Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.856345

52 (2014) 7906–7914
December

Taylor & Francis
Taylor & Francis Group

Lead biosorption from aqueous solution by raw and chemically modified green fresh water algae *Scenedesmus obliquus*

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Received 15 April 2013; Accepted 2 August 2013

ABSTRACT

Biosorption of lead (Pb) from aqueous solution by biomass of green algae, (*Scenedesmus obliquus*), was investigated as a function of initial solution pH, contact time, and temperature. Additionally, the effect of $CaCl_2$ pretreatment on the Pb uptake capacity of biomass has been investigated. The Langmuir isotherm analysis revealed that the modified biomass (Q_{max} = 207.2, $1/b$ = 19. 10) has a great uptake capacity and higher affinity towards the Pb metal than the raw biomass (Q_{max} = 112.0, $1/b$ = 56. 91). The absorption process was complied with Freundlich isotherm (R^2 = 0.9938 and 0.9629). The Freundlich isotherm analysis showed that the modified biomass (K_f = 78.10, $1/n$ = 0.6019) has a great uptake capacity and higher affinity toward Pb than the raw biomass (K_f = 22.35, $1/n$ = 0.7680). The mean biosorption energy calculated from Dubinin–Radushkevich plot (8.84 and 10.44 kJ/mol) suggested chemical biosorption. FTIR spectra indicated the presence of different functional groups, such as amino, carboxyl, hydroxyl, and carbonyl groups, on the cell wall of the *S. obliquus* biomass. The change in the band intensity and frequency indicate the involvement of these functional groups in Pb binding. Also, the severe decrease in all band intensity indicates that the $CaCl_2$ increases the biosorption capacity of the *S. obliquus* biomass. The obtained results proved that treatment with $CaCl_2$ has increased the uptake capacity of the *S. obliquus* biomass and could be used as a potential biosorbent for the removal of Pb from aqueous solutions.

Keywords: Biosorption; Lead; *Scenedesmus obliquus*; Pretreatment; Isotherm

1. Introduction

The release of toxic heavy metals into the environment mainly as a consequence of anthropogenic activities is considered a growing global problem. There are hundreds of sources of heavy metals, including various industries such as textile, pigments, plastics, mining, electroplating, metallurgical, etc. [1,2]. Heavy metals are considered persistent environmental pollutants, because they cannot be destroyed or degraded and remain indefinitely in the ecosystem [3,4]. Due to their toxic effect and accumulation tendency throughout the food chain, toxic heavy metals are a growing threat to the environment and

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human health consequences [5,6]. Pb is among the most toxic heavy metals affecting the environment [7]. Pb accumulates mainly in the bones, brain, kidney, and muscles and may cause many serious disorders, including anemia, kidney diseases, nervous disorders, and sickness even death [8].

Biosorption is an innovative technology that employs inactive and dead biomass of algae for the removal of heavy metals from aqueous solutions. It has gained important credibility in the last years, because of the high efficiency and low cost of these materials [6,9,10]. Green algae are mainly cellulose, and a high percentage of the cell wall is proteins bonded to polysaccharides to form glycoproteins. These compounds contain several functional groups (amino, carboxyl, sulphate, and hydroxyl) which could play an important role in the biosorption process [9].

The use of chemically pretreated micro-organisms seems to be a preferred alternative to the use of living cells in industrial applications for the removal of heavy metals from wastewater [11]. Chemical treatment of the dead biomass increases the metal capacity uptake due to the change in cell wall chemistry of the biosorbent [12]. The pretreated biomass of marine algae *Padina* sp. could be used as an effective biosorbent for treatment of copper (II) containing wastewater streams [13]. Pretreatment using $CaCl_2$ led to the precipitation of inorganic substances present in the biomass. Due to this precipitation, more free sites on the biomass surface will be available for metal interaction, resulting in the enhancement of Cr (VI) biosorption [14,15]. The pretreatment with $CaCl_2$ enhanced the biosorption efficiency 20–25% more than the control biomass [16].

