IMMOBILIZATION DRIED MIX OF ALGAE FOR COPPER REMOVAL

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ABSTRACT

This study was aimed to reveal the effectiveness of Immobilization of biomass (dried mix algae) in the form of bead for the removal of copper ions from synthetic polluted water. Various operational parameters such as pH (2–6), biosorbent dosage (0.5–20 g/L) and initial concentration (10–100 mg/L)The results concluded that a removal efficiency reached up to 90 % , which indicated the fascinated and easiest the handling of biomass. Characterization of the immobilized algae was determined by the Scanning electron microscope with Energy Dispersive X-Ray Analysis (SEM- EDX). The result reveals that the equilibrium time can be reached within 60–80 min. Experimental data were compiled well with Langmuir and Freundlich isotherm with $R^2 = 0.97$ and 0.93, respectively.

Keywords: heavy metal; equilibrium and kinetic parameters; wastewater; biosorption; SEM-EDX.

الامتزاز باستعمال الكتلة الحيوية لازالة عنصر النحاس من المياه باستخدام الطحالب المقيدة

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المستخلص

يهدف البحث لدراسة فعالية الكتلة الحيوية (الطحالب المجففة) المقيدة باستخام الجينات الكالسيوم على شكل حبات لإزالة أيونات النحاس من المياه الملوثة اصطناعيا اظهرت انها تعطي كفاءة إزالة تصل إلى 90٪ لعنصر النحاس عملية تقييد الكتلة الكتلة الحيوية تسهل التعامل معها والحفاظ عليها, الطحالب المقيدة قبل وبعد استعمالها بلازالة فحصت بواسطة تحليل الصورة المجهرية والاشعة السينية SEM–EDX، العديد من المتغيرات التشغيلية ادخلت لدراسة تاثيرها على عملية الازالة مثل الرقم الهيدروجيني (2–6) ، الكمية المضافة من الطحالب المقيدة (0.5 – 20 جم / لتر) والتركيز الأولي لعنصر النحاس (10–100 ميلي غرام لكل لتر). من خلال النتائج لوحظ ان وقت التوازن خلال 60–80 دقيقة من بدأ التجربة. تم تحليل البيانات ثابتة درجة الحرارة بإستخدام موديلات Langmiur وFrandulich. تم تحليل البيانات الحركية بإستخدام معادلات من الدرجة الأولى والثانية. تم تطابق بينات الإمتصاص ثابتة الحرارة جيدا مع الموديلين ومن خلال البيانات الحركية لوحظ انطباق معادلات الدرجة الثانية مع النتائج واللتي تعطي توضيح ان العملية هي عملية امتزاز كيميائي

الكلمات المفتاحية: المعادن الثقيلة، مواد ممتزة رخيصة الكلفة، المعاملات الحركية، فحص الصورة المجهرية

INTRODUCTION

In order to heavy metal removal from aqueous solutions, biosorption was the suggestion, which employs inactive and dead biomass for the recovery of pollutant. As an alternative to traditional methods, its results show promising method considered for application (5). Besides their toxic effects, accumulation of heavy metals throughout the food chain, leads to a serious ecological and health hazards problems because of their solubility and mobility. Copper ion, which is essential to human life and health, has adverse effects on human health and on the environment when exceed the permissible limits. In humans, serious problems occurs when copper exceed the limits such as stomach intestinal distress, kidney damage and anemia (6) (8). Many processes been used for the removal of heavy metals from contaminated effluents such as membrane separation; chemical precipitation; solvent extraction; coagulation; ion exchange and adsorption (19). For dilute metal concentrations, ion exchange, reverse osmosis and adsorption applied; however, ion exchange and reverse osmosis are costly processes, which makes adsorption a better alternative for heavy metals removal. Activated carbon is one of the most recommended sorbents. Nevertheless, the relatively high cost of production and regeneration of the spent carbon thus, many low-cost sorbents have been investigated (22). Biosorption, which is the accumulation and concentration of pollutants from polluted aqueous solutions by the use of material of biological origin, appears to offer an economically attractive approach (10) (11). Immobilization is an attractive technique to fix and retain biomass on suitable natural or synthetic support materials. The key advantages of immobilization include biomass retention within the working environment, easy separation of products from cells and relatively high local cell density. One of the application on biosorption processes, biomass immobilization so that the recovery of the adsorbed metal from the matrix easy and protect the sorbent material so that the system can be used more than once. Immobilization may also enhance biosorption capacity and can overcome obstacles arising from using powder biomass when contact with polluted water (12). Alginate, which is a biopolymer, been used extensively in cell immobilization studies. This biopolymer advantages include capability to retain cells by entrapment in its matrix fine pores, ease of preparation, and biocompatibility (10). In this study the investigation of the feasibility of using, immobilized algal biomass for the removal of copper ion from aqueous solutions. The effects of experiment parameters, such as initial pH, removal time, dose of sorbent and initial copper ion concentration on the sorption capacity studied.

