Performance of Immobilized Chlorella Algae for Removing pb(II) Ions from Aqueous Solution

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Abstract

This study aims to show the effectiveness of immobilization of Chlorella green algae biomass in the form of bead for the removal of lead ions from synthetic polluted water at various operational parameters such as pH (2–6), biosorbent dosage (0.5–20 g/L) and initial concentration (10–100 mg/L). More than 90 % removal efficiency was achieved. FTIR and SEM-EDX analysis of the biosorbent before and after sorption show differences in the functional groups on the adsorbent surface. Langmuir and Freundlich equilibrium isotherm, pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental and results and show good conformity with Langmuir isotherm model and pseudo-second-order kinetic model with correlation coefficient (0.994) and (0.998) respectively.

1- Introduction

Toxic metal ions removal from wastewater is important in economic and environmental problems. Heavy metals and other metal ions contaminants are aqueous waste streams of many industries, such as mining and tanneries.

Some metals associated or released with these activities are Pb, Hg, Cr, and Cd. Some of these metals accumulate in living organisms and cause various diseases and disorders. Metals such as lead, mercury, arsenic, zinc, copper, and cadmium are highly toxic when adsorbed into the body causing accumulative poisoning, brain damage, cancer, and so forth.

Lead is an enzyme inhibitor and general metabolic poison that has the ability to replace calcium in the bone to form sites for long-term release, hence, the need to remove these toxic metals from water and wastewater is a point of interest. Lead permissible limit in wastewater as set by the Environment Protection Agency is 0.1 mg/L, and in drinking water, it is 0.05 mg/L [1].

The conventional methods for heavy metals removal include chemical precipitation, electrodialysis, ion exchange, membrane separations, reverse osmosis, and solvent extraction which maybe not effective at low metal concentration and costly so the search for new, effective and economical technique for metal removal from wastewaters has directed attention to biosorption that uses various biological materials at little or no cost to remove heavy metal [2].

Biosorption, describes the removal of heavy metals from aqueous solution by using nonliving biomass.

Biosorption is favorable as an alternative to conventional methods of metal recovery from solutions due to availability and low-cost raw material.

Freely suspended biomass may have better contact with adsorbate during the removal process, suspended biomass maybe not the practical form to the direct use because of many problems, and one of them is the separation of the biomass from the treated water. Immobilization suggested as an easy handling of the biomass, enhance its stability, reusability, mechanical strength, and the ease of separation and regeneration [1].

This study aims to investigate the feasibility of using immobilized chlorella biomass for the removal of lead ions from aqueous solutions. The effects of different experimental parameters, such as initial pH, removal time, dose of sorbent and initial lead concentration on the sorption capacity were studied.

2- Materials and Methods

2.1. Sorbents and Contaminant

The algae used in the experiment were purchased from the buy algae web site (https://www.buyalgae.com/) as a pure dried sample of chlorella in a powdered form. The selected amount of the algal biomass mixed with 2% sodium alginate solution before that the algae wetted with a specific amount of distilled water, the mixture then dropped in a 5 % CaCl2 solution left there in the solution for 2 hr to full solidification. The formed beads of diameter 4 ± 0.1 mm were washed with distilled water before using in the experiments.

Lead ions stock solution was prepared by dissolving the known amount of Pb(NO3)2 powder, in a known volume of distilled water different concentrations were prepared by dilution from the stock solution.

Then the pH of the aqueous solution was controlled using 0.1 M HCl and 0.1 M NaOH to the required value. Fig. **1** shows the algae before and after immobilization.

(a)

(b)
Fig. 1. Chlorella algae (a) before (b) after immobilization

2.3. Experimental Work

250 mL conical-flasks were used in the experiments, each flask washed with HNO_3 diluted solution then washed with distilled water before starting the experiments. The flasks filled with 100 mL of Pb(II) ion solution and selected sorbent amount. In order to do the experimental work, several parameters were studied to examine their effect on the removal process such as pH, contact time, initial metal concentration, agitation speed, and sorbent dose. The agitation of flasks in the form of shaking was done for a defined time using orbital shaker (Edmund Buhler SM25, German). (10 mL) volume of the contaminated solution collected from each flask, without the need for further filtration, solutions analyzed to measure the remaining metal concentration. The measurements of metal ions carried out using atomic absorption spectrophotometer (AAS, Sens AA, Australian) Duplicate measurements of the samples were done for more accurate results. The removal efficiency of contaminants calculated from eq. (1):

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

Where C_o and C_e are the initial and equilibrium lead concentrations (mg/L).