In this study, the ability of the dead and chemically modified biomass of green alga (*Scenedesmus obliquus*) to eliminate Pb from aqueous solution has been investigated. Also, the effect of various parameters such as contact time, initial solution pH, initial metal concentration, temperature, and biomass dosage on the biosorbent characteristics have been investigated. The equilibrium and kinetic data of biosorption studies were modeled using isotherm models.

2. Materials and methods

2.1. Chemicals

All chemicals used throughout the experimental works were of analytical grade provided by Merck (Darmstadt, Germany). Pb salt used in the preparation of the synthetic metal bearing stock solution (1,000 mg/L) was $Pb(NO_3)_2$. The working solution was then prepared by diluting the stock standard. Deionized water was used throughout the experimental work. Standard solution of Pb (II) (1,000 mg/L) for atomic adsorption spectrophotometer was obtained from Merck, Germany.

2.2. Preparation of biomass

The microalgae employed for the current study was a fresh water *S. obliquus*, which belongs to the class Chlorophyceae. It has been isolated from the Nile River and maintained in the laboratory under suitable culture conditions. The medium used throughout the maintenance and experimental studies was BG11 [17]. *S. obliquus* was in the logarithmic phase of growth when introduced to the standard algal culture medium. Algal culture was incubated at 24 ± 2˚C under continuous illumination (2,500 lux) without aeration. After 8 days of cultivation period, exponentially grown algal cells were harvested by centrifugation. The algal biomass was washed with distilled water five times to avoid any effect of salt and then dried in an oven at 40˚C to constant weight. Afterwards, the dried biomass was grinded, sieved through a 0.2 mm size sieve, and stored in polyethylene bottles. All chemicals used throughout the experimental works were provided by Merck (Darmstadt, Germany).

2.3. Biomass pretreatment

A sample of 5 g of dry *S. obliquus* biomass (0.2 mm) was treated with 250 mL of 0.2 M $CaCl_2$ solution for 24 h under slow stirring. The solution was kept at constant pH 4 (optimum pH value for calcium activation). The calcium-treated biomass was filtered, washed several times with distilled water to remove the excess calcium, dried at 40˚C to constant weight, and then crushed and sieved through a 0.2 mm sieve.

2.4. Analytical methods

2.4.1. Determination of Pb concentration

The concentration of Pb in all samples was determined according to the APHA method [18] using graphite furnace atomic absorption spectrophotometer (Varian SpectrAA 220, USA) with deuterium arc background corrector.

2.4.2. Quality control

For each series of measurements, the constructed calibration curve composed of a blank and three or more standards. The accuracy and precision of Pb measurement were confirmed using National Institute Standards and Technology certified standard reference material 1643e trace elements in water.

2.5. Batch biosorption studies

The biosorption characteristics of the biosorbent *S. obliquus* were investigated as a function of pH, biosorbent dosage, contact time, and initial ion concentration on the absorption of Pb (II) ions. Each of the batch biosorption studies was carried out at room temperature (25 ± 0.1˚C) by contacting the *S. obliquus* biomass with Pb ions in 250 mL stopper conical flasks. The samples were shook at 120 rpm using mechanical shaker, then filtered through Whatman filter paper (No. 41) and the Pb ions concentration was determined in the filtrate.

To distinguish between possible metal precipitation and actual metal sorption, controls (blank) were used without biosorbent materials. All the experiments were carried out in triplicate and the mean of the quantitative results were reported and used for further calculations.

Standard deviation of results was calculated and if its value was greater than 5%, the data were discarded.

