L. was studied in a batch adsorption system as a function of pH, contact time, lead ion concentration, adsorbent concentration and adsorbent size. The biosorption capacities and rates of lead ions onto *S. cumini* L. were evaluated. The Langmuir, Freundlich, Redlich–Peterson and Temkin adsorption models were applied to describe the isotherms and isotherm constants. Biosorption isothermal data could be well interpreted by the Langmuir model followed by Temkin model with maximum adsorption capacity of 32.47 mg/g of lead ion on *S. cumini* L. leaves biomass. The kinetic experimental data were properly correlated with the second-order kinetic model. © 2006 Elsevier B.V. All rights reserved.

Keywords: *Syzygium cumini* L.; Adsorption; Adsorption isotherm; Kinetic studies

1. Introduction

The removal of toxic metal ions and recovery of valuable ions from mine wastewaters, soils and waters have been important in economic and environmental problems [1–4]. Heavy metals and other metal ions exist as contaminants in aqueous waste streams of many industries, such as tanneries and mining. Some metals associated with these activities are Pb, Hg, Cr and Cd. Some of these metals are accumulated in living organisms and produce diseases and disorders.

Heavy metals such as lead, mercury, arsenic, copper, zinc and cadmium are highly toxic when adsorbed into the body [5]. They can cause accumulative poisoning, cancer, brain damage, etc. Lead is a general metabolic poison and enzyme inhibitor. It can cause mental retardation and semi permanent brain damage in young children [6]. Lead has the ability to replace calcium in the bone to form sites for long-term release. Toxic metals are released into the environment in a number of ways. Coal combustion, sewage wastewaters, automobile emissions, battery industry, mining activities, and the utilization of fossil fuels are just a few examples [7]. Among the various water-treatment

techniques described, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness [8].

Earlier studies demonstrated that the living systems had been often unreliable because there were many problems to maintain active microbial populations under highly variable conditions of wastewaters [9]. Therefore, some types of biomass served as biosorbents to remove heavy metals [9–11]. Biosorption, a term that describes the removal of heavy metals by the passive binding to non-living biomass from an aqueous solution [12], is considered as an alternative to conventional methods of metal recovery from solutions [13]. Although freely suspended biomass may have better contact with adsorbates during biosorption process, the suspended biomass is normally not the practical form for the direct use in the removal of heavy metals. Since cell immobilization can enhance its stability, mechanical strength, reusability and the ease of treatment, the technique has been well used to remove toxic heavy metals [9,14–16]. Usually a fixed bed reactor, in which a certain type of immobilized biomass is packed, is designed for effective and continuous removal of heavy metals [9,16–19].

The effectiveness of biosorption for the removal of heavy metals has been shown in a number of studies. However, only when the cost of the biosorption process can complete with the

* Corresponding author. Tel.: +91 891 2844894.
E-mail address: p.king@rediffmail.com (P. King).

existing technologies will it be accepted commercially. Kuyucak indicated that the cost of biomass production played an important role in determining the overall cost of a biosorption process [20]. Therefore, low cost biomass becomes a crucial factor when considering practical application of biosorption.

The present work investigates the potential use of untreated *Syzygium cumini* L. biomass as metal sorbent for removal of lead from aqueous solution. *S. cumini* L. was chosen as a biosorbent because of the relative lack of information about its sorption ability. Environmental parameters affecting the biosorption process such as pH, contact time, metal ion concentration, adsorbent concentration and adsorbent size were evaluated. The equilibrium adsorption data were evaluated by Langmuir, Freundlich, Redlich–Peterson and Temkin isotherm models.

2. Materials and methods

2.1. Preparation of biosorbent

The green *S. cumini* L. leaves were collected from Andhra University College of Engineering campus of Visakhapatnam, Andhra Pradesh, India. Leaves were washed with deionized water several times to remove dirt particles. The dried leaves of 75–212 μm particle size were used as biosorbent without any pretreatment for lead adsorption.

2.2. Chemical

Analytical grades of $\text{Pb}(\text{NO}_3)_2$, HCl and NaOH were purchased from Merck, India. Lead ions were prepared by dissolving its corresponding nitrate salt in distilled water. The pH of solutions was adjusted with 0.1N HCl and NaOH.

All the experiments were repeated five times and the average values have been reported. Also, blank experiments were conducted to ensure that no adsorption was taking place on the walls of the apparatus used.

2.3. Biosorption experiments

Biosorption experiments were performed at room temperature ($30 \pm 1^\circ\text{C}$) in a rotary shaker at 180 rpm using 250 mL Erlenmeyer flasks containing 30 mL of different lead concentrations. After 1 h of contact (according to the preliminary sorption dynamics tests), with 0.1 g *S. cumini* L. leaves biomass, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The metal content in the supernatant was determined using Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) after filtering the adsorbent with 0.45 μm filter paper. The amount of metal adsorbed by *S. cumini* L. leaves was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$q = (C_0 - C_f) \frac{V}{M} \quad (1)$$

where q is the metal uptake (mg/g); C_0 and C_f the initial and final metal concentrations in the solution (mg/L), respectively;

V the solution volume (mL); M is the mass of biosorbent (g). The pH of the solution was adjusted by using 0.1N HCl and 0.1N NaOH.

