Biosorption of Pb(II) from aqueous solutions using chemically modified *Moringa oleifera* tree leaves

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ABSTRACT

Moringa oleifera leaves (MOL); an agro-waste material has been used as a precursor to prepare a new biosorbent. The leaves were washed with base and citric acid, and obtained new chemically modified MOL biosorbent (CAMOL) for sequestration of Pb(II) from aqueous solution. The biosorbent was characterized by SEM, FTIR spectral and elemental analyses. The effect of experimental parameters such as pH, dose, initial concentration, contact time and temperature on the biosorption was studied. The kinetic data were analyzed using three adsorption kinetic models: the pseudo-first and second-order kinetics and intraparticle diffusion. The equilibrium data were analyzed using Langmuir, Freundlich, Dubinin–Radushkevick and Temkin isotherm models. Langmuir model provided the best correlation with biosorption capacity of 209.54 mg g^{-1} at 313 K. The thermodynamic properties, ΔG°, ΔH° and ΔS° showed that biosorption of Pb(II) onto CAMOL was spontaneous, endothermic and feasible in the temperature range of 293–313 K. Desorption experiments showed feasibility of regeneration of the biosorbent for further use after treating with dilute HCl. The presence of other common metal ions like Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} did not affect the biosorption of lead. Investigations carried out proved that CAMOL is a biosorbent with good potential for removal of lead from the aqueous media.

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1. Introduction

Many industrial wastewaters produced by metal plating, metal finishing, mining, automotive, aerospace, battery and general chemical plants often contain very high concentrations of heavy metals [1]. Lead being the most toxic metal, ranks second in the list of prioritized hazardous substances issued by the US Agency for toxic substances and Disease Registry. Lead exists in several other industrial and mining wastes, such as chemicals and allied products, lead acid storage batteries, ceramic and glass industries printing, ammunition, lead smelting and mine tailings. Wastes that include lead are found in paints, pipes, batteries and in some petrol types [2]. Lead poisoning in human beings causes severe damage to the kidneys, liver, brain, nervous and reproductive systems [3,4]. It impairs hemoglobin synthesis and causes several neurological disorders. Based on its toxicity, the EPA, the US has set a maximum permissible limit for lead ions in drinking water as 0.05 mg L^{-1} [5] and the Bureau of Indian Standards as 0.1 mg L^{-1} [6]. The upper limit for lead in drinking water recommended by WHO and AWWA is 0.05 mg L^{-1} [7]. As a consequence, environmental disposal of the industrial effluents containing lead has become a serious cause of concern.

Common methods for reclamation of metal-contaminated waters are based on chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion exchange and adsorption techniques. These methods can ensure the complete removal of pollutants, but with varying costs, often higher costs. Intensive efforts are being made to find low-cost and effective materials and methods for the removal of heavy metals by sorption materials [8,9]. As a result, a few innovative and economic technologies have emerged for the treatment of metal-bearing effluents. Some of them are in the process of commercialization. Among these methods, biosorption, a property of different kinds of dead microbial organisms, seaweeds and agro-industrial biomass that binds and concentrates heavy metals even in very dilute aqueous systems has been demonstrated as a potential method to replace conventional methods for the removal of metal ions [10–12]. Biosorption is a passive adsorption process, based mainly on the affinity between biosorbent and the sorbate. The use of dead biomass is of particular economic interest, because the biomaterials have been used in the same way as synthetic adsorbents or ion exchangers and could be regenerated [13]. Further, the use of agricultural residues as adsorbents has not only provided a new class of benign alternatives for the removal of waste materials from industrial waters,

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but has also reduced the use of chemicals as adsorbents which are hazardous materials. A number of investigations have been carried out for the removal of heavy metals from aqueous systems using agricultural waste and by-products such as bael leaves [14], *Moringa oleifera* bark [15], eucalyptus bark [16] and pectin-rich fruit wastes [17]. It has been observed that pretreatment of plant wastes extracts soluble organic compounds with enhanced chelating efficiency [18]. Various chemical methods for modifying the biomass, such as introduction of additional functional groups to increase its efficiency for the metal biosorption have been reported. To site one instance, the chemical treatment of biomass with citric acid produces condensation product, citric acid anhydride that reacts with cellulosic hydroxyls initially to form an ester and finally carboxyl acid group residues in the cellulose [19]. The metal uptake disclosed improvement when the biomass was treated first with NaOH followed by citric acid. Treatment with NaOH would deesterify and remove tannins, making available more active binding sites for metal adsorption. This is a simple, efficient and environmentally acceptable method for the preparation of chelating agents from a majority of available agricultural residues.

This work is aimed at studying the biosorption of Pb(II) from aqueous solutions using the citric acid treated *M. oleifera* leaves. *M. oleifera* Lam; commonly known as horseradish tree is grown as a vegetable crop in India and other tropical countries. Its fruits are edible and consumed during all the seasons in India, and therefore these trees are widely cultivated species. Hence, massive amount of leafy waste is produced, which is disposed off. In order to use this massive amount of biomass effectively, studies have been carried out systematically to investigate the application of citric acid treated *M. oleifera* leaves as a biosorbent for the removal of lead ions from water/waste water. The optimum conditions for biosorption such as pH, initial metal ion concentration, biosorbent dosage and contact time have been experimentally investigated. An effort to discuss the equilibrium adsorption isotherms on the basis of Langmuir, Freundlich, Dubinin–Radushkevick and Temkin models together with thermodynamic studies has been made.

