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Environmentally benevolent urea modified *Saccharum bengalense* as a high capacity biosorbent for removal of Pb(II) ions: metal uptake modeling and adsorption efficiency

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ABSTRACT

Sorption studies of hyper toxic Pb(II) ions from aqueous solution were investigated on simple and urea modified *Saccharum bengalense* (UMSB) biosorbent. Various experimental parameters including pH, temperature, and contact time were studied to evaluate the adsorption behavior. The equilibrium modeling showed that the biosorption data were better represented by the Langmuir and Freundlich models rather than other studied models. Thermodynamic parameters such as changes in standard free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) revealed the spontaneous, endothermic, and feasible nature of adsorption process. The biosorption process followed the pseudo-second-order (PSO) model. The intraparticle diffusion model was applied to investigate the rate determining step. The biosorption efficiency of urea modified biosorbent has also been compared with unmodified material. It was found that the sorption capacity (q_m) increased from 4.73 to 12.65 mg/g on modification. The results of the present investigation suggested that UMSB can be used as an environmentally and economically feasible alternative biosorbent for the removal of Pb(II) from aqueous solutions.

Keywords: Microwave radiation; Lead; *Saccharum bengalense*; Activation energy

1. Introduction

The poisoning by hyper toxic lead can cause a number of diseases such as hypertension, nephritis, and behavioral changes, etc. [1]. Lead pollution has been attributed to disposal from the manufacturing of storage batteries, painting pigments, ammunition, solder, plumbing fixtures, automobiles, cable coverings, radioactivity shields, caulking, and bearings [2]. The permissible safe level for lead in drinking water is 0.05 mg/L according to the US Environmental Protection Agency (EPA). So, lead is very toxic even in low concentration [3]. The most widely used methods for removing Pb(II) from contaminated waters include ion exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration, and adsorption. Most of these methods suffer from drawbacks such as high capital and operational cost; the disposal of the residual metal sludge; and not suitable for small-scale

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industries [4]. Adsorption, by activated carbons, has the most widespread applications in this regard. Activated carbon has high surface area, mesoporous nature, and high adsorption capacity, yet it has limited use due to high operational cost and nonregenerable features. For this reason, there is a need for developing economical and eco-friendly alternative methods/materials for waste minimization [5]. Thus, there is a growing demand to find a low-cost, efficient, and locally available alternative adsorbent for the removal of lead (Pb(II)) from aqueous solutions. A number of attempts have been reported in literature for the use of alternative agro-based materials (biosorbents), such as coconut shell, sawdust, and sugar cane bagasse [6–9] for the treatment of Pb(II) contaminated waters. In such biosorbent materials, binding sites are available due to the presence of functional groups in cellulose, hemi-cellulose, lignin, and silica indicating that the use of biomass may hold potential in the detoxification of polluted waters in a more eco-friendly and cost-effective manner [10,11]. However, there is still a need to search for new inexpensive and locally available materials with high metal sorption capacity.

Modification of materials with different chemical compounds has resulted in an increase in the sorption efficiency [12,13]. It has been found that this causes a change in the functional groups present on the cell wall. Hence, these act as sorbent as well as complexing/chelating agents [14,15]. The modification of the biomass with urea under microwave radiation has been discussed as a green method to enhance the biosorption capacity of the material by increasing the nitrogen content in the form of amino ($-NH_2$) and amide ($-CONH_2$) group [16].

Saccharum bengalense (SB), locally known as "Kana" or "Sarkanda" distributed from North and North-West India to Pakistan and Afghanistan, is fast-growing annual herbage [17]. A large quantity of biomass can be obtained from the stem that may offer a good basis for the selection of SB as a low-cost biosorbent [18,19]. To the best of our knowledge, no investigations have been reported to explore the biosorption characteristics of this plant for the removal of Pb(II) metal ions from aqueous solutions. The present study is aimed to investigate and compare the adsorption efficiency and biosorption capacity of SB and microwave radiated urea modified *Saccharum bengalense* (UMSB) for the removal of hyper toxic Pb(II) metal ions from aqueous solution in a batch procedure. The study will help to decide the potential of the simple as well as the modified material as an alternate to the activated carbon to detoxify the metal contaminated waters.

2. Material and methods

2.1. Collection of *Saccharum bengalense* and its urea modification

Saccharum bengalense plants (1–1.5 years old) were collected from the banks of the river Sutlej in Bahawalpur, Pakistan. The dried plants were ground and the 60–80 mesh (ASTM standards) particles were collected and washed with deionized water. Finally, the biosorbent was oven dried (at 348 K) to constant mass and stored in airtight plastic bottles (oven dry bulk density 0.61 g/mL).

Microwaves were showered on the mixture of SB and reagent grade urea (1:2 by mass) for 14 min in a microwave oven (D131, Dawlance). After it, the mixture was boiled in water for 40 min and filtered while hot. It was further washed with hot water to remove any un-reacted urea. The residue was dried in an oven (348 K) to constant mass and designated as UMSB for use in further experiments. The modification under microwave radiation has been discussed in detail elsewhere [20].

2.2. Characterization of SB and UMSB

The unmodified and modified materials (SB and UMSB) were characterized by Fourier transformation infrared (FTIR), elemental analysis, and BET surface area. Elemental analyses were accomplished by *Perkin-Elmer 2400 Series* II *CHNS*/O Elemental *Analyzer using sulfanilamide as the standard.* BET surface area and single-point surface area of SB and UMSB were determined from the N_2 adsorption isotherm at 77 K in the range of relative pressure 10^{-6}–1.0 with a surface area and pore size analyzer (Autosorb 1, Quantachrome Instruments). Before measurement, the sample was degassed at 300°C for 2 h. A potassium bromide (KBr) disk method was used to scan the FTIR spectra in 4,000–600 cm^{-1} range by using FTIR spectrophotometer (Tensor 27, Bruker Germany).

2.3. Biosorption experiments

All the solutions were prepared from certified reagent grade chemicals and double distilled water was used for all solution preparation/dilution. Lead stock solution (1,000 mg/L) was prepared from $Pb(NO_3)_2$ by dissolving the calculated amount. Nitric acid (HNO_3, 0.1 M) and sodium hydroxide (NaOH, 0.1 M) were used for pH adjustments. Further dilutions were prepared daily as required. A PerkinElmer 2380 atomic absorptions spectrophotometer with air-acetylene flame was used for the determination of lead concentration at 283.3 nm. The stirring (150 rpm) of solutions was performed with a magnetic stirrer. All batch experiments were conducted with adsorbent in flasks closed with glass stoppers to avoid evaporation to elucidate the optimum experimental conditions. The effect of pH on the adsorption of Pb(II) ions onto SB and UMSB was determined by equilibrating the adsorption mixture with dried adsorbent and lead (50 mg/L and 50 mL) solution at different pH values between 1 and 10. The effect of adsorbate concentrations was studied by using concentrations ranging from 10 to 100 mg/L. The effect of time on the adsorption of Pb(II) ions onto SB and UMSB was determined by equilibrating the adsorption mixture with dried adsorbent and lead (50 mg/L and 50 mL) solution at different time intervals between 10 and 80 min. The difference of initial and equilibrium concentrations ($C_0 - C_e$) was considered to be sorbed by the biosorbent. The percentage removal efficiency of adsorbent and equilibrium uptake capacity (q_e) were calculated as follows,

$$\text{Percentage removal (R\%)} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e = (C_0 - C_e) \times \frac{V}{m} \tag{2}$$

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of metal ions in solution, respectively. V (L) is the volume of the solution and m (g) is the dry mass of the adsorbent.