The Langmuir [21] sorption model was chosen for the estimation of maximum lead sorption by the biosorbent. The Langmuir isotherm can be expressed as

$$q = \frac{Q_{\max} b C_{\text{eq}}}{1 + b C_{\text{eq}}} \quad (2)$$

where Q_{\max} indicates the monolayer adsorption capacity of adsorbent (mg/g) and the Langmuir constant b (L/mg) is related to the energy of adsorption. For fitting the experimental data, the Langmuir model was linearized as

$$\frac{1}{q} = \frac{1}{Q_{\max}} + \frac{1}{b Q_{\max} C_{\text{eq}}} \quad (3)$$

The Freundlich [22] model is represented by the equation:

$$q = K C_{\text{eq}}^{1/n} \quad (4)$$

where K (mg/g) is the Freundlich constant related to adsorption capacity of adsorbent and $1/n$ is the Freundlich exponent related to adsorption intensity (dimensionless). For fitting the experimental data, the Freundlich model was linearized as follows:

$$\ln q = \ln K + \frac{1}{n} \ln C_{\text{eq}} \quad (5)$$

The Redlich–Peterson [23] model is represented by the equation:

$$q = \frac{A C_{\text{eq}}}{1 + B C_{\text{eq}}^g} \quad (6)$$

where A (L/g) and B (L/mg) are the Redlich–Peterson isotherm constants and g is the Redlich–Peterson isotherm exponent, which lies between 0 and 1. The linearized form of equation is given by

$$\ln \left(\frac{A C_{\text{eq}}}{q} - 1 \right) = g \ln(C_{\text{eq}}) + \ln(B) \quad (7)$$

Redlich–Peterson isotherm equation contains three unknown parameters A , B , and g . Therefore a minimization procedure is adopted to maximize the coefficient of determination, between the theoretical data for q predicted from the linearized form of Redlich–Peterson isotherm equation and the experimental data.

The Temkin [24] isotherm has generally been applied in the following form:

$$q = \frac{RT}{b_T} \ln(A_T C_{\text{eq}}) \quad (8)$$

where A_T (L/mg) and b_T are Temkin isotherm constants.

2.4. Biosorption kinetics

The kinetics studies were carried out by conducting batch biosorption experiments with different initial lead concentrations. Samples were taken at different time periods and analyzed for their lead concentration.

3. Results and discussion

3.1. The effect of contact time

The data obtained from the biosorption of lead ions on the *S. cumini* L. showed that a contact time of 10 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. Therefore, the uptake and unadsorbed lead concentrations at the end of 10 min are given as the equilibrium values (q_{eq} , mg/g; C_{eq} , mg/L), respectively (Fig. 1).

3.2. Effect of pH

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the biomass cell walls, so pH is an important parameter on biosorption of metal ions from aqueous solutions [25–29].

S. cumini L. presents a high content of ionizable groups (carboxyl groups from mannuronic and gluronic acids) on the cell wall polysaccharides, which makes it, very liable to the influence of the pH. As shown in Fig. 2, the uptake of lead increased with the increase in pH from 2.0 to 6.0. Similar results were also reported in literature for different biomass systems [30–33]. At pH values lower than 2.0 lead removal was inhibited, possibly as a result of the competition between hydrogen and lead ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligands such as carboxylate groups in *S. cumini* L. would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface.

In this study, these lead cations at around 6 would be expected to interact more strongly with the negatively charged binding sites in the adsorbent. As a result, the optimum pH for lead adsorption was found as 6 and the other adsorption experiments were performed at this pH value.

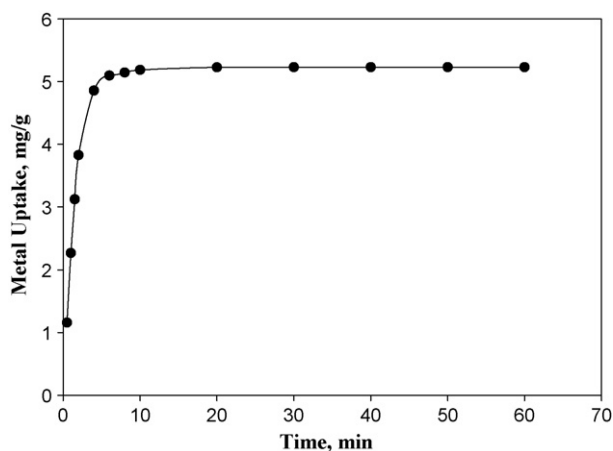


Fig. 1. Effect of contact time on lead uptake by *Syzygium cumini* L. for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentrations.