2. Material and methods

2.1. Biomass and chemical modification

The chemical modification of MOL has been undertaken and was carried out as described elsewhere [20]: MOL leaves were sieved to 20–30 mesh fractions. 200 g of sieved leaves powder was placed in 4 L of 0.1N NaOH. The slurry was stirred at 300 rpm for an hour at 23 °C to remove the excess base. The washed leaves powder was taken onto a 40 mesh sieve, rinsed with double distilled water and made upto 4 L. This procedure was repeated twice to ensure removal of the base from the leaves powder. This biomass named BWMOL was mixed with citric acid (CA) in the ratio of 1.0 g leaves powder to 7.0 mL of CA, where the leaves powder readily absorbed the acid and this ratio of leaves to acid was observed to ensure that the leaves had completely absorbed the liquid. The acid/leaves slurry was dried overnight at 50 °C.

The CA-treated BWMOL leaves were placed on a Whatmann 41 filter paper and washed in a Buchner funnel under vacuum with 150–200 mL of double distilled water per gram of the product to remove excess CA. This volume of water was sufficient to remove unreacted CA, since no turbidity from Pb(II) citrate was observed when the washed leaves were suspended in 10 mL of water, to which 10 mL of 0.1 M Pb(II) nitrate was added. The treated leaves powder was dried at 50 °C overnight and sieved to retain the 20–30 mesh fractions. Treating with a base as NaOH and a subsequent citric acid modification stabilizes the MOL due to insertion and crosslinking of carboxyl groups and thus increases its cation uptake

ability [21,22]. This modified MOL, named as CAMOL has been used in the present studies.

2.2. Reagents and equipments

All chemicals/reagents used in this study were of analytical grade from S.D. Fine Chem. Ltd. (Mumbai, India) and were used as obtained. An Elico (LI-129) pH meter was used for pH measurements. The pH meter was calibrated using standard buffer solutions of pH 4.0, 7.0 and 9.2. Vario EL, Elementar, Germany was used for elemental analysis of the CAMOL. The FTIR spectra were recorded using (Thermo-Nicolet FTIR, Nicolet IR-200, USA) infrared spectrophotometer between the wave numbers 4000 and 400 cm^{-1}. Scanning electron microscopy (Model Evo15, Carl Zeiss, England) has been used to study the surface morphology of the biosorbent.

2.3. Determination of the point of zero charge (PZC)

The PZC of the biosorbent was determined adopting the following procedure [23,24]: 100 mL of double distilled water was added to an Erlenmeyer flask, capped with cotton and was slowly and continuously heated until boiling for 20 min to expel the dissolved CO_2. The flask was capped immediately to prevent reabsorption of atmospheric CO_2 by water. 0.2 g of the biosorbent (CAMOL) was placed in another 25 mL Erlenmeyer flask with 15 mL of CO_2-free water. The flask was sealed with a rubber stopper and left in continuous agitation for 48 h at room temperature and then filtered. Then the pH of the filtrate was measured and this value has been taken as the point of zero charge.

2.4. Biosorption experiments

Batch adsorption experiments were repeated and carried out using stoppered conical flasks (100 mL) on a temperature-controlled water bath shaker set at 200 rpm and maintained at the desired temperature. The effects of solution pH (2.0–9.0), adsorbent dose (0.010–0.140 g), contact time (0–100 min) and concentration (10–1000 mg L^{-1}) were studied. Isotherms were obtained by equilibrating metal ion solutions of different initial concentrations with 0.1 g of sorbent at different temperatures (293–313 K) using a thermostatic shaking water bath. After the prescribed contact time, the solutions were filtered through Whatmann filter paper No. 41 and the concentration of metal in the filtrate was measured using AAS. All the experiments were carried out in duplicates and the average values were used. The adsorbent phase concentrations q_e of Pb(II) were calculated according to the following equation:

$$q_e = V \frac{C_0 - C_e}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of Pb(II) (mg L^{-1}), respectively, V is the volume of the solution (mL), and W is the mass of adsorbent (g).

3. Results and discussion

3.1. Characteristics of the biosorbent (CAMOL)

Elemental analysis results revealed that CAMOL is composed of $47.19 \pm 2.32\%$ carbon, $6.79 \pm 1.08\%$ hydrogen, $2.47 \pm 0.32\%$ nitrogen, $0.59 \pm 0.01\%$ sulphur and $42.96 \pm 1.28\%$ oxygen. Selected physicochemical properties of CAMOL are listed in Table 1. The vibrations of the main functional groups on CAMOL biosorbent surface that bind metals were investigated using infrared spectroscopy. FTIR spectra of MOL, BWMOL and CAMOL are shown in Fig. 1. The FTIR spectrum exhibits characteristic main skeleton cellulose peak in the finger print region of 1000–1200 cm^{-1}.
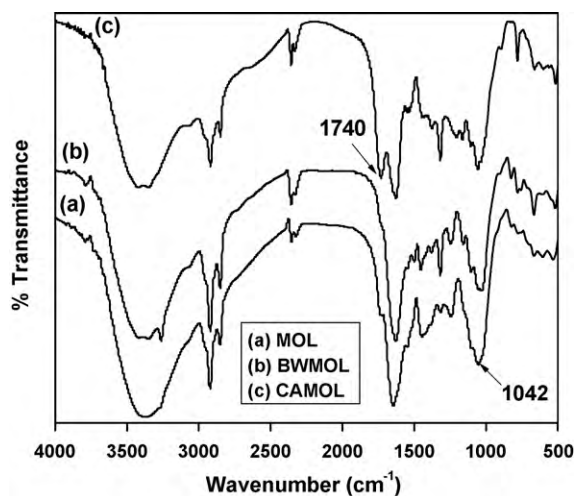
Fig. 1. FTIR spectra of (a) MOL, (b) BWMOL and (c) CAMOL.