The effect of other parameters like biosorbents dose (0.1–1.0 g), pH (1.0–10.0), contact time (10–80 min), and temperature (383–333 K) was studied in a similar manner. One parameter was varied at a time while keeping other parameters constant.

3. Results and discussion

3.1. Characterization of biosorbents

The results for elemental analysis and BET surface area are given in Table 1. SB contains large number of complex organic components, especially proteins, lipids, and carbohydrate, containing a variety of functional groups including –OH and –COOH. When urea was made to react with SB under microwave radiation, most of the carboxyl groups were modified to amide (–$CONH_2$) groups (Fig. 1). On modification, the nitrogen content increased from 0.9% (SB) to 3.1% (UMSB). This indicated the incorporation of a nitrogen containing group (amide from urea) into the biomass.

The BET surface area was determined by nitrogen adsorption at 77 K. It was found that surface area significantly increased from 9.43 m^2/g (SB) to 17.24 m^2/g (UMSB). This increase in BET surface area, on modification, indicated the increased probability to attach the metal ions with UMSB as compared to SB. Thus, the both materials are found to be porous in nature; considering that UMSB has greater ability to attach Pb(II) ions from aqueous solution.

3.2. Potential functional groups

3.2.1. Comparison of simple and urea modified biosorbents FTIR

The presence of a number of functional groups was confirmed by FTIR, a valuable tool for the purpose. The comparison of FTIR spectra of SB and UMSB can provide information about the changes in the functional groups during the modification process. Similarly, comparing FTIR spectra of biosorbents before and after Pb(II) attachment will help indicate the potential binding sites present in both types of materials. When Pb(II) ions attach a specific functional group, the change in the electron density on the site causes the FTIR band to shift from its original position. The extent of this change (shift) can be attributed to the strength of Pb(II) ions binding. Fig. 2 shows the FTIR spectra of the biosorbents before and after Pb(II) loading/binding.

In the spectrum of SB, the broad band centered at 3359.83 cm^{-1} is a characteristic band of O–H stretching vibration. The single peak at 2913.25 cm^{-1} is due to C–H stretching vibration of CH, CH_2, and CH_3 groups present in lignin. The absorption band at 1730.90 cm^{-1} is attributed to the vibrations by carbonyl groups of ester and carboxylic acid groups. The band at 1601.3 cm^{-1} is due to carbonyl groups of aldehydes

Table 1
BET surface area and elemental analysis for SB and UMSB

	Saccharum bengalense (SB)	Urea modified *Saccharum bengalense* (UMSB)
BET surface area (m^2/g)	9.43	17.24
Single point surface area (m^2/g)	5.78	7.04
Elemental analysis		
C (%)	41.2	42.6
H (%)	4.2	4.0
N (%)	0.9	3.1

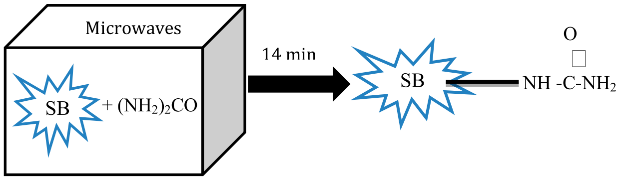

Fig. 1. Modification of SB under microwaves.

and ketones. The peaks at 1425.49 and 1372.42 cm^{-1} are due to C–H bending. The intense peak at 1039.40 cm^{-1} along with the weak peak at 1240.00 cm^{-1} and the shoulder at 1159.41 cm^{-1} are C–O stretching vibration of ethers and alcohols. Thus, SB mainly consists of compounds having oxygen containing functional groups [21].

When the spectrum of UMSB is observed and compared with that of SB, shifts in a number of bands was observed. The broad band appearing between 3,500 and 3,000 cm^{-1} is mainly due to O–H stretching; indicates the presence of hydroxyl functional groups on the surface of the material. The peak at 1697.72 cm^{-1} is attributed to the carbonyl groups from aldehydes and ketones. The medium peak in 1,695–1,630 cm^{-1} region arises due to amide I band. The C–C stretching vibrations of aromatic rings also give peaks in this region. The peaks at 1,455.77 cm^{-1} and 1,417.18 cm^{-1} are due to C–H bending (deformation). The band centered at 1,052.00 cm^{-1} is assigned to C–O–C stretching vibrations in carbohydrates. The peak at 761.60 cm^{-1} arises due to C–H bending of four or more methylene groups. Hence, UMSB is mainly comprised of compounds having oxygen and nitrogen containing functional groups. The shifts in the peaks and the emergence of amid I band indicates the introduction of $-NH_2$ into the biosorbent on modification [20] as shown in Fig. 1.

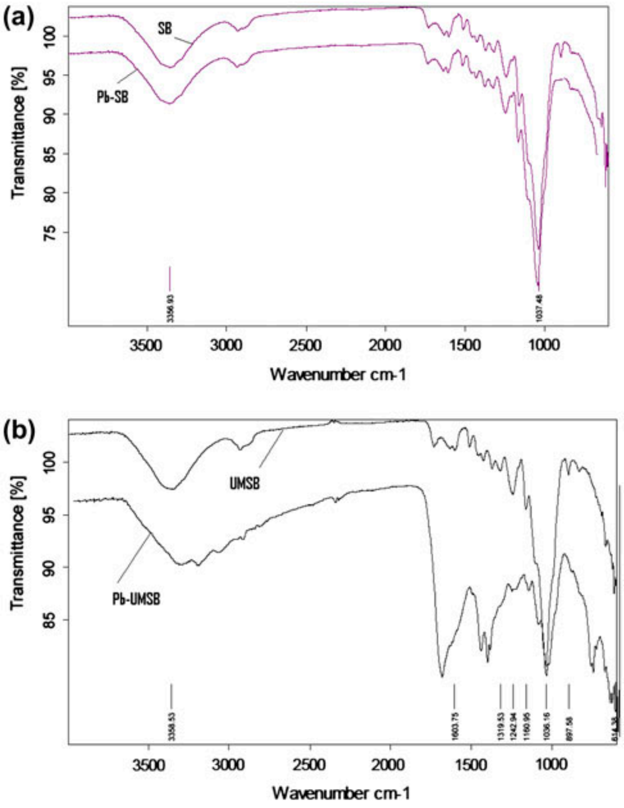

Fig. 2. FTIR spectra of (a) simple and Pb(II) loaded SB and (b) simple and Pb(II) loaded UMSB.

3.2.2. Comparison of Pb loaded SB and UMSB FTIR

In order to have an insight into to the potential functional groups present in SB and UMSB responsible for Pb(II) uptake, FTIR spectra were obtained after loading Pb(II) ions onto the biosorbents. It can be observed from Fig. 1 that there were clear shifts in the positions of the bands obtained from oxygen containing functional groups i.e. from 3,359.83 to 3,353.82 cm^{-1} (O–H), 1,039.44 to 1,052.23 cm^{-1} (–O–C), and from 1,730.99 to 1,601.57 cm^{-1} (–COOH).