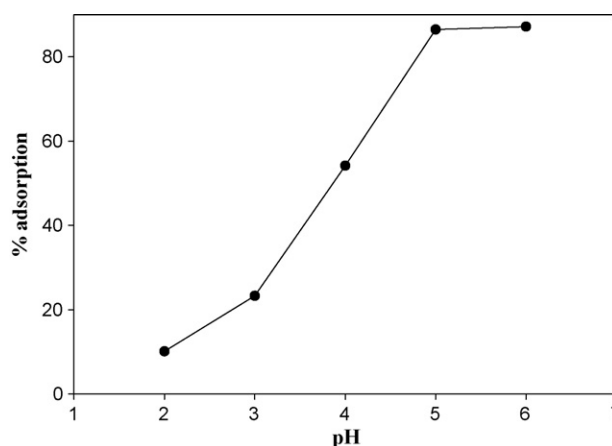


Fig. 2. Effect of pH on lead adsorption by *S. cumini* L. for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentration.

3.3. Effect of metal ion concentration

Fig. 3 shows the effect of metal ion concentration on the adsorption of lead by *S. cumini* L. The data shows that the metal uptake increases and the percentage adsorption of lead decreases with increase in metal ion concentration. This increase (5.23–21.77 mg/g) is a result of increase in the driving forces, i.e. concentration gradient. However, the percentage adsorption of lead ions on *S. cumini* L. was decreased from 87.18 to 72.57%. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of lead displays an opposite trend. At lower concentrations, all lead ions present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher lead ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

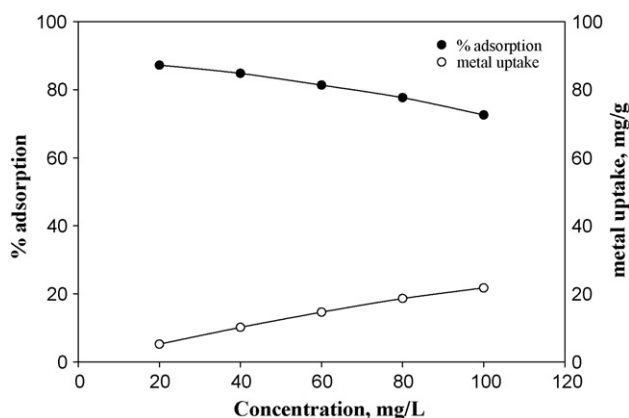


Fig. 3. Effect of metal concentration on the adsorption of lead by *S. cumini* L. at 0.1 g/30 mL of adsorbent concentration.

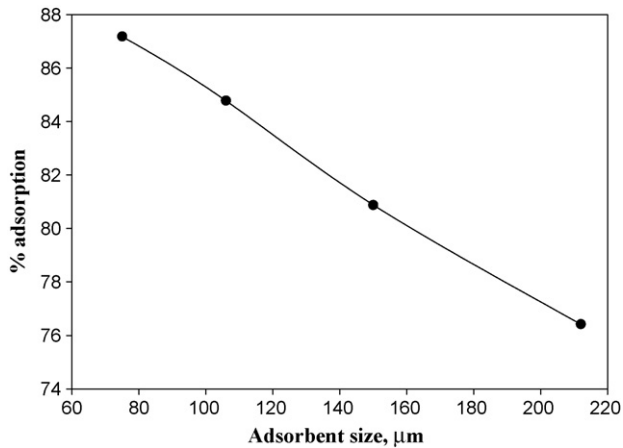


Fig. 4. Effect of *S. cumini* L. particle size on adsorption of lead for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentration.

3.4. Effect of adsorbent size

The effect of different adsorbent particle sizes on percentage removal of lead is investigated and showed in Fig. 4. It reveals that the adsorption of lead on *S. cumini* L. decreased from 87.18 to 76.42% with the increased particle size from 75 to 212 μm at an initial concentration of 20 mg/L. The smallest size obtained was 75 μm due to the limitation of available grinder configuration. It is well known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity.

3.5. Effect of adsorbent dosage

Fig. 5 shows the effect of adsorbent dosage on the % removed at equilibrium conditions. It was observed that the amount of lead adsorbed varied with varying adsorbent dosage. The amount of lead adsorbed increases with an increase in adsorbent dosage from 0.1 to 0.5 g. The percentage of lead removal was increased from 87.18 to 98.03% for an increase in biomass