The doublet peaks appeared in all the spectra at wave number 2921–2918 cm^{-1} and 2853–2850 cm^{-1}, respectively, due to the asymmetric and symmetric stretch of aliphatic chains (–CH) [25]. Comparison of the IR spectra of samples of the MOL and CA modified MOL revealed that a strong characteristic stretching vibration adsorption band for carboxyl group at 1742 cm^{-1} was present in the IR spectrum of the CAMOL. This confirms the esterification between alcohol groups of cellulose in MOL and citric acid. The broad absorptions between 2500 and 3500 cm^{-1} confirm the existence of carboxylic O–H groups and free COOH's after CA modification.

In this study, SEM (Fig. 2) is used to examine the change in the morphological features of MOL on treating with citric acid. The surface morphology of MOL is different from that of CAMOL, which might exhibit microstructure porosity for both untreated and CA-treated biomass. The surface morphology of raw-MOL powder showed that the powder was an assemblage of fine particles, which did not have regular, fixed shape and size. The particles were of various dimensions and all of them contained a large number of steps and kinks on the external surface, with broken edges. The size of the voids in the MOL was reduced after citric acid treatment and some distortion of the shape could be seen in the SEM of CAMOL.

3.2. Effect of solution pH on biosorption

The interaction between the metal ions and the functional groups of the biomass depends on the nature of the biosorbent as well as the solution chemistry of the biosorbate, which in turn depends on the pH of the solution that considerably influences the metal speciation, sequestration, and/or mobility [26]. To examine this effect, a series of experiments were carried out using 50 mg L^{-1}

Table 1
Physicochemical characteristics of CAMOL.

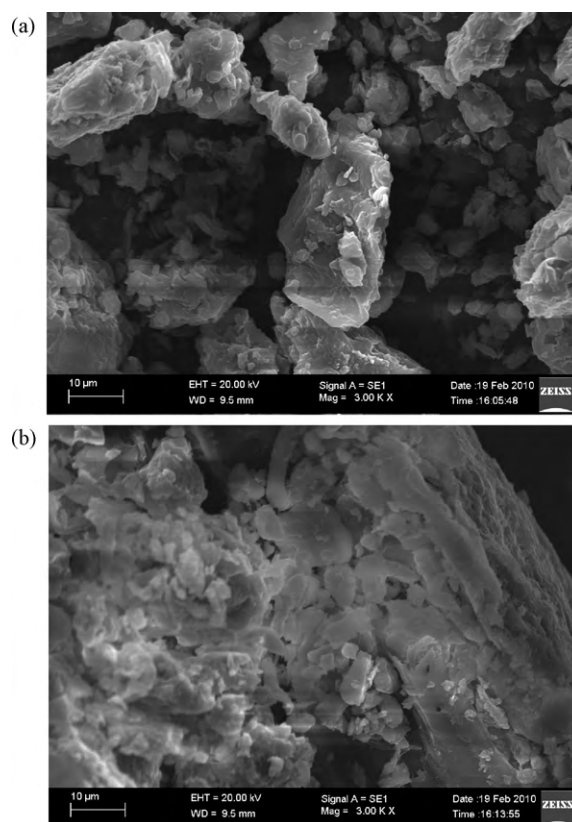| Parameter	CAMOL
Moisture content (%)	7.32 ± 1.23
Ash content (%)	6.23 ± 1.02
Bulk density (g mL^{-1})	0.43 ± 0.02
Conductivity (µs cm^{-1})	152.2 ± 10.1
PZC	3.72 ± 0.21
Carbon (%)	47.19 ± 2.32
Hydrogen (%)	6.79 ± 1.08
Nitrogen (%)	2.47 ± 0.32
Sulphur (%)	0.59 ± 0.01
Oxygen[a] (%)	42.96 ± 1.28

[a] Estimated by difference.

Fig. 2. Scanning electron micrographs of (a) MOL and (b) CAMOL.

lead-containing solutions, with varying pH from 2 to 9. Fig. 3 shows the equilibrium biosorption removal of Pb(II) on biosorbent increased with further increase in pH, and then decreased slightly with a further increase of pH. The main factors influencing the pH on biosorption process were Pb(II) species and surface functional groups on the adsorbents. It is generally known that at low pH values, concentration of H$^+$ ions far exceeds that of the metal ions and hence H$^+$ ions compete with Pb(II) ions for the surface of the adsorbent which would hinder the Pb(II) ions from reaching the binding sites of the adsorbent resulting in low adsorption amount of Pb(II). As the pH increases, there are fewer protons in the solution and consequently there is lesser competition with Pb(II) for bind-
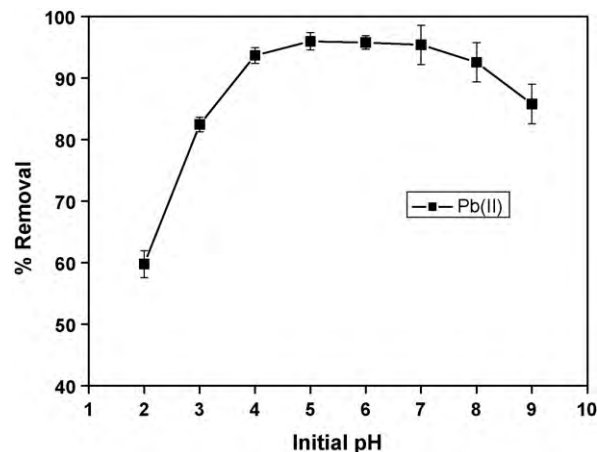