FTIR spectrum of Pb(II)-loaded-UMSB indicated the shifts in the frequency of a number of peaks/bands from phenolic (–OH), methoxy ($-OCH_3$), carboxylic acid (–COOH), and amide I ($-CONH_2$) functional groups. These shifts are 3,203.86–3,358.58 cm^{-1}, 1,416.32–1,603.75 cm^{-1}, 1,179.60–1,160.95 cm^{-1}, 1,051.76–1,036.16 cm^{-1}, and 616.38–614.38 cm^{-1}, respectively.

3.3. Equilibrium models

The equilibrium models are considered to be one of the most important tools in understanding the mechanism of the adsorption and thus the role of adsorption in biosorption. In order to have an insight into the mechanism of Pb(II) adsorption on SB and UMSB, the experimental data were fitted to the equilibrium isotherm equations. The different isotherm parameters determined from various plots are presented in Table 2.

3.3.1. Langmuir adsorption isotherm

The Langmuir adsorption model assumes that adsorption takes place at specific homogeneous sites within the adsorbent and a monolayer of the adsorbate is formed [22]. The linear form of the Langmuir model is shown as under [23]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{3}$$

A graph was plotted between C_e/q_e and C_e and the constants of the equations i.e. q_m the monolayer adsorption capacity of the adsorbent (mg/g) and K_L the Langmuir constant (L/mg) were determined from the slope and intercept (Fig. 3(a)). The values for these parameters are given in Table 2.

It was found that in the Langmuir model, the calculated q_m was higher for UMSB as compared to that for SB and almost three times increase was found in q_m value for UMSB than that for SB. The value of coefficient of determination, R^2, helps in deciding which of the mathematical models is being followed under particular set of conditions. The R^2 value was found to be 0.998 (SB) and 0.963 (UMSB). So, the Pb(II) biosorption onto SB and UMSB followed Langmuir model. Hence, it was concluded that q_m of the Pb–SB system was 4.73 mg/g and for Pb–UMSB it was 12.65 mg/g of the dried biomass. The increase in the Pb(II) sorption by UMSB was due to the modification by urea under microwave radiation. Due to the increased surface area and the increased number of sites on UMSB than on SB, the biosorption capacity was found to be greater.

The Langmuir specific surface area of SB and UMSB for monolayer sorption of Pb(II) ions was determined using Eq. (4).

$$S_L = \frac{q_m N A}{M} \tag{4}$$

where q_m (mg/g) is the biosorption capacity, N is Avogadro's number (6.022×10^{23}), A (A^{o2}) is the cross sectional area of metal ion, and M is the atomic mass of metal ion. The atomic mass of Pb(II) is 207 and the cross-sectional area is 5.56 A^{o2} (the radius of Pb(II) ions for close packed monolayer is 1.33 Å [24]). The specific surface area was found to be 0.94 m^2/g for SB and 40.42 m^2/g for UMSB.

3.3.2. Freundlich isotherm

The Freundlich model is an empirical equation and can be used to describe adsorption on heterogeneous systems [25]. The linear equation of the Freundlich adsorption model is,

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

where K_F (L/mg) and n (dimensionless) are the Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of nonlinearity, respectively. The plot of ln C_e vs. ln q_e for the adsorption was employed to determine the value of K_F and n, respectively (Fig. 3 (b)). The values for these parameters are given in Table 2.

The "n" value provides information about the process to be favorable or unfavorable under studied conditions. The values of "n" were greater than "1.00" in both cases i.e. for SB and UMSB. This shows that the adsorption onto the heterogeneous systems is quite favorable. The R^2 value is greater than 0.98 in both cases, thus the sorption of Pb(II) by SB as well by

Table 2
Equilibrium modeling of the biosorption of Pb(II) ions by SB and UMSB

Equilibrium model	Biosorbent		Parameters	
Langmuir model		q_m (mg/g)	K_L (L/mg)	R^2
	SB	4.73	0.043	0.998
	UMSB	12.65	0.032	0.963
Freundlich model		K_F (L/mg)	n	R^2
	SB	0.232	1.2	0.988
	UMSB	0.322	1.05	0.990
Temkin model		K_T (L/mg)	B	R^2
	SB	0.625	1.09	0.931
	UMSB	0.383	2.417	0.959
Dubinin–Radushkevich model		q_m (mg/g)	β	R^2
	SB	2.16	3×10^{-6}	0.855
	UMSB	4.37	4×10^{-6}	0.912

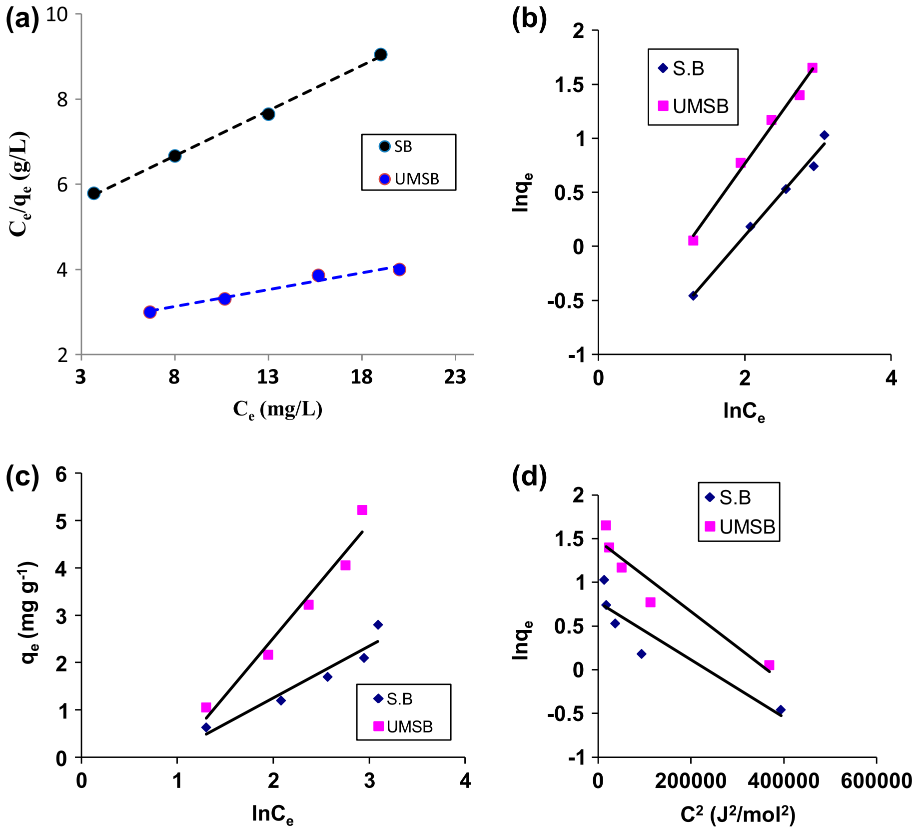

Fig. 3. (a) Langmuir adsorption Isotherm, (b) Freundlich adsorption Isotherms, (c) Temkin adsorption Isotherm, (d) Dubinin–Radushkevich (D–R) adsorption Isotherm for sorption of Pb(II) ions on SB and UMSB (pH 5.5, 50 min and 500 mg (SB), 40 min and 300 mg (UMSB), 313 K, 125 rpm).