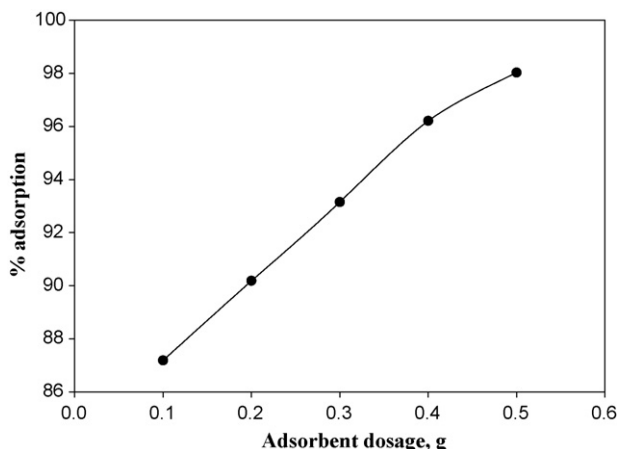


Fig. 5. Effect of *S. cumini* L. dosage on adsorption of lead for 20 mg/L of metal concentration.

dosage from 0.1 to 0.5 g at an initial concentration of 20 mg/L. The increase in the adsorption of the amount of solute is obvious due to increasing biomass surface area. Similar trend was also observed for lead removal using *Azadirachta indica* as adsorbent [34].

4. Biosorption equilibrium

The equilibrium biosorption of lead on the *S. cumini* L. as a function of the initial concentration of lead is shown in Figs. 6–10. There was a gradual increase of adsorption for lead ions until equilibrium was attained. The Langmuir, Freundlich models are often used to describe equilibrium sorption isotherms and Redlich–Peterson and Temkin models are also applied to describe equilibrium sorption isotherms. The calculated results of the Langmuir, Freundlich, Redlich–Peterson and Temkin isotherm constants are given in Table 1.

It is found that the adsorption of lead on the *S. cumini* L. was correlated well with the Langmuir equation and Temkin equation as compared to Freundlich and Redlich–Peterson equa-

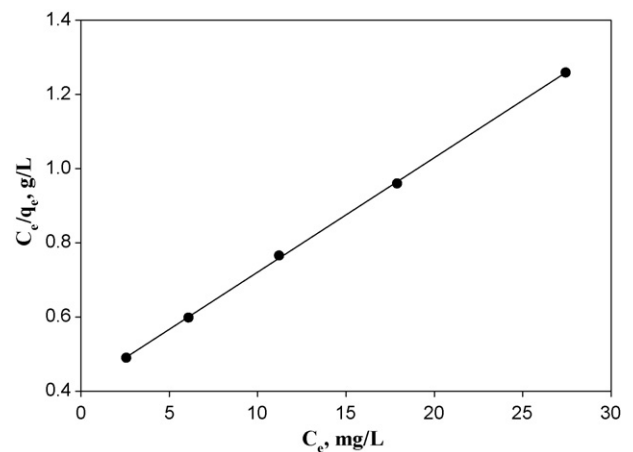


Fig. 6. Langmuir adsorption isotherm for lead at 0.1 g/30 mL of adsorbent concentration.

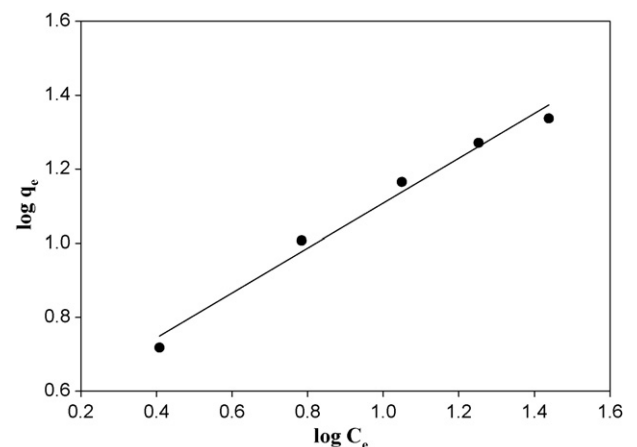


Fig. 7. Freundlich adsorption isotherm for lead at 0.1 g/30 mL of adsorbent concentration.

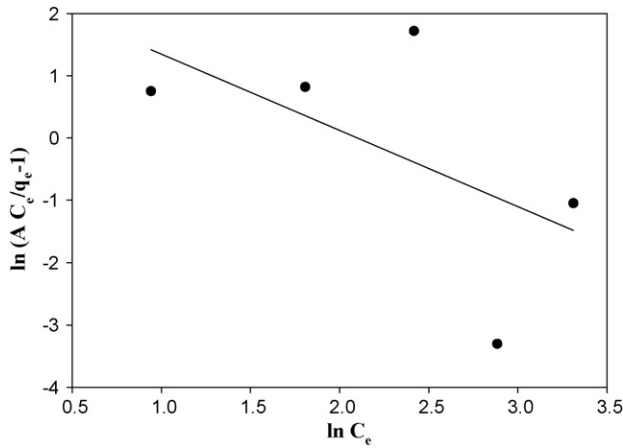


Fig. 8. Redlich–Peterson adsorption isotherm for lead at 0.1 g/30 mL of adsorbent concentration.