The amount of sorbate adsorbed on the sorbent material, q_e (mg/g), can be determined by:

$$q_e = (C_o - C_e)\frac{V}{m} \qquad (2)$$

Where m is the amount of sorbent on the flask (g) and V is the volume of contaminant solution (L)

3- Results and discussion

3.1. Characteristic of Immobilized Beads

a. FTIR Analysis

Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups present in the biosorbent. The biomass samples were examined using the FTIR spectrometer (model: FT/IR-4100typeA) within range of 400-4000 cm^{-1}.

Analysis as can be seen in Fig. **2** indicated the broad and strong bands at 3500 to 3000cm^{-1} which can be attributed to the overlapping of –OH and –NH stretching. The band at 2900 attributed to the C-H, at 1620 to 1590cm^{-1} due to the C=O, and amide groups, at 1400 cm^{-1} N-H bending in the amine groups, and at 1025 cm^{-1} to CO stretching of alcohols and carboxylic acids.

As compared to simple biosorbent, biosorbent loaded with chromium (VI) the broadening of -OH peak at 3440 cm^{-1} and carbonyl group peak at 1628 cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of metal ions [3].
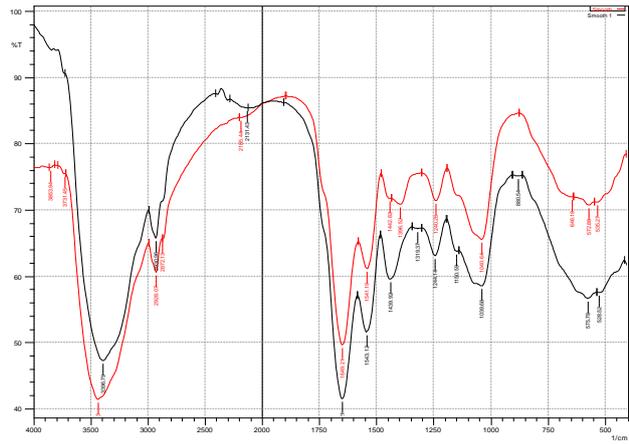
Fig. 2. FTIR of immobilized chlorella black before lead removal red after lead removal
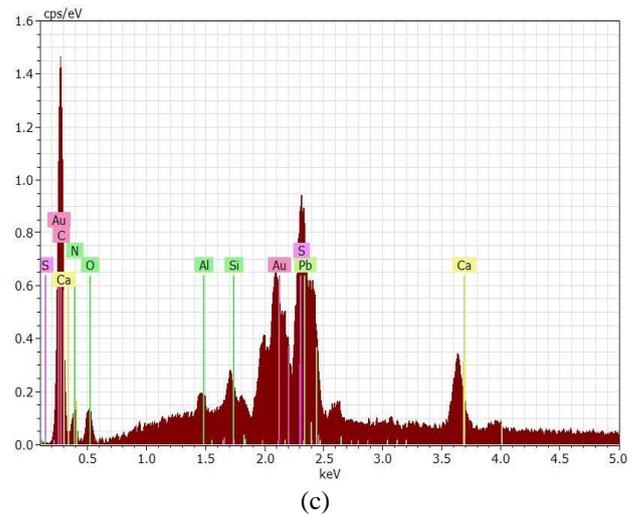
b. SEM-EDX Results