Fig. 3. Effect of pH on the biosorption of Pb(II) onto CAMOL (initial conc.: 50 mg L^{-1}, contact time: 2 h, agitation rate: 200 rpm, biosorbent dose: 0.40 g). Error bars represent ±S.D.
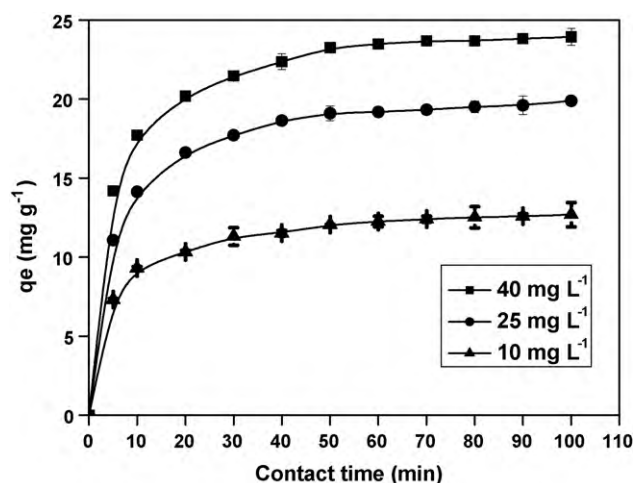
Fig. 4. Effect of contact time on the biosorption of Pb(II) onto CAMOL (biosorbent dose: 0.04 g, pH: 5.0). Error bars represent ±S.D.

ing sites. This results in the increase of the biosorption amount of Pb(II). In the case of CAMOL, a pH range of 4–6 is more suited for the quantitative removal of Pb(II) from the aqueous solution. pH 5 was selected as the optimum value for conducting further adsorption experiments. The adsorption decreased when pH was higher than 6, which might be attributed to the coordination of OH$^-$ with the metal ion.

Point of zero charge determination of the biosorbent is important in elucidating the biosorption mechanism. PZC, shown in Table 1 could be used to explain the effect of pH on Pb(II) adsorption. The pH at PZC, the surface charge of biosorbents was neutral and the electrostatic forces between Pb(II) and surface of adsorbents were balanced. This balance is disturbed when pH is deviated from PZC. At pH < PZC, the biosorbent, surface charge is positive which results in an electrostatic repulsion with Pb(II) and causes low lead sorption. At pH > PZC, the surface charge of the biosorbent becomes negative and Pb(II) in solution are attracted to its surface. Maximum sorption is likely to occur at pH values greater than PZC when adsorbents have a net negative charge. The principle of PZC agrees with the adsorption behaviors of adsorbents for Pb(II).

3.3. Effect of the biosorbent dose

The biosorption efficiency for Pb(II) as a function of biomass concentration has been investigated. The influence of biosorbent dose on the percentage removal of Pb(II) has also been examined by carrying out concurrent experiments with biomass concentrations from 0.01 to 0.140 g, while the total volume, initial concentration of the metal solution, the temperature and the pH value were kept constant. The amount of Pb(II) adsorbed had increased with an increase in the biosorbent dosage from 0.01 to 0.14 g. This result could be explained by the fact that for optimum biosorption, extra sites must be available for biosorption reaction, whereas by increasing the biomass concentration, a number of sites available for bisorption site had increased. The maximum biosorption percentage reached 99% for Pb(II) as biomass concentration reached 0.04 g as shown in Fig. S1 (see the Supporting Information). However, further increase in sorbent mass beyond 0.04 g did not result in sufficient improvement in the percentage removal of lead ions by CAMOL. Therefore, the optimum biomass concentration has been taken as 0.040 g for conducting further batch experiments.

Table 2
Parameters of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

Initial Pb(II) concentration (mg L^{-1})	Experimental value, $q_{e,exp}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order				Weber ad Morris		
		$q_{e,cal}$ (mg g^{-1})	k_1 (×10^{-3} mg g^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 (×10^{-2} mg g^{-1} min^{-1})	h_0 (mg g^{-1} min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	K_{id} (mg g^{-1} min$^{-1/2}$)	R^2
10	12.7343	4.35 ± 0.12	29.22 ± 0.41	0.9033	13.26 ± 0.13	15.35 ± 1.40	0.20 ± 0.02	0.9974	7.20 ± 0.26	0.61 ± 0.01	0.9353
25	19.8988	6.65 ± 0.03	39.11 ± 0.72	0.8011	20.64 ± 0.12	10.08 ± 0.78	0.21 ± 0.01	0.997	11.39 ± 0.53	0.94 ± 0.06	0.9213
40	23.9233	6.65 ± 0.13	38.92 ± 0.65	0.7999	25.01 ± 0.01	9.3 ± 0.10	0.23 ± 001	0.9995	14.17 ± 0.17	1.11 ± 0.02	0.9243

3.4. Effect of contact time and initial concentration

In order to determine the equilibrium time for maximum uptake, a contact time study was performed with different initial concentrations of Pb(II) of 10, 25 and 40 mg L^{-1}. A graphical representation of the contact time as a function of initial concentrations, as given in Fig. 4 suggests that the adsorption increased sharply with contact time in the first 20 min and equilibrium adsorption was established within 50 min. It is also clear from Fig. 4 that the efficiency of biosorption had increased with an increase in the initial concentration of Pb(II). The equilibrium biosorption amount of Pb(II) was found to increase from 12 to 23 mg g^{-1} as the initial concentration of metal ion increased from 10 to 40 mg L^{-1}. The higher adsorption capacity and rate of Pb(II) adsorption on CAMOL indicated its suitability to treat wastewater polluted with Pb(II).