2.5.1. Effect of pH

The batch experiment was carried out at different pH value (from 2 to 6) by contacting 0.1 g of algal biomass with 100 of 50 mg/L of Pb solution in 250 mL stopper conical flask (below 2, the high proton concentration minimizes the metal sorption and above 6 the metal precipitation is favored). The pH of the solutions was adjusted either by hydrochloric acid or sodium hydroxide. The mixture was shaken for 2 h at room temperature, filtered, and the final pH of each sample was determined.

2.5.2. Effect of contact time

The effect of contact time was carried out at optimum pH by conducting batch biosorption experiments with an initial Pb ions concentration of 50 mg/L, 1 g/L biosorbent dosage and at different time intervals (5, 15, 30, 60, 90, and 120 min).

2.5.3. Effect of biosorbent dosage

The biosorbent dosages were varied from 0.025 to 0.25 g using a fixed volume of 100 of 50 mg/L of metal solution at the optimum pH and the optimum contact time.

2.5.4. Effect of temperature

The effect of temperature was carried out at optimum pH, dose, and contact time by conducting batch biosorption experiments with an initial Pb ions concentration of 50 mg/L, biosorbent dosage, and at different temperature (25, 40, and 60˚C)

2.5.5. Biosorption isotherms

Isotherms were measured by varying the initial metal ion concentrations at the optimum conditions. Different biosorption models were used for comparison with experimental data such as Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) [19].

3. Results and discussion

3.1. Biosorbent

The biosorbent used in this study was green algae *S. obliquus* which isolated from the Nile River water and was purified and recultivated in BG11 medium [17].

3.2. Characterization of dried biosorpent

FTIR analysis has been carried out for the raw *S. obliquus*, raw Pb-loaded *S. obliquus*, modified *S. obliquus*, and modified Pb-loaded *S. obliquus* biomass to identify the functional groups present in the different biomass cell wall structure that may play an important role in metal binding.

FTIR spectra (Fig. 1) indicate the presence of different functional groups in the cell wall of the different biomasses. The strong broadband at 3,382 cm^{-1} represents O–H stretch carboxylic, while band at 2,920 cm^{-1} represents carboxylic/phenolic stretching. The band at 1,652 cm^{-1} might be attributed to asymmetric C=O (COOH) stretching, while bands at approximately 1,530, 1,429, 1,249, and 1,059 cm^{-1} could be attributed to N–H stretch, symmetric C=O (COOH), C–O stretch of COOH, and C–O stretch (Alcohol), respectively.

The changes in bands intensity and wavenumber suggest the involvement of these functional groups in Pb binding. As shown in Fig. 1, the intensity of the peaks has been changed to a lower value after the interaction of the raw biomass with Pb ((a), (b)). Also, the same trend has been observed in case of $CaCl_2$ pretreated biomass.

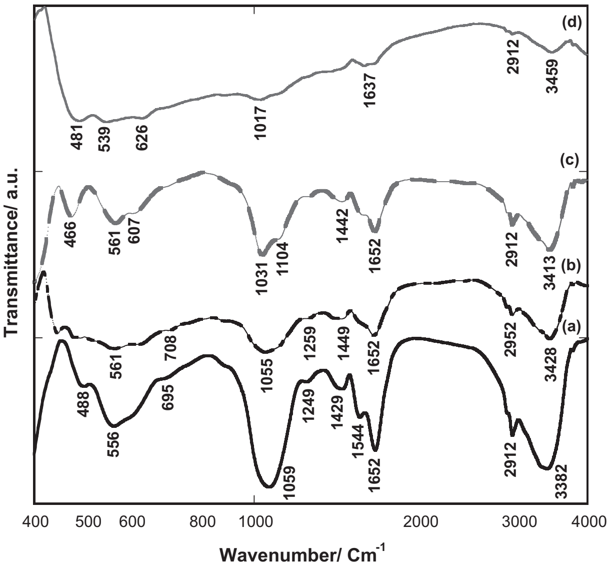

Fig. 1. FTIR spectra of *S. obliquus* biomasses: (a) raw *S. obliquus* (b) raw S. *obliquus* + Pb (c) modified *S. obliquus* (d) modified *S. obliquus* + Pb.