SEM-EDX result of chlorella algae bead before and after pb (II) ion deposit on the surface of beads as shown in **Fig.3**. The EDX also shows the composition of the surface of the alginate bead before and after sorption which indicate that change in light metal on alginate surface which support the theory of ion exchange during the removal process.
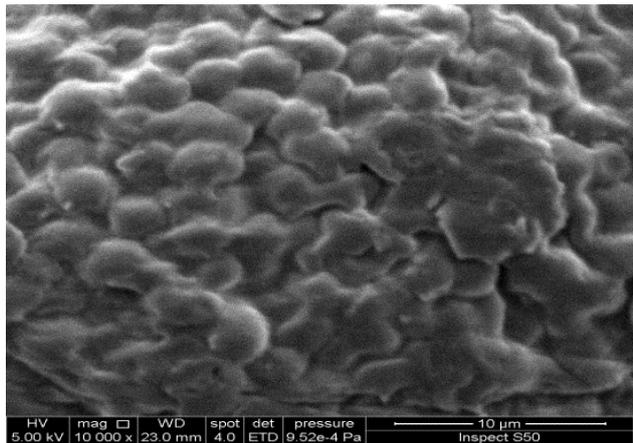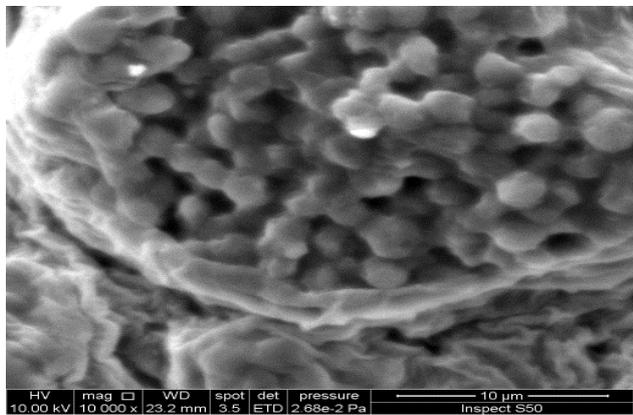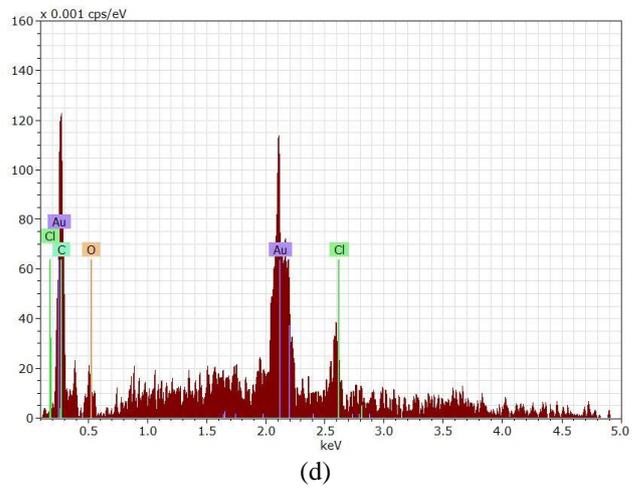

Fig. 3. SEM-EDX analysis of immobilized chlorella algae A SEM before and B after lead removal C and D EDX before and after lead removal respectively

3.2. Effect of Different Parameter

a. pH of the solution

In the biosorption the initial pH of the solution is a very important parameter. The effect of this parameter was studied in a pH range, 2-6, and not exceeded 6 to avoid precipitation of heavy metal. Fig. **4** shows removal efficiency variation with the variation of pH value. At pH value 2, the removal efficiency was low due to solution protonation that lower lead ion passing and compete with it.

The removal efficiency starts to increase because functional groups such as carboxyl, phosphate, imidazole and amino groups, would be exposed due to deprotonation and carried negative charges, thus facilitating the biosorption of metal.

3

At higher pH in basic conditions, the amount of OH- ions is increased in the solution, so metal ions react with it and precipitated as a metal hydroxide [4], [5].
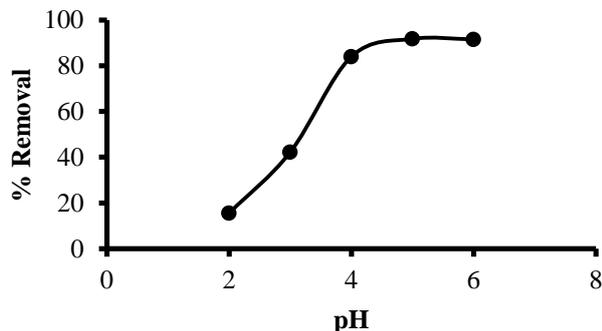

Fig. 4. Effect of pH on removal process

b. Sorbent Dose

Doses of (0.05, 0.2, 0.6, 1 and, 2 gm) were used in different flasks with the same conditions to study their effect on the sorption process and the results are represented in **Fig.5** .The uptake capacity of the sorbent increased when decreasing biosorbent dosage because of interference between the binding sites on the surface, while increasing sorbent dose more than 1 gm/100, ml the quantity of metal ions uptake decreases because of the sites on the biosorbent surface remain unsaturated during the removal process [6], [7], [8].
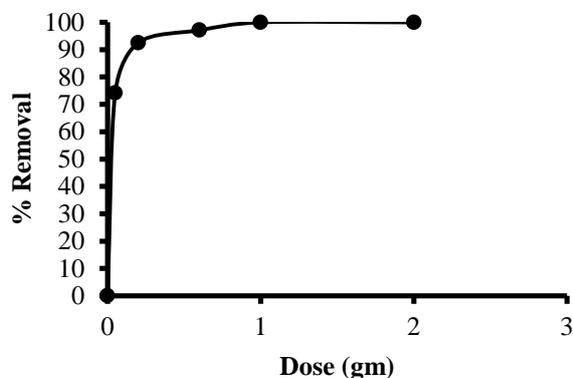