3.5. Biosorption kinetics

Kinetic experiments have been employed to evaluate the rate of the adsorption process and to examine the potential rate-controlling step. In the present work, the kinetic data obtained from the batch studies have been analyzed by using pseudo-first and pseudo-second-order models. The first order equation of Lagergren [27] is expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{2}$$

where q_t and i_e (mg g^{-1}) are the amounts of metal ions adsorbed per unit weight of the adsorbent at time t and equilibrium, respectively; and k_1 (min^{-1}) is the pseudo-first-order rate constant of the sorption process. The model is based on the assumption, that the adsorption rate is proportional to the number of free sites available. By applying the boundary conditions $t = 0$ to $t = t$ and correspondingly $q_t = 0$ to $q_t = q_t$ and integrating, Eq. (2) the resultant solution in the linear form is shown in the following equation:

$$\log(q_e - q_t) = \frac{\log q_e - k_1 t}{2.303} \tag{3}$$

Linear plots of $\log(q_e - q_t)$ versus t have been used to evaluate the data, to determine the rate constant and q_e from the slope and intercept, respectively. The experimental and calculated q_e values, pseudo-first-order rate constant and coefficient of determination (R^2) values are given in Table 2. The theoretic values ($q_{e,cal}$) were far lower than the corresponding experimental data, $q_{e,exp}$, implying that the biosorption process had not fully followed the pseudo-first-order adsorption rate expansion.

The pseudo-second-order kinetic rate equation [28] is based on the assumption that the adsorption follows the second-order chemisorption. The linear form can be written as follows:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of adsorption. From the plots of t/q_t against t, q_e and k_2 has been evaluated. The initial sorption rate h_0 (mg g^{-1} min^{-1}), could be obtained by the following equation [29]:

$$h_0 = k_2 q_e^2 \tag{5}$$

Plotting t/q_t versus t at different adsorbate concentrations has provided the second-order sorption rate constant (k_2) and q_e values from slopes and intercepts. The linear plots of t/q_t versus t for all the experimental concentrations are shown in Fig. 5a. The values of the correlation coefficients, R^2, and k_2 are presented in Table 2. The correlation coefficient for the linear plots is superior (close to 1), confirming the applicability of the pseudo-second-order model.
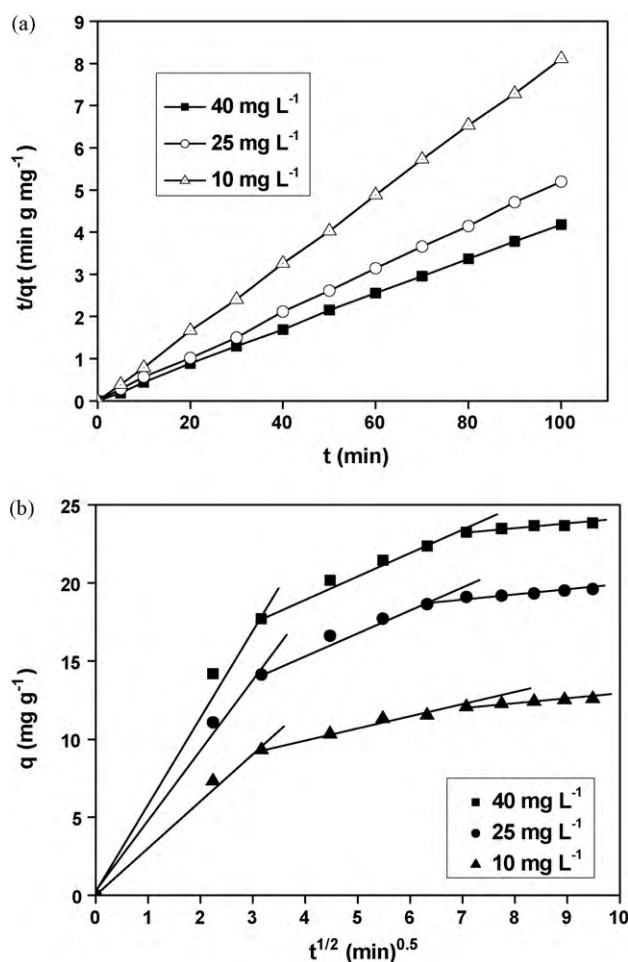

Fig. 5. (a) Pseudo-second-order plots for the biosorption of Pb(II) onto CAMOL. (b) Weber and Morris plots for the biosorption of Pb(II) onto CAMOL. (conditions: pH: 5.0, biosorbent dose: 0.04 g).

The calculated sorption capacity values were more consistent with the experimental values of the predicted sorption capacity.

The lower correlation factors obtained for pseudo-first-order model (0.9033–0.7999) as compared with that obtained for the pseudo-second-order model (0.9974–0.9995) for the biosorption of Pb(II) ions, implies that the pseudo-first-order model is not conducive for explaining the kinetics of the biosorption of the metal. Therefore, the option exercised in favor of the pseudo-second-order model better represented the sorption kinetics and thus supported the assumption behind the model. The obtained results support the hypothesis that chemical sorption as rate-limiting step of adsorption mechanism and a mass transfer was not involved in the solution [29,30].

Since neither the pseudo-first-order nor the pseudo-second-order models could identify the diffusion mechanism, the kinetic results were analyzed by the intraparticle diffusion model. In many cases, there is a possibility that intraparticle diffusion would be the rate-limiting step and this normally is determined by using the equation described by Weber and Morris [31]:

$$q = k_{id} t^{1/2} + c \tag{6}$$

where q (mg g^{-1}) is the amount adsorbed at time t, c (mg g^{-1}) is the intercept, and k_{id} (mg g^{-1} min$^{-1/2}$) is the intraparticle diffusion rate constant. Fig. 5b shows the amount of metal sorbed versus $t^{1/2}$ at three different concentrations with a fixed biosorbent dose. It can be deciphered that these plots have three distinct regions. The initial region of the curve relates the adsorption on the external sur-

Table 3
Isotherm parameters for Pb(II) biosorption onto CAMOL at different temperatures.