In case of the interaction of the pretreated biomass with Pb (d), a severe decrease in the intensity has been noticed in all bands that may have an involvement in the Pb binding. These results revealed that the $CaCl_2$ increased the biosorption capacity of the *S. obliquus* biomass; also the biosorption took place on the surface functional groups of the biomass.

3.3. Optimum conditions

3.3.1. Effect of pH

Metal uptake arises from coordination of the metal cations with the different functional group in the algal cell wall including amino, hydroxyl, and carboxyl. It is well known that pH affects the dissociation degree of functional groups on the biomass surface, the speciation, and the solubility of metal ions [20]. Consequently, the pH is considered as an important parameter that could affect the biosorption of metal ions from solutions [21,22].

The biosorption of Pb from aqueous solution using raw and chemically modified *S. obliquus* biomass was examined at various pH values (2–5). The experiments were not conducted beyond a pH of 5.0 to avoid metal precipitation.

It can be observed that the biosorption of Pb increased by increasing pH in both raw *S. obliquus* and modified *S. obliquus* biomass (Fig. 2). In case of raw *S. obliquus* biomass, the removal percentage was increased from 30 to 87 by increasing pH from 2 to 3, respectively. After pH 3, the removal percent remains constant even by increasing pH until 5. While in case of modified biomass, the removal percent increased from 18 to 97.5 by increasing the pH from 2 to 4, after pH 4 the removal percent remains constant. Therefore, the optimum pHs for raw and modified biomasses are 3 and 4, respectively.

At low pH, the positively charged hydrogen ions may compete with the metal ions for binding sites on the cell wall of the biomass and this leads to fewer binding site being available for metal ions to bind. As the pH increases, there are fewer H^+ ions in solution resulting in less competition for binding sites available. It is believed that carboxyl groups may be responsible for some of the metal binding, since carboxyl groups have pKa values between 3 and 4 [23]. The obtained results indicated that the pH 4 was considered to be the optimum pH for the biosorption of Pb by the raw *S. obliquus* and modified *S. obliquus* biomasses.

In the current study, the pretreatment of *S. obliquus* biomass by 0.2 M $CaCl_2$ solution at pH = 4 led to increase the uptake capacity of the biomass. The obtained results were in agreement with the results obtained by Ghasemi et al. [24] who investigated the uptake capacity of uranium (II) from aqueous solution by natural and different pretreated (0.1 M $CaCl_2$ solution at pH = 4) biomasses and the results showed increase in the uptake capacity.

3.3.2. Effect of biosorbent dosage

To study the effect of biomass dose on the biosorption of Pb, different doses (0.025–0.1 g/100 mL) of raw *S. obliquus* and modified *S. obliquus* biomasses were applied to 100 mL of 50 mg/L of Pb solution at optimum pH. The effect of the biosorbent dosage on

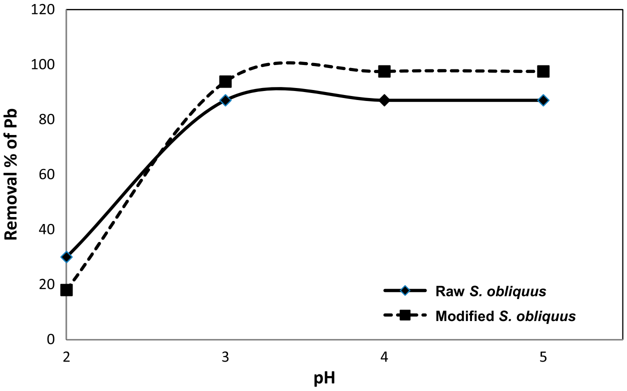

Fig. 2. Effect of pH on the biosorption of Pb by raw and modified *S. obliquus* biomasses.

the removal of Pb is shown in Fig. 3. In the current study low biomass doses (0.025–0.1 g/100 mL) were applied to avoid the decreasing in the sorption capacity due to mutual interaction between binding sites at high dose [25,26].