UMSB followed Freundlich model and the sorption is favorable under the specific set of conditions.

3.3.3. Temkin isotherm

Temkin isotherm [26] is expressed, in linear form by Eq. (6).

$$q_e = B \ln K_T + B \ln C_e \tag{6}$$

where $B = RT/b$ is related to the heat of adsorption, T (K) is the absolute temperature, R is the universal gas constant (8.3143 J/molK), b indicates the adsorption potential of the adsorbent (J/mol), and K_T is the equilibrium binding constant (L/mg). The parameters for the Temkin model are obtained from the plot of q_e vs. ln C_e (Fig. 3(c)). The values for these parameters are given in Table 2. The R^2 values indicated that the adsorption of Pb(II) on SB and UMSB did not follow Temkin model. Hence, it is clear that heat of adsorption does not decrease linearly with adsorption onto SB as well as UMSB.

3.3.4. Dubinin–Radushkevich (D–R) model

The linear equation of D–R isotherm [27] is shown in Eq. (7).

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{7}$$

where β (mol^2/kJ^2) is a constant connected with the mean free energy of adsorption per mole of the adsorbate and ε (J/mol) is the Polanyi potential, which is equal to,

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{8}$$

where R (J/mol K) is the gas constant and T (K) is the absolute temperature. By plotting ln q_e vs. ε^2, it is possible to determine the value of q_m from the intercept and the value of β from the slope. The values of parameters determined from Fig. 3(d) are given in Table 2.

The biosorption mean free energy (E_s; kJ/mol) can be calculated as follows,

$$E_s = \frac{1}{\sqrt{2\beta}} \tag{9}$$

Physical and chemical nature of adsorption can be predicted by biosorption mean free energy (E_s, kJ/mol) [28]. The adsorption is physical in nature, if $E_s < 8$ kJ/mol and adsorption will be chemical in nature for E_s between 8 and 16 kJ/mol. The mean free energy of adsorption (E_s) was found to be 0.409 and 0.353 kJ/mol for SB and UMSB, respectively. These values showed that the adsorption was physical in nature.

There are two indicators for D–R model to decide whether the system follows it or not i.e. R^2 value and comparison of experimental and calculated q_m values. The calculated q_m value for SB is 2.8 mg/g which is not comparable with experimental q_m value (2.16 mg/g). Similarly, the experimental q_m (4.37 mg/g) and calculated q_m (5.2 mg/g) values for UMSB were found to be significantly different. The R^2 values were less than 0.98 in both cases, hence it is indicated that the adsorption of lead onto SB as well as onto UMSB did not follow the Dubinin–Radushkevich isotherm. The description of the sorption of Pb(II) on UMSB by the Dubinin–Radushkevich (D–R) equation is a pointer to the heterogeneity of the surface of the SB.

Since, D–R model is not being followed by the both systems; these E_s values provide only an assessment of the nature of the processes. So, further studies are required to understand the nature of the adsorption.

From the comparison of different mathematical models, it was found that biosorption of Pb(II) by SB as well as UMSB followed Langmuir and Freundlich models. The R^2 values were quite close for other adsorption models. Due to the complex nature of the biosorbent, the nature of forces responsible to attach Pb(II) (the mechanism) is not fully understood. The present studies show the potential role of adsorption in the mechanism of biosorption and is in conformity with the previous studies reported in literature about the removal of Pb(II) by various biosorbents.

3.4. *Effect of contact time: kinetics of the process*

Effect of contact time on adsorption was studied in the range of 10–80 min. In both cases, it was observed that the equilibrium biosorption capacity (q_e, mg/g) increased rapidly with the increase in the contact time. Increase in removal efficiency with increase in time of contact is due to the fact that more time becomes available for metal ions to sorb onto the biosorbents (SB and UMSB). Initial removal occurred immediately as soon as the metal and the adsorbent came into contact, but after some time, the number of active sites available for the biosorption decreased and so the metal needed more time to reach available active sites for binding. Thus, the slope of the q_e versus t curve decreased and the curve became almost parallel to the time axis after 40 min (UMSB) and 50 min (SB). No more significant variation/increase in the q_e value, after this time, was observed in both cases. It was concluded that metal should remain in contact for at least 40 min for UMSB and 50 min for SB for the optimum uptake/sorption. This time of contact is relatively smaller as compared to a number of other biosorbents reported for the minimization of Pb(II) from aqueous solutions [20,29,30].

The pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models have been applied for the experimental data to analyze the kinetics of Pb(II) ions. The linear mathematical equations for PFO and PSO are shown in Eqs. (10) and (11), respectively

$$\ln(q_e - q_t) = \ln q_e - k_f t \tag{10}$$

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{t}{q_e} \tag{11}$$

where q_t and q_e (mg/g) are amounts of metal ions sorbed at time "t (min)" and at equilibrium, respectively, k_f (1/min) and k_s (mg/g min) are the rate constants for PFO and PSO kinetics.

The plots for PFO and PSO kinetic models are shown in Fig. 4(a) and (b). The kinetic parameters for the adsorption of Pb(II) ions onto SB and UMSB are summarized in Table 3. Comparison of the calculated and experimental q_e values indicated a significant difference when calculated for PFO for both the biosorbent materials. R^2 value also supports this inference. For PSO, the R^2 values are quite near to 0.98. In addition, the calculated q_e values are comparable to the experimental q_e values, for SB as well as UMSB. Hence, it can be inferred that the biosorption of Pb(II) by SB and UMSB followed the PSO kinetic model. Several authors who studied the biosorption of divalent metal ions on various sorbents reported that the biosorption mostly followed PSO kinetics [20,29–32].

In order to have an insight into the rate determining step, Weber and Morris model i.e. intraparticle diffusion model was employed [33]. The linear form is shown in Eq. (12).

$$q_t = k_{WM}\sqrt{t} + C \tag{12}$$

where k_{WM} is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and C is the intercept. The Weber–

Morris sorption model assumes that the three steps involved in the biosorption process are: (a) surface saturation, (b) external transport of the mass, and (c) intraparticle diffusion.

The rate determining step among these steps can be determined on the basis of a graph between q_t and $t^{1/2}$. The values of parameters of the model determined from Fig. 4(c) are given in Table 3. Fig. 4(c) shows dual nature of the curves due to the varying extent of biosorption in the initial and final stages of the process for lead biosorption on SB as well on UMSB. This can be explained on the grounds that more than one types of diffusion processes are involved in the biosorption. The initial part of curves, having an increasing slope, indicated the boundary layer diffusion, whereas the linear parts at the later stages of the curves indicated the intraparticle diffusion. Since, the curves are not linear and do not pass through the origin (intercept "C" is not zero), the boundary layer diffusion was found to be the rate determining step for the biosorption of Pb(II) on SB and UMSB. However, further studies are required to establish this observation.