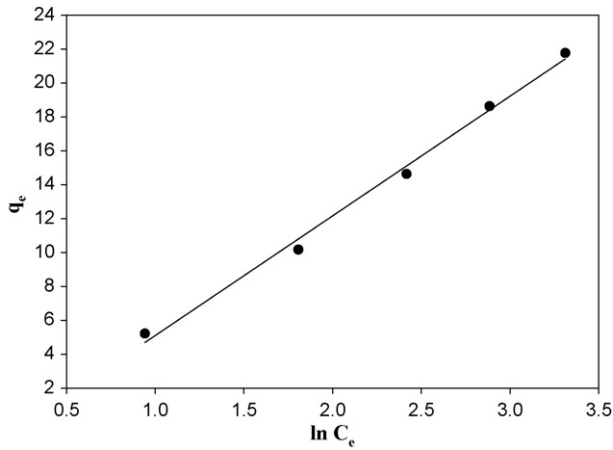


Fig. 9. Temkin adsorption isotherm for lead at 0.1 g/30 mL of adsorbent concentration.

tions under the concentration range studied. Examination of the Freundlich and Redlich–Peterson data shows that these two isotherms are not modeled as well across the concentration range studied.

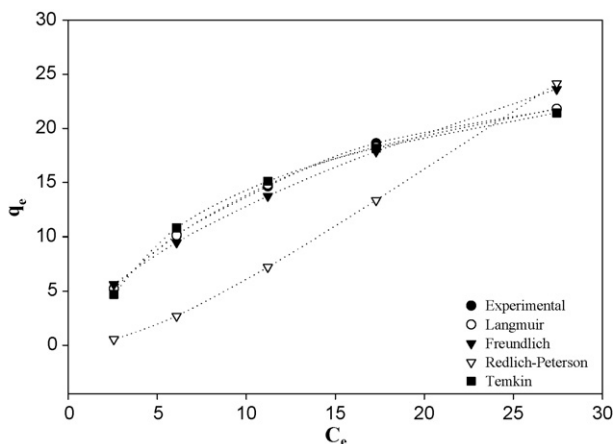


Fig. 10. Equilibrium curves for lead onto *S. cumini* L.

Table 1

Langmuir, Freundlich, Redlich–Peterson and Temkin isotherm constants and correlation coefficients

Langmuir	
Q (mg/g)	32.47
b (L/mg)	0.0746
R^2	0.9997
Freundlich	
K_f (mg/g)	3.1761
n	0.606
R^2	0.9834
Redlich–Peterson	
A (L/mg)	1.08
B (L/mg)	13.1129
g	−1.2261
R^2	0.3259
Temkin	
A_T (L/mg)	0.7584
b_T	356.72
R^2	0.9938

5. Kinetics of adsorption

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Fig. 1 shows the plot between amount adsorbed, q (mg/g) versus time, t (min) for different initial solute concentrations. From the figure it was observed that q value increased with increase in initial lead concentration. The adsorption rate within the first 5 min was observed to be very high and thereafter the reaction proceeds at a slower rate till equilibrium and finally a steady state was obtained after equilibrium. The kinetics of the adsorption data was analysed using two kinetic models, pseudo-first-order and pseudo-second-order kinetic model. These models correlate solute uptake, which are important in predicting the reactor volume. These models are explained as follows:

5.1. The pseudo-first-order equation

The pseudo-first-order equation of Lagergren and Kungliga [35] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q - q_t) \tag{9}$$

where q and q_t are the sorption capacities at equilibrium and at time t , respectively (mg/g) and k_1 is the rate constant of pseudo-first-order sorption (1/min). After integration and applying boundary conditions, $q_t = 0 - q_t$ at $t = 0 - t$; the integrated form of Eq. (9) becomes

$$\log(q - q_t) = \log(q) - \frac{k_1}{2.303}t \tag{10}$$

The equation applicable to experimental results generally differs from a true first-order equation in two ways [36]:

- The parameter $k_1 (q - q_t)$ does not represent the number of available sites;

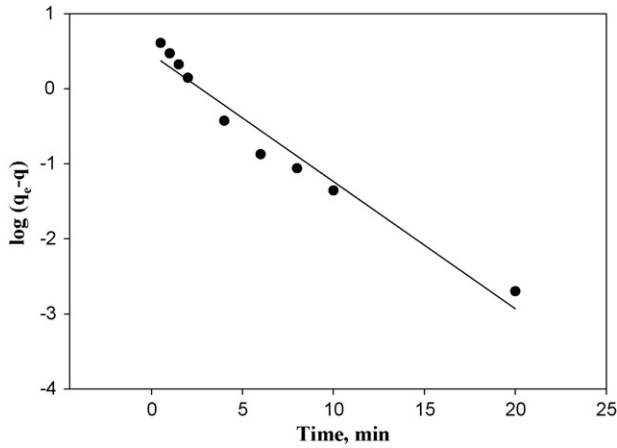


Fig. 11. Pseudo-first-order adsorption of lead by *S. cumini* L. for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentration.