Metal ion	Temp. (K)	Langmuir		Freundlich		Dubinin–Radushkevick		Temkin	
		Q_{max} (mg g^{-1})	b (L mg^{-1})	K_F (mg g^{-1})	n	Q (mg g^{-1})	K	b	K
Pb(II)	293	186.63 ± 6.29	0.027 ± 0.004	16.36 ± 4.076	2.55 ± 0.28	159.68 ± 11.09	0.005 ± 0.034	0.94 ± 0.02	0.42 ± 0.02
	303	195.62 ± 6.69	0.0361 ± 0.006	19.63 ± 4.035	2.67 ± 0.25	173.05 ± 11.06	0.006 ± 0.02	0.89 ± 0.02	0.62 ± 0.06
	313	209.54 ± 9.06	0.038 ± 0.007	22.09 ± 4.663	2.71 ± 0.27	185.01 ± 12.78	0.007 ± 0.02	0.89 ± 0.04	0.68 ± 0.10

face. The second region corresponds to the gradual uptake, which reflects the intraparticle diffusion as the rate-limiting step. The final plateau region indicates the equilibrium uptake. It denotes that the intraparticle diffusion is not the only rate-controlling step [32]. The k_{id} values were obtained from the slope of the linear portions of the curve of different initial concentrations and have been indicated in Table 2.

3.6. Biosorption isotherms

The biosorption isotherm for the Pb(II) removal has been studied using an initial concentration of Pb(II) between 10 and 1000 mg L^{-1} at three different temperatures 293, 303 and 313 K keeping the other conditions constant. The biosorption equilibrium data have been conveniently represented by biosorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e. The correlation coefficients, R^2 and the Chi-square (χ^2) test were also carried out to find the best fit among the adsorption isotherm models which has been used. The equation for evaluating the best fit model is to be evolved as:

$$\chi^2 = \sum \frac{q_e - q_{e,m}^2}{q_{e,m}} \qquad (7)$$

where $q_{e,m}$ is the equilibrium capacity obtained by calculating from a model (mg g^{-1}) and q_e is the experimental data of equilibrium capacity (mg g^{-1}).

There are many theoretical models to describe the adsorption process of heavy metal ions. The Langmuir isotherm [33] is valid for monolayer sorption onto surfaces containing finite number of identical sorption sites, which is given by Eq. (8):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (8)$$

where C_e (mg L^{-1}) is the equilibrium solute concentration in mg L^{-1}, q_e (mg g^{-1}) is the amount of adsorbate adsorbed per unit mass of adsorbent in mg g^{-1} and K_L is the Langmuir bisorption constant (L mg^{-1}) relating the free energy of biosorption. The value of Q_{max} was enhanced and raised from 186.63 to 209.54 mg g^{-1} (Table 3) with an increase in the temperature from 293 to 313 K, which could be attributed to a rise in kinetic energy of the sorbent particles due to the rise in temperature. This rise in kinetic energy increases the frequency of collisions between the biosorbent and the sorbate, resulting in enhanced sorption on to the surface of the sorbent [34]. The data obtained with the correlation coefficients (R^2) and (χ^2) at the three varied and different temperatures have been listed in Table S1 (see the Supporting Information). Higher R^2 values >0.99 indicate that the biosorption of Pb(II) onto CAMOL follows the Langmuir model.

The type of the Langmuir isotherm could be predicted based on whether the adsorption was favorable or unfavorable in term of equilibrium parameter or dimensionless constant separation factor R_L, which has been defined and disclosed by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (9)$$

where K_L is the Langmuir constant (L mg^{-1}) and C_0 is the initial adsorbate concentration (mg L^{-1}). While $0 < R_L < 1$ denotes favorable adsorption, $R_L > 1$ is an indication of unfavorable adsorption [35]. The values of R_L 0.15, 0.12 and 0.11 at the three varied and different temperatures were all in the range of 0–1, which indicates the favorable biosorption of Pb(II) by CAMOL.

The Freundlich isotherm [36] is an empirical relationship established upon sorption onto a heterogeneous surface on the assumption that different sites with several adsorption energies are involved, which is given by Eq. (10):

$$q_e = K_F C_e^{1/n} \qquad (10)$$

where K_F (mg g^{-1}) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption, respectively. The values of K_F increased from 16.36 to 22.09 mg g^{-1} (Table 3) with increase in the temperature of the solution from 293 to 313 K. As the K_F is a measurement of adsorption capacity, the increase in the value again confirms that the adsorption process of Pb(II) onto CAMOL is an endothermic process. The $1/n$ values are found in the range of 0.39–0.36, when the temperature was altered from 293 to 313 K. The $1/n$ values between 0 and 1 indicate that the biosorption of Pb(II) onto CAMOL is favorable under the conditions studied. Freundlich correlation coefficients (R^2) and (χ^2) values at 293–313 K have been presented in Table S1 (see the Supporting Information). The R^2 values were in the range 0.902–0.982 for Pb(II) biosorption, respectively. Since these values were lower than the Langmuir values, these results indicate that the Freundlich model was not altogether properly describing the relationship between the amounts of sorbed metal ion and their equilibrium concentrations in the solution.