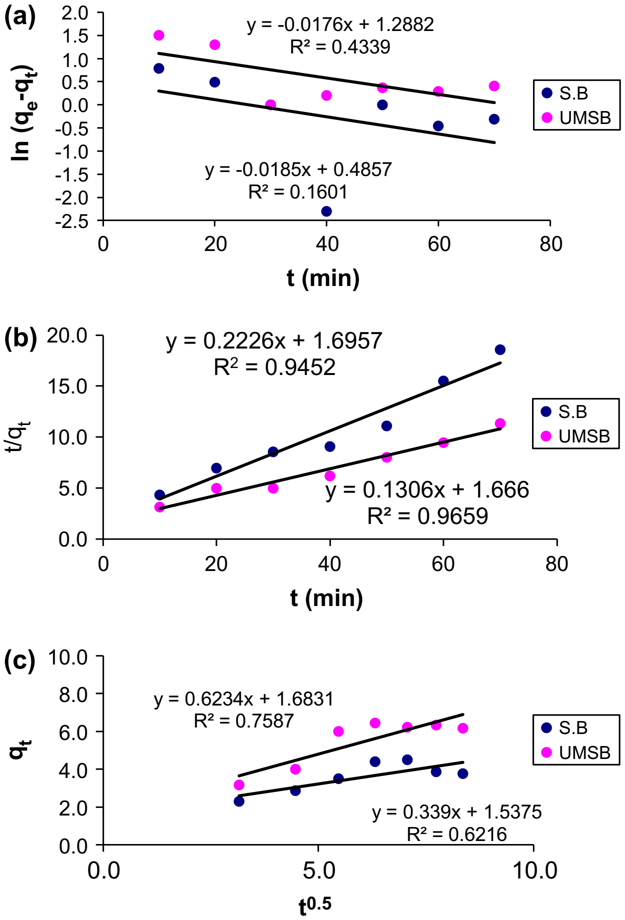

Fig. 4. (a) Pseudo-first-order kinetics, (b) pseudo-second-order kinetics, and (c) intra-particle diffusion kinetic model for sorption of Pb(II) ions on SB and UMSB (pH 5.5, 50 mg/L Pb(II), 500 mg (SB), 300 mg (UMSB), 313 K, 125 rpm).

3.5. Effect of pH

The pH of the medium is a very important parameter as it affects the biosorption process in two ways: it not only affects the characteristics of the biosorbent material but the speciation of metal ions is also influenced by change in pH. Lead ions are present as Pb(II) at a $\text{pH} < 6$. Above a pH of 6, Pb(II) ions start precipitating as $Pb(OH)_2$. This precipitation causes decrease in the interaction of Pb(II) ions with the biomass. On the other hand, at a very low pH, there is excess of H^+ ions in the solution and they dominantly cover the active sites on the biosorbent making it a positive species [20].

In the present investigation, the biosorption of lead was studied at pH range 1–10 with biomass dose 0.5 g for SB and 0.3 g for UMSB in an orbital shaker for 50 min at 313 K ($C_0 = 50$ mg/L). Agitation was continued for 50 min for Pb(II)–SB system and 40 min for Pb(II)–UMSB system. It was observed that pH significantly affected the biosorption process (Fig. 5(a)). As the pH rises, biosorption removal efficiency increases for the both adsorbents till a pH of 5.5 and then it decreases. The best results are obtained at pH 5.5. The maximum removal efficiency for SB was 89.3% ($q_e = 4.46$ mg/g) and for UMSB it was 96% ($q_e = 8.0$ mg/g). At lower pH, H^+ competes with metal cations for the available adsorption site, whereas at higher pH, the overall surface charge on the SB and UMSB became negative and biosorption decrease. As the pH of the medium is increased, the competition between positively charged metal ions and H^+ ions decreases and metal ions become the dominant species to sorb on the biosorbent. This is true as far as the metal ions are present as positively charged species in the solution. So an optimum pH is expected to lie in the acidic region [16]. Similar results have been reported by a number of earlier researchers studying metal biosorption on different biomasses [30,32,34,35].

3.6. Effect of the adsorbent dosage

The variation in adsorption capacities between the various adsorbent dosages could be related to the number of available active sites responsible for the adsorption of metal ions from solution. With increasing adsorbent dosage, greater number of active sites and more surface area are available for adsorption.

Table 3
Kinetic modeling of the biosorption of Pb(II) by SB and UMSB

Kinetic model	Biosorbent		Parameters		
Pseudo-first-order		k_f (1/min)	Calculated q_e (mg/g)	Experimental q_e (mg/g)	R^2
	SB	0.018	1.62	4.5	0.160
	UMSB	0.017	3.60	7.67	0.437
Pseudo-second-order		k_s (g/mg min)	Calculated q_e (mg/g)	Experimental q_e (mg/g)	R^2
	SB	0.029	4.49	4.50	0.945
	UMSB	0.010	7.65	7.67	0.965
Intra-particle diffusion		k_{WM} (mg/g min$^{1/2}$)	C (intercept)		R^2
	SB	0.621	1.53		0.339
	UMSB	0.623	1.68		0.758

Hence, the increase in the dose caused an increase in the q_e value (Fig. 5(b)). When the dose of biomass was increased above 0.5 g/L, the q_e value decreased. The decrease in q_e value may be attributed to the overlapping or aggregation of active sites of SB and UMSB. Thus, the total surface area of the biomass decreases. It can be found that the optimum amount of UMSB for further adsorption experiments was selected as 0.3 g/50 mL ($q_e = 7.9$ mg/g) and for SB was 0.5 g/50 mL ($q_e = 4.5$ mg/g). Similar results have been reported earlier on different biomasses, studying metal biosorption [20,29,30,36].

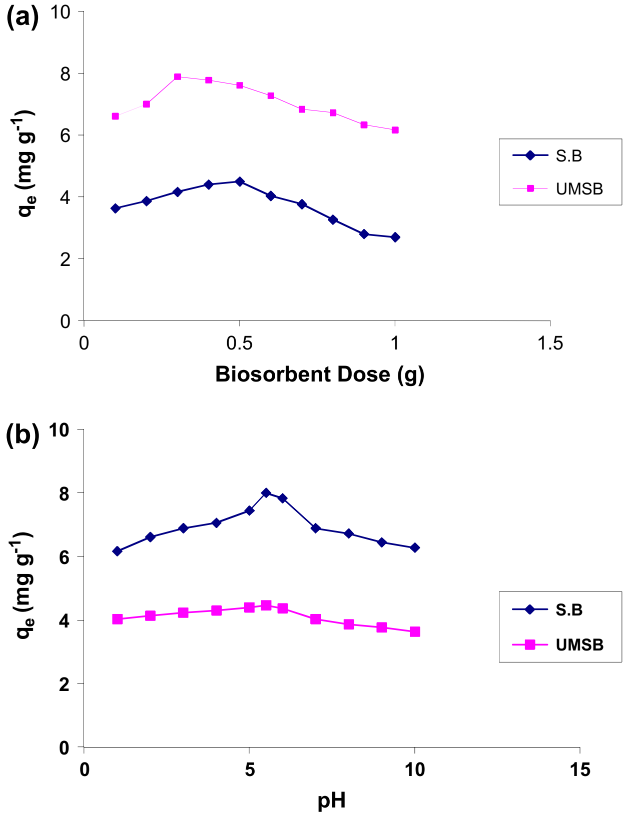

Fig. 5. (a) Effect of pH (50 min and 500 mg (SB), 40 min and 300 mg (UMSB), 313 K, 125 rpm) and (b) effect of biosorbent dose for sorption of Pb(II) ions on SB and UMSB (pH 5.5, 50 min (SB), 40 min (UMSB), 313 K, 125 rpm).