Fig. 5. effect of dose on the removal process

c. Sorption Time

Fig. **6** presents the removal efficiency of pb(II) ions during different time periods. It can be seen from this figure that biosorption rate was increased rapidly at the initial stage of time from 0 to 30 and thereafter become nearly constant at around 90% then gradually the biosorption retarded due to the decrease in biosorption sites on the sorbent surface [9].
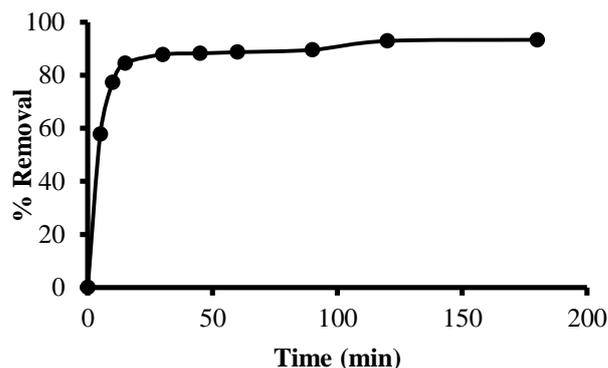

Fig. 6. Effect contact time on the removal process

d. Initial lead Concentration

With increasing initial metal ions concentration the biosorption capacity also increased, high metal ions concentration provides a driving force that overcomes the resistance of the mass transfer layer between the beads and the metal in the solution. Also, the biosorption process enhanced because of the number of collisions between metal ions and biosorbent increases when increasing initial metal concentration. The reduction in metal removal efficiency might be attributed to the insufficient binding sites for adsorption associated with increasing metal concentration, and that the binding was saturated [9], [10] as showed in Fig. **7**
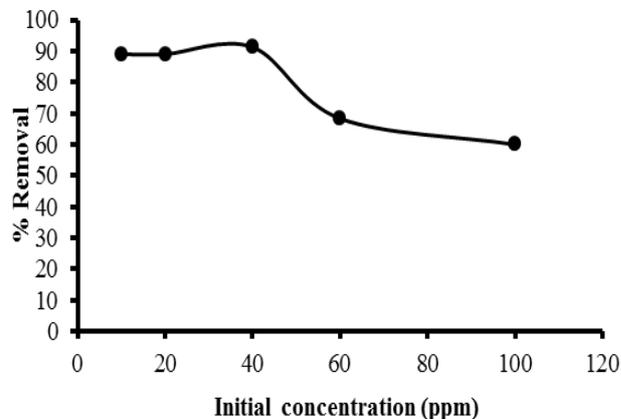
Fig. 7. Effect of initial concentration on the removal efficiency of lead ions

4- Isotherm and kinetic studies

4.1. Isotherm

Desorption isotherm which is the equilibrium relationship at a given temperature were studied by. Langmuir, and Freundlich, Equations are used widely to describe sorption process. The importance of these models is finding the relationship between the sorbed amount of sorbate onto adsorbent (q_e) and the concentration of sorbate remaining at equilibrium (C_e) in the aqueous solution [11].

a. Langmuir model

This model, suggests that sorption process occurs uniformly on the active sites of the sorbent at the surface, and once a sorbate occupies a site, no further sorption can take place at that site, Langmuir model can be represented as [12]

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

Where b and q_{max}, are the Langmuir constants, represent the saturated monolayer sorption capacity (mg/g), and the sorption equilibrium constant, and refer to the slope of the model.

b. Freundlich model

$$q_e = k C_e^{1/n} \tag{4}$$

Is an empirical Model which suggests that sorption based on multilayer heterogeneous surface given by eq. (4) where *1/n* is the intensity of sorption and *k* is a constant related to the maximum adsorption capacity [13], [14].

4.2. Sorption Kinetics

The transformation rate of pollutant from aqueous solution to solid phase [6] and the kinetic in the present study were represented using two models:

a. Pseudo-first order kinetic model

$$q_t = q_e(1 - e^{-k_1 t}) \tag{5}$$

The q_e and q_t are the equilibrium and the amount of sorbate removed from the solution at time *t* respectively in (mg/g), and k_1 is the pseudo first order rate constant (1/min) [15]

b. Pseudo-second order kinetic model

This model can be described as:

$$q_t = \frac{t}{\left(\frac{1}{k_2 q_e^2} + \frac{t}{q_e}\right)} \tag{6}$$

Where k_2 is the pseudo second order rate constant (g/mg min) [16].