The biosorption uptake of Pb ions on *S. obliquus* was significantly affected by the dose of the biomass in the solution. The biosorption of Pb ions increased with subsequent increase of the biomass dose, where increasing biomass dose led to increase in the biomass surface area and more functional groups will be available for binding to Pb ions. The results obtained indicated that $CaCl_2$ pretreatment enhanced the biosorption efficiency than the raw biomass at the different doses. The highest removal percent 92 and 97.3 was detected at 0.075 g/100 mL and 0.05 g/100 mL for raw *S. obliquus* and modified *S. obliquus* biomasses doses, respectively. Therefore, these doses were selected as the optimum doses of the biosorbent for the rest of the study.

3.3.3. Effect of contact time

The effect of contact time is highly influencing the biosorption process. Fig. 4 shows the effect of contact time on the biosorption of Pb ions using raw and modified *S. obliquus* biomasses.

The biosorption of both biomasses was rapid in the first 5 min where the removal percent reached 70 and 80, and then the equilibrium was reached at 60 and 90 min for raw *S. obliquus* and modified *S. obliquus* biomasses, respectively. Therefore, a contact time of 60 and 90 min was used as the optimum time for the rest of the experiments. In this concern, similar behavior was recorded for the biosorption of Ni and Cu on treated alga *Undaria pinnatifida* [27] and the adsorption of Cd by fungal biomass [28].

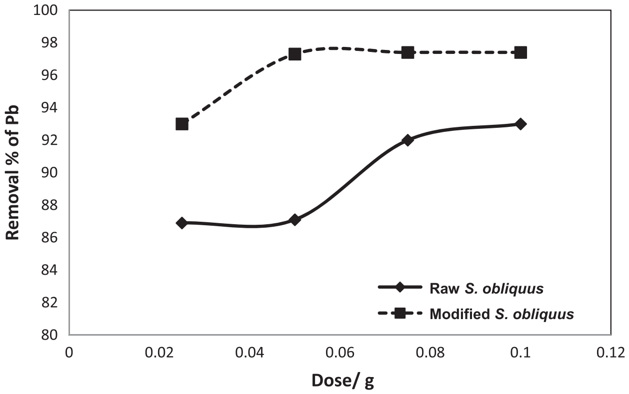

Fig. 3. Effect of dose on the biosorption of Pb by raw and modified *S. obliquus* biomasses.

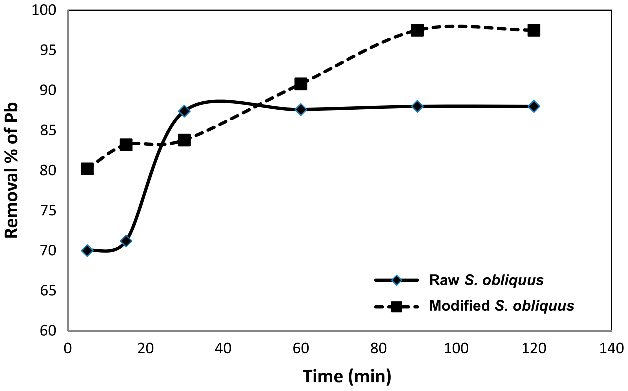

Fig. 4. Effect of contact time on the biosorption of Pb by raw and modified *S. obliquus* biomasses.

3.3.4. Effect of temperature

The effect of three different temperatures (25, 40, and 60˚C) on the biosorption of Pb has been illustrated in Fig. 5. By increasing the temperature from 25 to 60˚C, there was no significant increase in the removal percent in the case of modified biomass, while in case of raw biomass an increase in the removal percent was observed.