3.7. *Effect of temperature: thermodynamics*

Temperature is an important parameter as the change in the temperature provides information about the feasibility and nature of the process. It also helps to determine the thermodynamic quantities. As the temperature of solution varies, the kinetic energy and diffusion of ions are affected.

Effect of temperature was studied in the range of 283–313 K. It was observed that the biosorption removal efficiency increased from 56.92 to 93.42% (for SB) and from 67.33 to 96.30% (for UMSB) as the temperature of the system increased from 283 to 313 K. The increase in adsorption can be assigned to the changes in pore size or an increase in kinetic energy of the adsorbents. The increase in percentage of Pb(II) adsorption with increase in temperature indicated the endothermic nature of biosorption [37].

In order to describe thermodynamic properties of the adsorption of Pb onto SB and UMSB, changes in standard Gibbs free energy (ΔG°), enthalpy ($\Delta \overset{\circ}{H}$), and entropy ($\Delta \overset{\circ}{S}$) were determined. The Gibbs free energy tells about the feasibility of the reaction/process. It also indicates the degree of spontaneity of the sorption process and the higher negative value reflects a more energetically favorable sorption. It is calculated as follows,

$$\Delta G^0 = -RT\ln K_D \tag{13}$$

where R is the universal gas constant (8.314 J/mol K), T is the temperature (K), and K_D is the distribution coefficient. K_D is calculated as [38,39].

$$K_D = \frac{C_0 - C_e}{C_e} \tag{14}$$

C_0 (mg/L) and C_e (mg/L) are initial and equilibrium concentrations of Pb(II) ions.

To calculate other thermodynamic parameters, a graph was plotted using Eq. (15) (Fig. 6(a)). The values are given in Table 4.

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{15}$$

It was found that the values of ΔG° decreased with an increase in temperature, thereby indicating an increase in adsorption at higher temperature and endothermic nature of the adsorption process. Hence, an increase in temperature favors the removal process. The negative values of ΔG° confirmed the thermodynamic feasibility of the process and spontaneous nature of biosorption on SB and UMSB. The positive value of ΔH° indicated the endothermic nature of the process, while the positive values of ΔS° reflected the increase in randomness at solid/solution interface and affinity of the adsorbent material [40,41]. As the process is endothermic in nature, the materials can be used to detoxify polluted waters at higher temperatures. This is an added advantage for the treatment of industrial wastewaters as these usually are disposed off at temperatures higher than room temperature.

3.8. Activation energy

The kinetic parameters at different temperatures were plotted in terms of the Arrhenius Equation [42] as shown below:

$$\ln k_s = \ln k_0 - \frac{E_a}{RT} \tag{16}$$

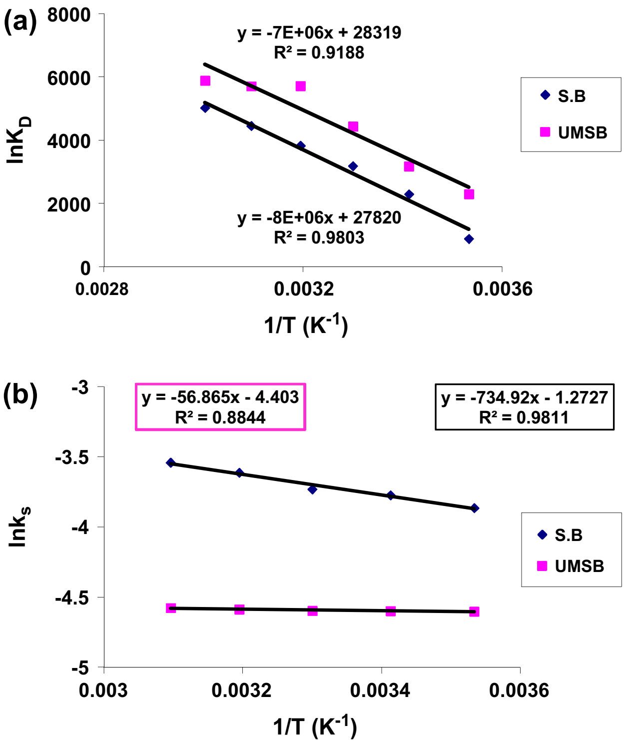

Fig. 6. (a) Thermodynamics parameters and (b) activation energy by Arrhenius plot for sorption of Pb(II) ions on SB and UMSB (pH 5.5, 50 min and 500 mg (SB), 40 min and 300 mg (UMSB), 125 rpm).

where k_s (g/mg min) is the PSO rate constant, k_0 (g/mg min) is the independent temperature factor, R (J/mol K) is the gas constant, and T (K) is the solution temperature [41]. The k_s values were determined at different temperatures (figure not shown). A plot of ln k_s vs. $1/T$ produced a straight line and the corresponding activation energy was determined from the slope of linear plot shown in (Fig. 6(b)). The activation energy for the biosorption of Pb(II) on SB and UMSB is given in Table 4. From the values of activation energy, it appears that the biosorption of Pb(II) on SB and UMSB is a physical adsorption process.

The magnitude of activation energy gives an idea about the nature of adsorption which is mainly physical or chemical. Low activation energies (5–50 kJ/mol)

Table 4
Thermodynamic modeling of biosorption of Pb(II) by SB and UMSB in temperature range of 283–313 K

Biosorbent	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K mol)	E_a (kJ/mol)
SB	(−0.8)–(−5.0)	+66.51	+231.30	6.110
UMSB	(−2.3)–(−5.9)	+58.20	+235.45	0.472

Table 5
Comparison of biosorption performance of SB and UMSB with some other biosorbents

Biosorbent	$q_{\max}$ (mg/g)	pH	Equilibrium time (min)	Equilibrium model	Kinetic model	
EDA-modified seaweed (*Caulerpa serrulata*)	2.16	4.5	10	Freundlich	PSO	[51]
Biochar rice husk (R300)	2.40	5.0	300	Langmuir	PSO	49
Hydrogen peroxide treated Bagasse fly ash	2.5	6.0	60	Langmuir	PSO	[47]
Biochar pinewood (P300)	4.25	5.0	300	Langmuir	PSO	[49]
Sacharum bengalense	4.73	5.5	50	Freundlich	PSO	Present work
Formaldehyde in sulfuric acid modified sawdust (*Pinus sylvestris*)	9.78	5.5	20	Langmuir	PSO	[50]
Modified peanut husk	29.14	4	180	Freundlich	PSO	[48]
Urea-modifed *Triticum aestivum*	31.85	6.0	10	Langmuir	PSO	[20]
Gossypium hirsutum (Cotton)	196.40	5.0	–	Langmuir	PSO	[30]
Urea modified *Sacharum bengalense*	12.65	5.5	40	Freundlich	PSO	Present work

are characteristics for physical adsorption, while higher activation energies (60–800 kJ/mol) suggest chemical adsorption [43]. This is because the temperature dependence of the pore diffusivity is relatively weak. Here, the diffusion process refers to the movement of the solute to an external surface of adsorbent and not diffusivity of material along micropore wall surfaces in a particle [44]. Therefore, the affinity of Pb(II) for SB as well as for UMSB may be assigned to van der Waals forces and electrostatic attractions between the metal and the surface of the particles. This low value of E_a generally indicates a diffusion controlled process and higher values represent a chemical reaction process. It can, therefore, be concluded that the E_a value calculated from the data suggests a diffusion-controlled process; a physical step in the adsorption process [45,46].