MATERIALS AND METHODS

Biosorbents

Algae collected from the canal in the University of Baghdad where the algae floated at the canal water. The physical characteristics of the canal water from where the algae collected were pH 7.7, Conductivity 846 (µs/cm), TDS 447 (mg/l), Salinity 2$\cdot$, Temp 38.8 (°C), Turbidity 48.6 (NTU), NO_3 16.9 (mg / L), and NH_4 22.3 (mg / L). The distinguished algal groups are Chlorophyceae (37.77$\cdot$), Cyanophyceae (32.88$\cdot$), and Bacillariophyceae (29.34 $\cdot$) these test made at the ministry of science and technology. The collected algae were washed several times with distilled water to remove all dirt and impurities, sun dried for 3 days and then crashed and sieved to a mesh size < 63 µm. A selected amount of dried algal biomass mixed with a specific amount of distilled water then it mixed with 2% alginate solution, the mixture then dropped by a syringe in a 5 % $CaCl_2$ solution left in the solution for 3 hr for complete solidification. The formed beads of algal entrapped in calcium alginate matrix with 4 ± 0.1 mm average diameter washed with distilled water and then used in the experiments.
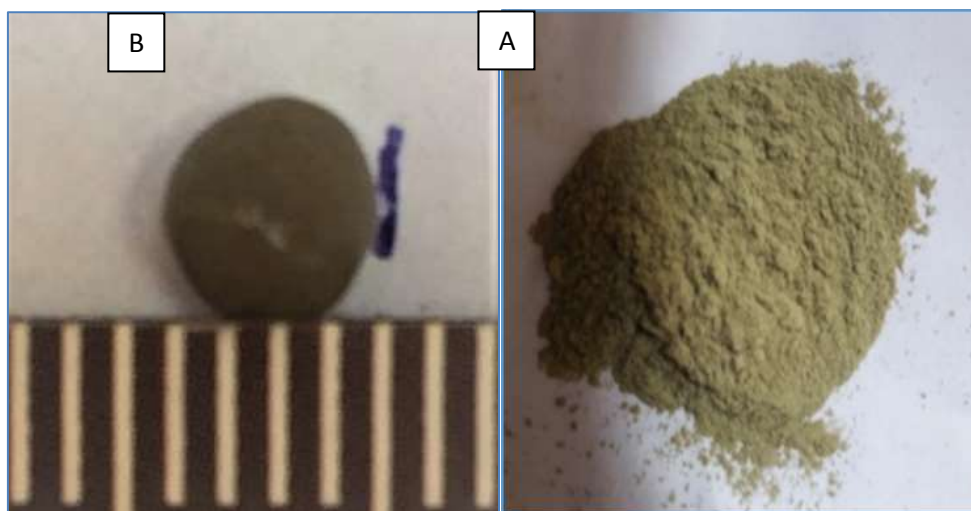
Figure.1 Collected algae (A) after drying and sieving (B) after immobilization

Chemicals

The stock solution of copper sulfate (1000 mg/L) of Cu (II) was prepared by dissolving appropriate amount of the analytical grade powders of copper sulfate ($CuSO_4.5H_2O$, purchased from BDH Company, England) different concentration for experiment prepared by dilution from the stock. The stock solutions were stored in a refrigerator under slightly acidic medium to prevent metal precipitation until further used for biosorption experiments. Solution pH adjusted using 0.1 M HCl and 0.1 M NAOH solutions throughout the experimental work to reach the desired pH value.