The obtained results were in agreement with the results obtained in other studies [29] in which we have observed an increase in the biosorption of Pb from aqueous solutions by green algae *Spirogyra* species by changing the temperature from 25 to 45˚C. The almost removal percent (97.5 and 97.6) was recorded in raw biomass at temperature 60˚C, while in case of modified biomass it was recorded at 25˚C. This finding is economically important where pretreatment of the biomass with $CaCl_2$ led to save energy consumption by at least 58%.

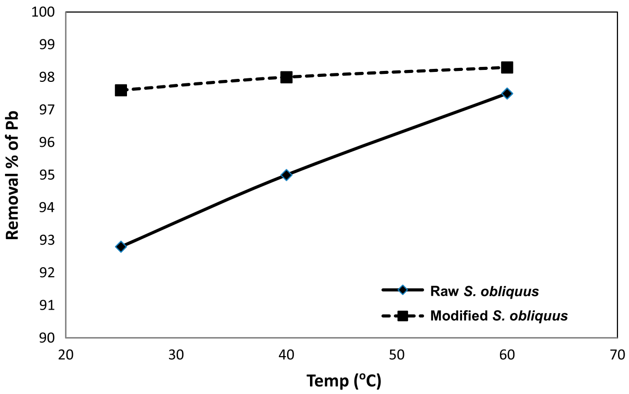

Fig. 5. Effect of temperature on the biosorption of Pb by raw and modified *S. obliquus* biomass.

3.3.5. Equilibrium studies and isotherm modeling

The biosorption isotherm models described the biosorption data at equilibrium and showed the correlation between the mass of solute adsorbed per unit mass of sorbent at equilibrium.

The biosorption isotherms were calculated using three different isotherm models including the Langmuir, Freundlich, and (D–R) isotherms [30]. Due to their simplicity, the Freundlich and Langmuir equations are the most widely used models to describe the relationship between metal biosorption equilibrium q_e (mg/L) and final concentrations C_e (mg/L) at equilibrium. The Freundlich equation is given by Eq. (1):

$$q_e = K_f C_e^{1/n} \tag{1}$$

where K_f and n are the Freundlich constants and are related to the adsorption capacity of the sorbent and the adsorption intensity. To simplify the determination of K_f and $1/n$, Eq. (1) can be linearized in logarithmic form, which allows the determination of the unknown parameters by plotting log q_e vs. log C_e (Eq. (2)):

$$\log q_e = \log K_f + 1/n \log C_e \tag{2}$$

The Langmuir isotherm relationship is given as Eq. (3) [31] :

$$C_e/C_{ads} = 1/Q_b + C_e/Q \tag{3}$$

where C_e (mg/L) is the concentration of metal in solution at equilibrium, C_{ads} (mg/g) is the amount of metal sorbed per unit mass of *S. obliquus* biomass, Q (mg/g) and b are Langmuir constants related to mono layer capacity sorption and sorption energy, respectively.

The selection between Freundlich and Langmuir isotherms is mainly controlled by the equilibrium data [32]. These isotherms commonly describe the adsorption phenomena at the solid–liquid interface and the isotherm data were used for the design of adsorption systems and to understand the relation between adsorbent and adsorbate [33].

3.3.5.1. Langmuir isotherm. According to the Langmuir model, sorption occurs uniformly on the active site of the sorbent, and once a sorbate occupies a site, no further sorption can take place on this site [34]. The values of the Langmuir isotherm parameters can be used to predict the affinity between the sorbent and sorbate. A high value of b (low value of $1/b$) indicates that there is a high affinity between sorbent and sorbate, while a large Q_{max} value indicate that the sorbent has a large uptake capacity [35].

S. obliquus biomasses. The Langmuir isotherm analysis of the biosorption of Pb onto *S. obliquus* biomass (Fig. 6 and Table 1) revealed that the modified biomass (Q_{max} = 207.2) has a great uptake capacity than the raw biomass (Q_{max} = 112.0). Also, there is a high affinity between the Pb ions and the modified biomass ($1/b$ = 19.10) than that of the raw biomass ($1/b$ = 56. 91). These results proved that treatment with $CaCl_2$ increased the uptake capacity of the *S. obliquus* biomass and could be used as a potential biosorbent for the removal of Pb from aqueous solutions.