3.9. Comparison of SB and UMSB with other biosorbents

Due to differences in the growth, experimental, and modification conditions, it is quite difficult to directly compare different biosorbents employed for the eradication of Pb(II) ions from aqueous solutions. Hence, SB and UMSB have been compared in terms of biosorption capacity, time of contact, and dose of material. The materials have also been compared with other biosorbents in order to observe its potential as an alternative to these materials (Table 5). It can be easily observed that the biosorption capacity of SB is low as compared to a number of other materials, since it provides a shorter time of contact and indicates a faster removal of toxic metal ions [47–51]. On modification, not only the time of contact decreases for UMSB, but the biosorption capacity also increased at a very high rate. So, it can be concluded that UMSB has potential as an alternative to these materials for the removal of hyper toxic Pb(II) ions from aqueous solutions.

4. Mechanism of Pb(II) biosorption by SB and UMSB

The results of characterization of the SB and UMSB, for example the alteration of functional groups and change in surface are on urea modification, can be used as evidences in proposing the mechanism of biosorption of Pb(II) on SB and UMSB. Also, biosorption kinetics can be used to explain the biosorption mechanism.

From the comparison of FTIR spectra of SB, UMSB, and Pb(II) loaded biosorbents, it was found that Pb(II) mostly attached with the oxygen containing functional groups, in addition to the introduced amide group. Thus, the functional groups like –OH, –COOH, $–OCH_3$ and $–NH_2$ play an important role in the biosorptive removal of Pb(II) from aqueous solutions. It was also possible that Pb(II) ions were bound with carboxylate groups in the lignocellulosic structure of SB by making ionic forces with carboxylic oxygen atoms. These oxygen atoms exhibited negative charge in their structure as a result of the dissociation of carboxylic groups. The negatively charged oxygen atom in carboxylate anions will coordinate with lead cations, resulting in the formation of metal–carboxylate complexes (COO–Pb) on the SB and UMSB surface.

On the basis of kinetics studies, the pseudo-second-order models fitted well on experimental data. Therefore, a chemisorption controlled mechanism can be proposed as the mechanism leading the biosorption process. Similar mechanisms have been reported earlier, studying metal biosorption [52,53].

5. Conclusions

Sorption studies of Pb(II) from aqueous solution were investigated for un-modified and UMSB. The isotherms exhibited the Langmuir and Freundlich behavior, which indicates a heterogeneous surface binding. The adsorption data followed the pseudo-second-order kinetic model and boundary layer diffusion was rate controlling for metal ion adsorption process. Thermodynamic parameters, such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), have been calculated and these revealed the spontaneous, endothermic, and feasible nature of adsorption process. Urea modification is a cost effective process for increasing surface area and metal uptake capacity of biomaterial. The strength of this research work is that both biomass and modification material urea are easily available, biodegradable, and cost-effective and the modification process is also simple. It can be concluded that UMSB can be an economic alternate material for the removal of toxic metal Pb(II) in wastewater treatment processes.

References

[1] C.L. Ake, K. Mayura, H. Huebner, G.R. Bratton, T.D. Phillips, Development of porous clay-based composites for the sorption of lead from water, J. Toxicol. Environ. Health A 63 (2001) 459–475.

[2] S. Tunali, T. Akar, A.S. Özcan, I. Kiran, A. Özcan, Equilibrium and kinetics of biosorption of Pb(II) from aqueous solutions by *Cephalosporium aphidicola*, Sep. Purif. Technol. 47 (2006) 105–112.

[3] S.C.S. Bhattacharjee, S. Maity, S. Kar, P. Thakur, G. Bhattacharyya, Removal of lead from contaminated water bodies using sea nodule as an adsorbent, Water Res. 37 (2003) 3954–3966.

[4] M. Kobya, E. Demirbas, E. Senturk, M. Ince, Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone, Biores. Technol. 96 (2005) 1518–1521.

[5] Ö. Gerçel, H.F. Gerçel, Adsorption of lead(II) ions from aqueous solutions by activated carbon prepared from biomass plant material of *Euphorbia rigida*, Chem. Eng. J. 132 (2007) 289–297.

[6] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol. 98 (2007) 2243–2257.

[7] S. Doyurum, A. Çelik, Pb(II) and Cd(II) removal from aqueous solutions by olive cake, J. Hazard. Mater. 138 (2006) 22–28.

[8] R. Ayyappan, A. Carmalin Sophia, K. Swaminathan, S. Sandhya, Removal of Pb(II) from aqueous solution using carbon derived from agricultural wastes, Process Biochem. 40 (2005) 1293–1299.

[9] K. Zhang, W.H. Cheung, M. Valix, Roles of physical and chemical properties of activated carbon in the adsorption of lead ions, Chemosphere 60 (2005) 1129–1140.

[10] H. Gao et al., Characterization of Cr (VI) removal from aqueous solutions by a surplus agricultural waste–rice straw, J. Hazard. Mater. 150 (2008) 446–452.

[11] U. Farooq, J.A. Kozinski, M.A. Khan, M. Athar, Biosorption of heavy metal ions using wheat based biosorbents – a review of the recent literature, Bioresour. Technol. 101 (2010) 5043–5053.

[12] J. Wang, C. Chen, Biosorption of heavy metals by *saccharomyces cerevisiae*: A review, Biotechnol. Adv. 24 (2006) 427–451.

[13] S. Deng, Y.P. Ting, Polyethylenimine-modified fungal biomass as a high-capacity biosorbent for Cr(VI) anions: Sorption capacity and uptake mechanisms, Environ. Sci. Technol. 39 (26) (2005) 8490–8496.

[14] K.L. Kadam, L.H. Forrest, W.A. Jacobson, Rice straw as a lignocellulosic resource: Collection, processing, transportation, and environmental aspects, Biomas. Bioener. 18 (2000) 369–389.

[15] U.S. Orlando, A.U. Baes, W. Nishijima, M. Okada, Preparation of chelating agents from rice straw by microwave radiation as an alternative ecologically benign procedure, Green Chem. 4 (2002) 555–557.

[16] U. Farooq, M.A. Khan, M. Athar, J.A. Kozinski, Effect of modification of environmentally friendly biosorbent wheat (*Triticum aestivum*) on the biosorptive removal of cadmium (II) ions from aqueous solution, Chem. Eng. J. 171 (2011) 400–410.

[17] S.A. Tirmzi et al., Inorganic nutrients of *Saccharum bengalense*, J. Chem. Soc. Pak. 27 (2005) 186–189.

[18] M.I. Din, M.L. Mirza, Biosorption potentials of a novel green biosorbent *Saccharum bengalense* containing cellulose as carbohydrate polymer for removal of Ni(II) ions from aqueous solutions, Int. J. Biol. Macromol. 54 (2013) 99–108.

[19] M. Imran Din, M.L. Mirza, S. Ata, M. Athar, I.U. Mohsin, Thermodynamics of biosorption for removal of Co(II) ions by an efficient and ecofriendly biosorbent (*Saccharum bengalense*): Kinetics and isotherm modeling, E-J. Chem. 2013 (2013) 11.