From the experimental results the relationships between the sored quantity (qe, mg/g) and the equilibrium concentration (Ce) for Pb(II) ions in the solution. The values of the calculated parameters and the correlation coefficients (R_2) are listed in Table **1** and the models are represented in Fig. **8** from the table the high correlation coefficients were found for the Langmuir model which suggested that homogeneous surface of the sorbent with all the sorption sites assumed to have an equal sorbate affinity and the sorption occurs uniformly on sorbent active sites [15].

The Pseudo-second order model gave a better fit based on the R_2 values. This indicating that sorption process occurred was chemisorption [16].

Table 1. Constants of isotherm models for sorption of pb (II) ion onto alginate bead

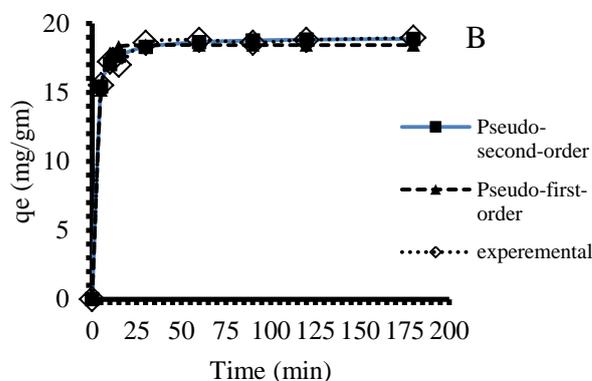| Isotherm model	Parameter	value	Kinetic model	Parameter	value
Langmuir	q_{max} (mg/g)	30.06		q_e (mg/g)	18.42
	b (L/mg)	0.245	Pseudo-first order	k_1 (min^{-1})	0.346
	R^2	0.994		R^2	0.74
Freundlich	k(mg/mg)(L/mg)^n	7.757	Pseudo-second order	q_e (mg/g)	18.table 199
	n	2.762		k_2 (g/mg min)	0.045
	R^2	0.873		R^2	0.998

Fig. 8. Isotherms and kinetic models for sorption pb (II) ions onto alginate bead

Conclusions

A non-conventional bio-carrier of immobilized Chlorella green algal is a good way for lead ions removal from simulated wastewater without losing their ability to adsorb. Different parameters studied and the isotherm shows that. Langmuir isotherm model gives the best fit model for lead ions removal than Freundlich models with the adsorption capacity. The monolayer adsorption capacity of pb(II) ions calculated from the Langmuir model was found 30.06mg/g, Pseudo-second order kinetic model gives good fitting to present the process of removal which indicates according to the model controlling mechanism in the removal process is the chemisorption process.

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كفاءة الطحالب المقيدة في ازالة الرصاص من المحاليل المائية

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الخلاصة

تهدف هذه الدراسة إلى إظهار فعالية تجميد الكتلة الحيوية (الكلوريلا المجففة الخضراء) في شكل حبة كروية الشكل لإزالة أيونات الرصاص من المحاليل المائية المحضرة مختبريا في معايير تشغيلية مختلفة مثل الرقم الهيدروجيني (2–6) ، الجرعة البيولوجية (L / g (20–0.5) والتركيز الأولي (10 – 100 مجم / لتر. تم الحصول على كفاءة إزالة بلغت أكثر من 90 ٪ ومن خلال عمل تحليل FTIR وتحليل المجهرية والاشعة السينية SEM–EDX لكرات الالجنيت المقيدة فيها الطحالب قبل وبعد الامتصاص ظهر الفرق في المجموعات الوظيفية على سطح المادة المازة نتيجة التبادل الايوني الحاصل خلال عملية الازالة. كما تم تطبيق موديلات التوازن (Langmuir وFreundlich) وكان اكثرها انطباقا مع النتائج موديل (Langmuir) بمعامل الرتباط (0.994) =R^2 والموديلات الحركية (pseudo–first–order وpseudo–second–order) كان اكثرها تماشيا مع النتائج موديل (pseudo–second–order) بمعامل ارتباط(0.998) = R^2.

الكلمات الدالة: تقييد، المعادن الثقيلة، طحالب الكلوريلا الميته، الامتزاز الحيوي ، موديلات رياضية وحركية