3.3.5.2. Freundlich isotherm. Similarly to the Langmuir isotherm, the values of the Freundlich parameters can also be used to predict the affinity between the sorbent and sorbate [36]. A high value of n (low value of $1/n$) indicates that there is a high affinity between sorbent and sorbate, while a large K_f value indicates that the sorbent has a large uptake capacity. The Freundlich isotherm plot (Fig. 7) indicated that

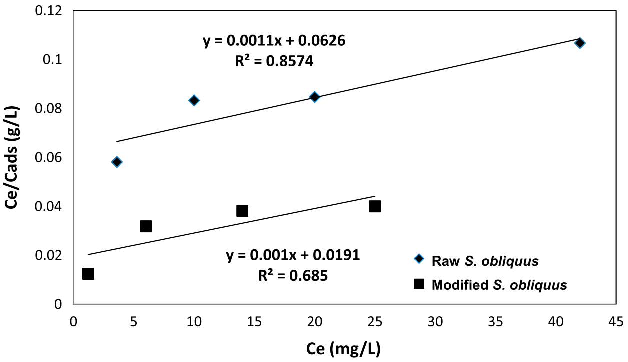

Fig. 6. Langmuir isotherm for Pb biosorption by raw and modified *S. obliquus* biomasses.

Table 1
Summary of isotherm model parameters for raw and modified *S. obliquus* biomass

	Freundlich model			Langmuir model		
	K_f	$1/n$	R^2	Q_{max} (mg/g)	$1/b$	R^2
Raw biomass	22.35	0.7680	0.9938	112.0	56.91	0.8574
Modified biomass	78.10	0.6019	0.9629	207.2	19.10	0.6580

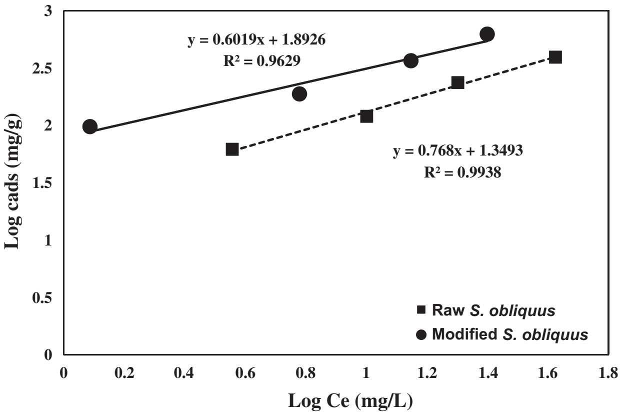

Fig. 7. Freundlich isotherm for Pb biosorption by raw and modified *S. obliquus* biomasses.

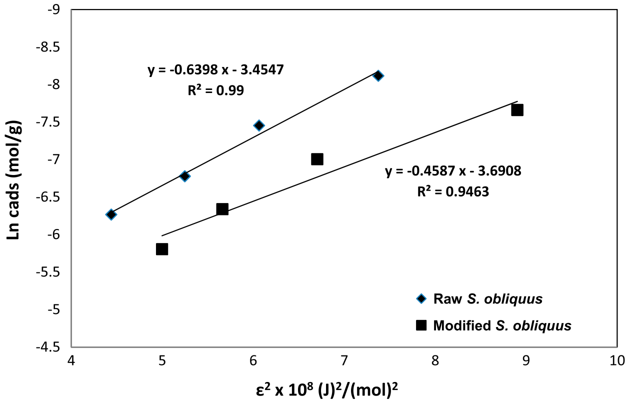

Fig. 8. DKR sorption isotherm of Pb ion by raw and modified *S. obliquus* biomasses.

the biosorption of Pb was complied with Freundlich isotherm (R^2 = 0.9938 and 0.9629).