- The parameter $\log(q)$ is an adjustable parameter which is often not found equal to the intercept of a plot of $\log(q - q_t)$ against t , whereas in a true first-order sorption reaction $\log(q)$ should be equal to the intercept of a plot of $\log(q - q_t)$ against t .

In order to fit Eq. (10) to experimental data, the equilibrium sorption capacity, q , must be known. In many cases q is unknown and as chemisorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount [37]. In most cases in the literature, the pseudo-first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20–30 min of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to $t = \infty$, on treat (q) as an adjustable parameter to be determined by trial and error. For this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity (q), in order to analyse the pseudo-first-order model kinetics. In over 50% of literature references, based on analyzing sorption kinetics, the authors did not measure an equilibrium isotherm.

The pseudo-first-order rate constant k_1 can be obtained from the slope of plot between $\log(q - q_t)$ versus time, t . Fig. 11 shows the Lagergren pseudo-first-order kinetic plot for the adsorption of lead onto *S. cumini* L. The pseudo-first-order rate constant k_1 values were calculated from the slope of Fig. 11. The calculated k_1 values and their corresponding linear regression correlation coefficient values are shown in Table 2. The linear regression correlation coefficient R_1^2 found as 0.9633, which shows that

Table 2
Kinetic constants for lead onto *Syzygium cumini* L.

Initial concentration (mg/L)	20
Pseudo-first-order	
Rate constant, k_1	0.3901
Amount of lead adsorbed on adsorbent, q_e (mg/g)	2.8661
Correlation coefficient, R_1^2	0.9633
Pseudo-second-order	
Rate constant, k_2	0.2498
Amount of lead adsorbed on adsorbent, q_e (mg/g)	5.3242
Correlation coefficient, R_2^2	0.9995

this model can be applied to predict the adsorption kinetic model.

5.2. The pseudo-second-order equation

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k(q - q_t)^2 \tag{11}$$

where q and q_t are the sorption capacity at equilibrium and at time t , respectively (mg/g) and k is the rate constant of pseudo-second-order sorption (g/mg min). For the boundary conditions $q_t = 0 - q_t$ at $t = 0 - t$; the integrated form of Eq. (11) becomes:

$$\frac{1}{q - q_t} = \frac{1}{q} + kt \tag{12}$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. (12) can be rearranged to obtain:

$$q_t = \frac{t}{1/kq^2 + (t/q)} \tag{13}$$

which has linear form:

$$\frac{t}{q_t} = \frac{1}{kq^2} + \frac{1}{q}t \tag{14}$$

where t is the contact time (min), q (mg/g) and q_t (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, t . Eq. (14) does not have the problem of assigning as effective q . If pseudo-second-order kinetics are applicable, the plot of t/q_t against t of Eq. (14) should give a linear relationship, from which q and k can be determined from the slope and intercept of the plot (Fig. 12) and there is no need to know any parameter beforehand.

The pseudo-second-order rate constant k_2 , the calculated q value and the corresponding linear regression correlation coefficient values R_2^2 are given in Table 2. At all initial copper concentrations, the linear regression correlation coefficient R_2^2 values

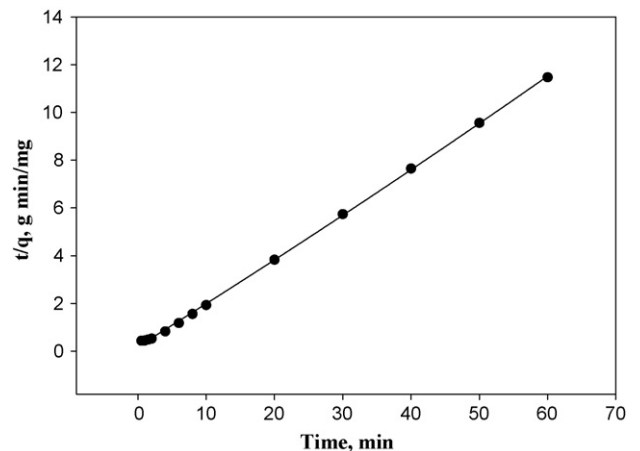


Fig. 12. Pseudo-second-order adsorption of lead by *S. cumini* L. for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentration.

Table 3
Maximum adsorption capacities for lead adsorption to different adsorbents

Adsorbent material	Adsorption capacity (mg/g)	pH	Reference
Na-Mont morillonite	9.58	5	[38]
Crushed concrete fines	37	5.5	[39]
Turkish Beypazari low rank coal	13.579	5	[40]
Olive stone waste	1.48×10^{-5}	5.5–6	[41]
<i>Oryza sativa</i> L. husk	8.6	5	[42]
Fly ash	10	5	[43]
Marine green macroalga <i>Caulerpa lentillifera</i>	28.72	5–6	[44]
Coir	18.9	5.5	[45]
Barley straw	15.2	5.5	[45]
Rice husk	4.0	5.5	[45]
Oak stem	0.75	5.5	[45]
Powdered waste sludge	82	5.5	[45]
Hazelnut shell	1.78	5.5	[45]
<i>Syzygium cumini</i> L.	32.47	6	Present study

were higher. The higher R_2^2 values confirm that the adsorption data are well represented by pseudo-second-order kinetics and supports the assumption behind the model that the adsorption is due to chemisorption.