[20] U. Farooq, M.A. Khan, M. Athar, M. Sakina, M. Ahmad, Environmentally benign urea-modifed *triticum aestivum* biomass for lead(II) elimination from aqueous solutions, Clean – Soil, Air, Water 38 (2010) 49–56.

[21] M.Á. Martín-Lara, I.L.R. Rico, I.d.l.C.A. Vicente, G.B. García, M.C. de Hoces, Modification of the sorptive characteristics of sugarcane bagasse for removing lead from aqueous solutions, Desalination 256 (2010) 58–63.

[22] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[23] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J. 156 (2010) 2–10.

[24] M.F. Sawalha, J.R. Peralta-Videa, J. Romero-González, J.L. Gardea-Torresdey, Biosorption of Cd(II), Cr(III), and Cr(VI) by saltbush (*Atriplex canescens*) biomass: Thermodynamic and isotherm studies, J. Colloid Interf. Sci. 300 (2006) 100–104.

[25] H.M.F. Freundlich, Über die adsorption in lo¨sungen, Z. Phys. Chem. 57 (1906) 385–470.

[26] M.I. Temkin, Adsorption equilibrium and the kinetics of processes on nonhomogeneous surfaces and in the interaction between adsorbed molecules, Zh. Fiz. Chim. 15 (1941) 296–332.

[27] B. Hameed, I. Tan, A. Ahmad, Adsorption isotherm, kinetic modeling and mechanism of 2, 4, 6-trichlorophenol on coconut husk-based activated carbon, Chem. Eng. J. 144 (2008) 235–244.

[28] S.N. Milmile, J.V. Pande, S. Karmakar, A. Bansiwal, T. Chakrabarti, R.B. Biniwale, Equilibrium isotherm and kinetic modeling of the adsorption of nitrates by anion exchange Indion NSSR resin, Desalination 276 (2011) 38–44.

[29] O.S. Lawal, A.R. Sanni, I.A. Ajayi, O.O. Rabiu, Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of *Calophyllum inophyllum*, J. Hazard. Mate. 177 (2010) 829–835.

[30] M. Riaz, R. Nadeem, M.A. Hanif, T.M. Ansari, K.-U. Rehman, Pb(II) biosorption from hazardous aqueous streams using *Gossypium hirsutum* (Cotton) waste biomass, J. Hazard. Mater. 161 (2009) 88–94.

[31] S. Tunali Akar, D. Arslan, T. Alp, Ammonium pyrrolidine dithiocarbamate anchored *Symphoricarpus albus* biomass for lead(II) removal: Batch and column biosorption study, J. Hazard. Mater. 227–228 (2012) 107–117.

[32] A. Sarı, M. Tuzen, Ö.D. Uluözlü, M. Soylak, Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass, Biochem. Eng. J. 37 (2007) 151–158.

[33] A. Witek-Krowiak, Analysis of influence of process conditions on kinetics of malachite green biosorption onto beech sawdust, Chem. Eng. J. 171 (2011) 976–985.

[34] J.P. Chen, S. Wu, K.-H. Chong, Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption, Carbon 41 (2003) 1979–1986.

[35] S. Tunali Akar, S. Arslan, T. Alp, D. Arslan, T. Akar, Biosorption potential of the waste biomaterial obtained from *Cucumis melo* for the removal of Pb^{2+} ions from aqueous media: Equilibrium, kinetic, thermodynamic and mechanism analysis, Chem. Eng. J. 185–186 (2012) 82–90.

[36] V.S. Munagapati, V. Yarramuthi, S.K. Nadavala, S.R. Alla, K. Abburi, Biosorption of Cu(II), Cd(II) and Pb(II) by acacia leucocephala bark powder: Kinetics, equilibrium and thermodynamics, Chem. Eng. J. 157 (2010) 357–365.

[37] K. Sato, T. Kusuyama, K. Tnimura, Adsorption of heavy metal ions onto the surface of metal-incorporated hydrous ferric oxide particles, Mater. Sci. Forum 439 (2003) 210–214.

[38] A. Sari, D. Mendil, M. Tuzen, M. Soylak, Biosorption of palladium (II) from aqueous solution by moss (*Racomitrium lanuginosum*) biomass: Equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater. 162 (2009) 874–879.

[39] M. Imamoglu, O. Tekir, Removal of copper (II) and cadmium (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks, Desalination 228 (2008) 108–113.

[40] I.A. Horsfall, Spiff, effects of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by caladium bicolor (*wild cocoyam*) biomass, Electron. J. Biotechnol. 8 (2005) 162–169.

[41] M. Al-Ghouti, M.A.M. Khraisheh, M.N.M. Ahmad, S. Allen, Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: A kinetic study, J. Colloid Interf. Sci. 287 (2005) 6–13.

[42] M. Ajmal, R. Ali Khan Rao, S. Anwar, J. Ahmad, R. Ahmad, Adsorption studies on rice husk: Removal and recovery of Cd (II) from wastewater, Bioresour. Technol. 86 (2003) 147–149.

[43] B. Crittenden, W.J. Thomas, Adsorption Technology and Design, Reed Educational and Professional Publishing, 1998, pp. 32–68.

[44] H. Nollet, M. Roels, P. Lutgen, P. Van der Meeren, W. Verstraete, Removal of PCBs from wastewater using fly ash, Chemosphere 53 (2003) 655–665.

[45] M. Doğan, H. Abak, M. Alkan, Adsorption of methylene blue onto hazelnut shell: Kinetics, mechanism and activation parameters, J. Hazard. Mater. 164 (2009) 172–181.

[46] T.S. Anirudhan, P.G. Radhakrishnan, Thermodynamics and kinetics of adsorption of Cu(II) from aqueous solutions onto a new cation exchanger derived from tamarind fruit shell, J. Chem. Thermodyn. 40 (2008) 702–709.

[47] V.K. Gupta, I. Ali, Removal of lead and chromium from wastewater using bagasse fly ash – a sugar industry waste, J. Colloid Interf. Sci. 271 (2004) 321–328.

[48] Q. Li, J. Zhai, W. Zhang, M. Wang, J. Zhou, Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk, J. Hazard. Mater. 141 (2007) 163–167.

[49] Z. Liu, F.-S. Zhang, Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass, J. Hazard. Mater. 167 (2009) 933–939.

[50] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*, J. Hazard. Mater. 105 (2003) 121–142.

[51] I.W. Mwangi, J.C. Ngila, Removal of heavy metals from contaminated water using ethylenediamine-modified green seaweed (*Caulerpa serrulata*), Phys. Chem. Earth Part A/B/C 50–52 (2012) 111–120.

[52] A. Kurniawan, A.N. Kosasih, J. Febrianto, Y.-H. Ju, J. Sunarso, N. Indraswati, S. Ismadji, Evaluation of cassava peel waste as lowcost biosorbent for Ni-sorption: Equilibrium, kinetics, thermodynamics and mechanism, Chem. Eng. J. 172 (2011) 158–166.

[53] I. Alomá, M.A. Martín-Lara, I.L. Rodríguez, G. Blázquez, M. Calero, Removal of nickel (II) ions from aqueous solutions by biosorption on sugarcane bagasse, J. Taiwan Inst. Chem. Eng. 43 (2012) 275–281.