The equilibrium data were examined using the Dubinin–Radushkevick isotherm [37] model in order to determine the nature of the biosorption processes as physical or chemical. The Dubinin–Radushkevick sorption isotherm is more general than the Langmuir isotherm as its derivation is not based on the ideal assumption such as equipotence of the sorption sites, absence of stoic hindrance between sorbed and incoming particles and surface homogeneity on a microscopic level. The Dubinin–Radushkevick equation has been used to determine the mean free energy of biosorption. The non-linear presentation of the equation is given as:

$$q_e = Q_m \exp\left(-K \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2\right) = Q_m \exp(-k\varepsilon^2) \qquad (11)$$

where Q_m is the maximum amount of the ion that can be sorbed onto a unit weight of sorbent (mg g^{-1}), ε is the polanyi potential which is equal to $RT \ln(1 + 1/C_e)$, where R and T are the universal gas constants (kJ mol^{-1} K^{-1}) and the absolute temperature (K), respectively. The Dubinin–Radushkevick isotherm parameters for the three varied and different temperatures are also listed in Table 3. K is related to the mean free energy of sorption per mole (E) of the sorbate, when it is transferred to the surface of the solid from infinity in the solution and E can be computed using the following relationship:

$$E = \frac{1}{\sqrt{2K}} \qquad (12)$$

From Table 3, the mean sorption energy (E) was evaluated as 8.11–9.80 kJ mol^{-1} for the biosorption of Pb(II) at temperatures ranging from 293 to 313 K. According to the available literature, the E value ranges from 1.0 to 8.0 kJ mol^{-1} for physical adsorption and from 8.0 to 16.0 kJ mol^{-1} for chemical ion exchange [38,39]. Therefore, these results indicate that the adsorption of Pb(II) onto CAMOL might be attributed to chemical ion-exchange mechanism.

The Temkin isotherm [40] is represented by the following equation:

$$q_e = \frac{RT}{b} \ln(K_T C_e) = B_1 \ln(K_T C_e) \tag{13}$$

where the constant $B_1 = RT/b$, which is related to the heat of adsorption, R is the universal gas constant (J mol^{-1} K^{-1}), T is the temperature (K), b is the variation of the adsorption energy (J mol^{-1}) and K_T is the equilibrium binding constant (L mg^{-1}) corresponding to the maximum binding energy. Temkin isotherm assumes that (i) the heat of adsorption of all the molecules in a layer decreases linearly due to the adsorbent–adsorbate interactions and (ii) adsorption is characterized by a uniform distribution of binding energies, to up some maximum binding energy [40,41]. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B_1 and K_T from the slope and the intercept, respectively. Temkin isotherm parameters have also been listed in Table 3. From non-linear regression, the R^2 values which were in the range of 0.9954–0.9823 for CAMOL at the three varied and different temperatures were also lower than the Langmuir values. Therefore, the biosorption of CAMOL did not follow the Temkin isotherm closely.

The χ^2 values of four isotherms are given in Table S1 (see the Supporting Information). The χ^2 values for four isotherms are in the following order Langmuir < Freundlich < Dubinin–Radushkevick < Temkin. Hence the biosorption data of the Pb(II) better fits the Langmuir model as its χ^2 value is less than that of the Freundlich, Dubinin–Radushkevick and Temkin models.

3.7. Thermodynamic analysis

Thermodynamically, in an isolated system, energy cannot be gained or lost; the entropy change is the driving force. In the practice of environmental engineering, both energy and entropy factors ought to be considered in order to determine the processes that occur spontaneously. The thermodynamic parameters including the Gibbs free energy change of adsorption ΔG° (kJ mol^{-1}), enthalpy (ΔH°), and entropy (ΔS°) for the biosorption of Pb(II) onto CAMOL were calculated using the following equations:

$$\Delta G^\circ = -RT \ln K \tag{14}$$

where R is the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T is a absolute temperature (K) and K (L g^{-1}) is an equilibrium constant obtained by multiplying the Langmuir constant Q_{max} and K_L [41].

The enthalpy (ΔH°) and entropy (ΔS°) values were estimated from the following equations:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{15}$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{16}$$

The values of ΔG were calculated from Eq. (14). Reciprocal of temperature ($1/T$) was plotted against $\ln K$, which was a straight line (Fig. S2, see the Supporting Information). The values of ΔH° and ΔS° were evaluated from the slope and intercept of the line in Fig. S2 (see the Supporting Information). The values of ΔG°, ΔH°, and ΔS° for the biosorption of Pb(II) onto CAMOL powder are given in Table S2 (see the Supporting Information). The negative values of ΔG° imply that the biosorption of Pb(II) ions onto CAMOL was

Table 4
Comparison of biosorption capacity of CAMOL with different biosorbents.

Biosorbent	Biosorption capacity (mg g^{-1})	pH	Ref.
Ficus religiosa leaves	37.5	4.0	[44]
Caulerpa lentillifera	29.0	5.0	[45]
Oryza sativa L. husk	8.6	5.0	[46]
Ponkan peel	112.1	5.0	[47]
Grape stalk waste	49.9	5.5	[48]
Yellow passion-fruit waste	151.6	5.0	[49]
Sugar beet pulp	43.5	5.0	[50]
Barley straws	23.20	6.0	[51]
Snowberry	62.16	5.5	[52]
Rice husk	58.1	6.0	[53]
Hazelnut shell	28.18	6.0	[54]
Pecannut shell	211.7	5.5	[55]
Pine bark	76.8	4.0	[56]
Sawdust	88.49	5.0	[57]
Acacia leucocephala bark powder	185.2	4.0	[58]
CAMOL	209.54	5.0	This work

spontaneous. The magnitude of ΔG° also increased with increase in the temperature indicating that the biosorption was more favorable at higher temperatures. The value of ΔH° was positive, indicating the endothermic nature of the biosorption of Pb(II) onto CAMOL in the temperature range of 293–313 K. One plausible explanation of endothermicity of the enthalpy of adsorption is the well-known fact that ions like Pb(II) are well solvated in water. In order that these ions get adsorbed, they are to some extent denuded of their hydration sheath. This dehydration process of ions requires energy. The investigators assume that this energy of dehydration exceeds the exothermicity of the ions attaching to the surface. The implicit assumption is that after adsorption, the environment of the metal ions is less aqueous than it was in the solution state. The removal of water from ions is essentially an endothermic process, and it appears that the endothermicity of the desolvation process exceeds that of the enthalpy of adsorption to a considerable extent [42]. The positive value of ΔS° suggested an increase in randomness at the solid/liquid interface during the biosorption of Pb(II) onto CAMOL [43].