A comparison of the maximum capacity Q_{\max} of *S. cumini* L. with those of some other adsorbents reported in literature is given in Table 3. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

6. Conclusions

The present study shows that the *S. cumini* L. was an effective biosorbent for the adsorption of lead ions from aqueous solution. The biosorption capacity of *S. cumini* L. was superior due to the higher content of hydroxyl and amine groups. The effect of process parameters like pH, metal ion concentration, adsorbent concentration and adsorbent size on process equilibrium were studied. The uptake of lead ions by *S. cumini* L. was increased by increasing the metal ion concentration and the adsorbent concentration and decreased by increasing the adsorbent size. The uptake was also increased by increasing pH up to 6. The adsorption isotherms could be well fitted by the Langmuir equation followed by Temkin equation. The biosorption process could be best described by the second-order equation.

References

- [1] B. Thomson, W. Turney, Mineral and mine drainage, *Water Environ. Res.* 67 (1995) 527–529.
- [2] K. Seki, N. Saito, M. Aoyama, Removal of heavy metal ions from solutions by coniferous barks, *Wood Sci. Technol.* 31 (1997) 441–447.
- [3] A. Hong, T. Chen, R. Okey, Chelating extraction of copper from soil using S-carboxymethylcysteine, *Water Environ. Res.* 67 (1995) 971–978.
- [4] J. Monteagudo, M. Ortiz, Removal of inorganic mercury from mine waste water by ion exchange, *J. Chem. Technol. Biotechnol.* 75 (9) (2000) 767–772.
- [5] L. Friberg, G.F. Nordberg, B. Vouk (Eds.), *Handbook on the Toxicology of Metals*, Elsevier/Biomedical Press, North-Holland/Amsterdam, 1979.
- [6] A. Mohammad, M. Najar, *J. Sci. Ind. Res.* 51 (1997) 523–532.
- [7] A. Denizli, E. Buyuktuncel, O. Genc, E. Piskin, *Anal. Lett.* 31 (1998) 2791–2804.
- [8] R.A. Beauvais, S.F. Alexandratos, *React. Funct. Polym.* 36 (1998) 113–121.
- [9] J.T. Matheickal, Q. Yu, Biosorption of lead from aqueous solutions by marine alga *Ecklonia radiata*, *Water Sci. Technol.* 34 (9) (1996) 1–7.
- [10] J.-S. Chang, J. Hong, Biosorption of mercury by the inactivated cells of *Pseudomonas aeruginosa* PU21 (Rip64), *Biotechnol. Bioeng.* 44 (1994) 999–1006.
- [11] K.H. Chu, M.A. Hashim, S.M. Phang, V.B. Samuel, Biosorption of cadmium by algal biomass: adsorption and desorption characteristics, *Water Sci. Technol.* 35 (7) (1997) 115–122.
- [12] T.A. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, *Water Res.* 37 (2003) 4311–4330.
- [13] S. Singh, S. Pradhan, L.C. Rai, Comparative assessment of Fe^{3+} and Cu^{2+} biosorption by field and laboratory-grown *Microcystis*, *Process Biochem.* 33 (5) (1998) 495–504.
- [14] B. Volesky, Z.R. Holan, Biosorption of heavy metals, *Biotechnol. Prog.* 11 (1995) 235–250.
- [15] J.-S. Chang, J.-C. Huang, C.-C. Chang, T.-J. Tarn, Removal and recovery of lead fixed-bed biosorption with immobilized bacterial biomass, *Water Sci. Technol.* 38 (4/5) (1998) 171–178.
- [16] D. Kratochvil, B. Volesky, G. Demopoulos, Optimizing Cu removal/recovery in a biosorption column, *Water Res.* 31 (9) (1997) 2327–2339.
- [17] S. Pradhan, L.C. Rai, Copper removal by immobilized *M. aeruginosa* in continuous flow columns at different bed heights: study of the adsorption/desorption cycle, *World J. Microbiol. Biotechnol.* 17 (2001) 829–832.
- [18] D. Kratochvil, B. Volesky, Advances in the biosorption of heavy metals, *Trends Biotechnol.* 61 (1998) 291–300.
- [19] B. Volesky, J. Weber, J.M. Park, Continuous-flow metal biosorption in a regenerable *sargassum* column, *Water Res.* 37 (2003) 297–306.
- [20] N. Kuyucak, Feasibility of biosorbents application, in: B. Volesky (Ed.), *Biosorption of Heavy Metals*, CRC Press, Boca Raton, 1990.
- [21] I. Langmuir, The adsorption gasses on plane surface of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1916) 1361–1368.
- [22] H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem.* 57 (1906) 385–470.
- [23] O. Redlich, D.L. Peterson, A useful adsorption isotherm, *J. Phys. Chem.* 63 (1959) 1024.
- [24] C. Aharoni, M. Ungarish, Kinetics of activated chemisorption Part 2. Theoretical models, *J. Chem. Soc. Faraday Trans.* 73 (1977) 456–464.
- [25] R. Gong, Y.D. Ding, H. Liu, Q. Chen, Z. Liu, Lead biosorption by intact and pretreated *spirulina maxima* biomass, *Chemosphere* 58 (2005) 125–130.
- [26] F.A. Abu Al-Rub, M.H. El-Naas, F. Benyahia, I. Ashour, Biosorption of nickel on blank alginate beads, free and immobilized algal cells, *Process Biochem.* 39 (2004) 1767–1773.
- [27] P.X. Sheng, Y.P. Ting, J.P. Chen, L. Hong, Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, *J Colloid Interf. Sci.* 275 (2004) 131–141.
- [28] G. Ozdemir, N. Ceyhan, T. Ozturk, F. Akirmak, T. Cosar, Biosorption of chromium(VI), cadmium(II) and copper(II) by *Pantoea* sp. TEM 18, *Chem. Eng. J.* 102 (2004) 249–253.
- [29] A. Iyer, K. Mody, B. Jha, Accumulation of hexavalent chromium by an exopolysaccharide producing marine *Enterobacter cloacae*, *Mar. Pollut. Bull.* 49 (2004) 974–977.
- [30] Y. Sag, A. Kaya, T. Kutsal, The simultaneous biosorption of Cu(II) and Zn(II) on *Rhizopus arrhizus*: application of the adsorption models, *Hydrometallurgy* 50 (3) (1998) 297–314.
- [31] J.L. Zhou, P.L. Huang, R.G. Lin, Sorption and desorption of Cu and Cd^{2+} by macroalgae and microalgae, *Environ. Pollut.* 101 (1) (1998) 67–75.
- [32] J.T. Matheickal, Q. Yu, Biosorption of lead(II) and copper(II) from aqueous solution by pre-treated biomass of Australian marine algae, *Biores. Technol.* 69 (1999) 223–229.