The Freundlich isotherm analysis of the biosorption of Pb onto *S. obliquus* biomass (Table 1) revealed that the modified biomass (K_f = 78.10) have a great uptake capacity than the raw biomass (K_f = 22.35). Also the Freundlich isotherm analysis revealed that there is a high affinity between the Pb and the modified biomass ($1/n$ = 0.6019) than that of the raw biomass ($1/n$ = 0.7680).

3.3.5.3. D–R isotherms. Freundlich and Langmuir isotherms could not provide any information about the biosorption mechanism. The D–R isotherm is an analog of Langmuir type, however it is more general because it does not assume a homogeneous surface or constant sorption potential [37].

The D–R isotherm model was used to predict the nature of adsorption processes as physical or chemical [38]. The linearized D–R isotherm equation can be written as shown (Eq. (4)):

$$\ln q_e = \ln X_m - \beta\varepsilon^2 \tag{4}$$

where q_e is the amount of metal ions adsorbed per unit mass of adsorbent (mol/g), X_m is the maximum sorption capacity, b is the activity coefficient related to mean sorption energy, and E is the Polanyi potential, which is equal to Eq. (5):

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{5}$$

where R is the gas constant (J/mol K) and T is the temperature (K). The saturation limit X_m may represent the total specific micro pore volume of the sorbent. The sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate [39]. The sorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces having the same sorption potential. The sorption energy can also be calculated using the following equation Eq. (6):

$$E = 1/\sqrt{-2\beta} \tag{6}$$

The data illustrated in Fig. 8 and Table 2 represent the D–R plot of the biosorption of Pb onto *S. obliquus* biomass. It is well known that the mean free energy of biosorption gives information about biosorption mechanism, physical or chemical.

If the E value lies between 8 and 16 kJ/mol, the biosorption process occurs chemically and if $E < 8$ kJ/mol, the biosorption process takes place physically [40,41]. In the current study, the mean biosorption energy was calculated as 8.84 and 10.44 kJ/mol for

Table 2
Summary of DKR model parameters for raw and modified *S. obliquus* biomass

	X_m (mol/g)	β (mol^2/J^2)	Sorption energy (E, kJ/mol)
Raw biomass	31.6×10^{-3}	-0.6398×10^{-8}	8.84
Modified biomass	24.9×10^{-3}	-0.4587×10^{-8}	10.44

the biosorption of Pb onto the raw and modified *S. obliquus* biomasses, respectively (Table 2).

These results indicated that the biosorption process of Pb onto both biomasses may be carried out chemically via involving valence forces through sharing or exchange of electrons between sorbent and sorbate [42].

4. Conclusions

The current study provides useful information about the biosorption of Pb from aqueous solution using raw and chemically modified biomasses of the green algae, *S. obliquus*, as a function of initial solution pH, contact time, and temperature. The FTIR spectra indicated the presence of different functional groups on the cell wall of the *S. obliquus* that could play an important role in the biosorption process. The Langmuir and Freundlich isotherms analysis revealed that the modified biomass ($Q_{\max}$ = 207.2, $1/b$ = 19.10, K_f = 78.10, $1/n$ = 0.6019) has a great uptake capacity and higher affinity toward Pb than the raw biomass ($Q_{\max}$ = 112.0, $1/b$ = 56.91, K_f = 22.35, $1/n$ = 0.7680). The mean biosorption energy calculated from D–R plot (8.84 and 10.44 kJ/mol) indicated the chemical nature of the biosorption of Pb on the *S. obliquus* biomass. It was proved that treatment with $CaCl_2$ increases the uptake capacity of the biomass toward Pb. The modified biomass could be used as a potential biosorbent for the removal of Pb from aqueous solutions.

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