3.8. Comparison of CAMOL with other biosorbents

The biosorption capacities of various biosorbents towards Pb(II) as reported in literature have been presented in Table 4. A comparison between this work and other reported data from the literature [44–58] shows that CAMOL is a better biosorbent for Pb(II) compared to other biosorbents. Therefore, it could be safely concluded that the CAMOL biomass has a considerable potential for the removal of Pb(II) from an aqueous solution.

3.9. Desorption experiment

Desorption is of utmost importance when the biomass preparation/generation is expensive. A successful desorption process requires the proper selection of the eluents, which strongly depends on the type of biosorbent and the mechanism of bisorption. Dilute solutions of mineral acids could be employed for desorption studies. In this study, HCl solution was selected as an eluent to desorb Pb(II) ions from the metal-loaded CAMOL biomass. Various concentrations of HCl (0.1–0.6 M) were used as desorbing media for the enumerated batch sorption studies for the lead loaded CAMOL. From the results of this study, more than 65% desorption of lead occurred by 0.1 M HCl, however the complete desorption (>98%) was achieved with 0.4 M HCl, indicating that moderately higher concentration of HCl was more efficient in releasing Pb(II) ions.
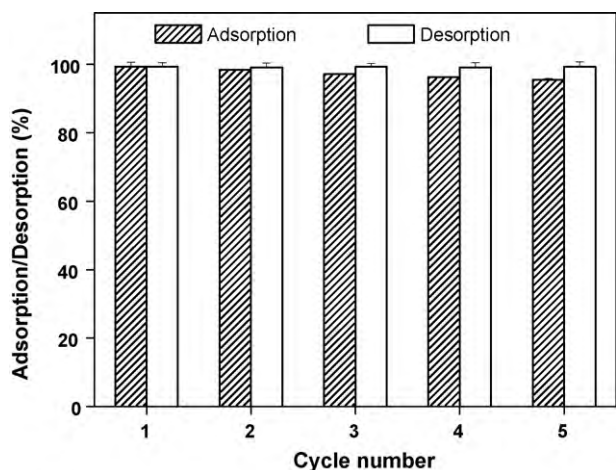
Fig. 6. Five cycles of Pb(II) adsorption–desorption with 0.4 M HCl. Error bars represent ±S.D.

3.10. Recovery of Pb(II) by adsorption–desorption cycle

To make the biosorption process more economical for recovery of Pb(II) using CAMOL and regeneration of spent biosorbent, five cycles of adsorption–desorption studies were carried out using 0.4 M HCl. Desorption and regeneration data have been presented in Fig. 6. An efficiency of 99.34% Pb(II) was obtained using 0.4 M HCl in the first cycle, indicating its suitability for regeneration of the biosorbent. There is a gradual decrease in Pb(II) biosoprtion with an increase in the number of cycles. The small fraction of sorbed metal not recoverable by regeneration presumably represents the metal that is bound through strong interaction and, as a result, sorption capacity is reduced in the subsequent cycle. After a sequence of four cycles, the Pb(II) uptake capacity of the biosorbent had reduced from 99.34% to 95.45%. The desorption efficiency in all four cycles was very high; >98% recovery of Pb(II) was observed in each cycle. The results indicate that the CAMOL can be reused for the biosorption of Pb(II).

3.11. The effect of alkali metal ions over the biosorption yield of Pb(II) ions

Industrial wastewaters and natural waters often contain alkali metal ions such as Na^+, K^+, Mg^{2+} and Ca^{2+}, which may interfere in the uptake of heavy metals by a sorbent [59,60]. Hence, the effect of these ions onto uptake of Pb(II) has been investigated. Calcium and magnesium are particularly important in the area where the hardness of water is high. The biosorption studies were performed by adding 100 mg L^{-1} of Na^+, K^+, Mg^{2+} and Ca^{2+} individually, in 100 mg L^{-1} of Pb(II) solution containing 100 mg of CAMOL and the results have been presented in Fig. S3 (see the Supporting Information). The results indicated that as the concentration of the alkali metal ions increased between 0 and 400 mg L^{-1}, the uptake of Pb(II) ions by CAMOL decreased. Besides, the effect of bivalent Mg^{2+} and Ca^{2+} was much more pronounced than that of single valent Na^+ and K^+.

4. Conclusion

The results of the study revealed that MOL wastes could be converted into an innovative low-cost biosorbent with good biosorption capacity by modifying it with NaOH and citric acid. The biosorption of Pb(II) by CAMOL from aqueous solution was found to be greatly dependent on solution pH. The studies of adsorption isotherms suggests that Langmuir isotherm better explained the experimental data of Pb(II) biosorption by CAMOL than Freundlich, Dubinin–Radushkevick and Temkin isotherms with correlation coefficients greater than 0.99. The values of the maximum adsorption capacity Q_{max} calculated from Langmuir model were also closer to the experimental value of q_e than that of other models. A pseudo-second-order model was more suitable than a pseudo-first-order model with correlation coefficients greater than 0.99. CAMOL could be used for five cycles regenerating with 0.4 M HCl. Results of this investigation proved that CAMOL is a reliable and dependable biosorent with good potential for removal of lead from aqueous media.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.06.010.

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