- [33] Y. Prasanna Kumar, P. King, V.S.R.K. Prasad, Removal of copper from aqueous solution using *Ulva fasciata* sp.—a marine green algae, *J. Hazard. Mater.*, in press.
- [34] Krishna G. Bhattacharyya, Arunima Sharma, Adsorption of Pb(II) from aqueous solution by *Azadirachta indica* (Neem) leaf powder, *J. Hazard. Mater. B* 113 (2004) 97–109.
- [35] S. Lagergren, S. Kungliga, Svenska Ventenskapsakademiens, Handlingar Band 24 (4) (1898) 1.
- [36] C. Ahroni, D.L. Sparks, Kinetics of soil chemical reactions—a theoretical treatment, in: D.L. Sparks, D.L. Suarez (Eds.), Rates of Soil Chemical Processes, Soil Society of America, Madison, WI, 1991, p. 1.
- [37] M. Ungarish, C. Aharoni, *J. Chem. Soc. Faraday Trans.* 77 (1981) 975.
- [38] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances”, *Water Res.* 37 (2003) 1619–1627.
- [39] N.J. Coleman, W.E. Lee, I.J. Slipper, Interactions of aqueous Cu^{2+} , Zn^{2+} and Pb^{2+} ions with crushed concrete fines, *J. Hazard. Mater. B* 121 (2005) 203–213.
- [40] C. Arpa, E. Basyilmaz, S. Bektas, O. Genc, Y. Yurum, Cation exchange properties of low rank Turkish coals: removal of Hg, Cd and Pb from wastewater, *Fuel Process. Technol.* 68 (2000) 111–120.
- [41] N. Fiol, I. Villaescusa, M. Martinez, N. Miralles, J. Poch, J. Serarols, Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste, *Sep. Purif. Technol.*, in press.
- [42] M.M.D. Zulkali, A.L. Ahmad, N.H. Norulakmal, *Oryza sativa* L. husk as heavy metal adsorbent: optimization with lead as model solution, *Biores. Technol.* 97 (2006) 21–25.
- [43] H. Cho, D. Oh, K. Kim, A study on removal characteristics of heavy metals from aqueous solution by fly ash, *J. Hazard. Mater. B* 127 (2005) 187–195.
- [44] P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, T.F. Marhaba, Biosorption of Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*, *Biores. Technol.*, in press.
- [45] K. Conrad, H.C.B. Hansen, Sorption of zinc and lead on coir, *Biores. Technol.*, in press.