Experimental work

A series of 250 mL conical-flasks used in the experiments, each flask filled with 100 mL of Cu (II) ion solution of the desired concentration and sorbent amount. Several parameters changed to study the removal process as pH, initial metal concentration; contact time, sorbent dose, and agitation speed varied to study its effect on the metal removal. Kinetic and isotherm of the removal process were calculated. Agitation of flasks in the form of shaking performed for a defined time using orbital shaker (Edmund Buhler SM25, German). Volume of (10 mL) of the contaminated solution withdrawn from each flask, without the need for filtration; solution was analyzed to measure of the remaining metal concentration. The measurements carried out using atomic absorption spectrophotometer (AAS, Sens AA, Australian) the experiment done with duplicate

for more accurate result. The removal efficiency for contaminant calculated as follows:

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

Where C_o and C_e are the initial and equilibrium concentrations of copper (mg/L). The amount of sorbate retained in the sorbent material phase, 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 that added to the flask (g) and V is the volume of aqueous contaminant solution (L). The sorption data were fitted with Langmuir, and Freundlich isotherm models. In addition, kinetic data represented using models of Pseudo-first order, and Pseudo-second order.

Biosorbent characterization

The surface and textural morphology of the biosorbents was analyzed using Scanning Electron Microscopy and the Energy Dispersive X-Ray Analysis (SEM-EDX, (TESCAN, Vega III, Czech Republic) the test was made at the department of physics in al Nahreen university. The micrographs captured at an accelerating voltage of 15KV in various lower and higher magnification points, while the SEM technique used to analyze the external aspect of the adsorbent whereas the EDX spectrometer used to reveal the surface qualitative mineral components. Samples of the prepared bead were dried then send for analysis before and after adsorption to see the change made on the bead surface after removal process.

Equilibrium and kinetic studies
Equilibrium studies
Adsorption isotherm that is the equilibrium relationship at a given temperature studied. Equations that used widely to describe adsorption isotherms are Langmuir, and Freundlich, 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 (14).
a) Langmuir model
According to this model, sorption process occurs uniformly on the active sites of the sorbent at surface, and once a sorbate occupies a site, no further sorption can take place at that site, Langmuir model represented as (16):

$$q_e = \frac{q_{max}bC_e}{1+bC_e} \qquad (3)$$

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.
Freundlich model

$$q_e = kC_e^{1/n} \qquad (2)$$

Is an empirical Model that is based on sorption on heterogeneous surface and is given by eq (2) where *1/n* (usually less than 1) is the intensity of sorption and *k* is a constant related to the maximum adsorption capacity of the adsorbent (2). This empirical isotherm model is applicable for multilayer sorption and heterogeneous surfaces (3).
Sorption kinetics
The rate transformation of pollutant from aqueous solution to solid phase is very important parameter in the design of appropriate sorption treatment processes (22).

The kinetic data that measured in the present study represented using the following two models:
Psedo first order model

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad (3)$$

Integrating linearize Eq. (3) with the conditions; "t = 0 to t = t and q_t= 0 to q_t= q_t ", gives:

$$\ln(q_e - q_t) = \ln q_e - k_1t \qquad (4)$$

The non-linear form of Eq. (4) rewritten as the following form:'

$$q_t = q_e(1 - e^{-k_1t}) \qquad (5)$$

Where q_e and q_t are the equilibrium and the amount of sorbate removed from the aqueous solution time *t* respectively in (mg/g), and *k_1* is the pseudo first order rate constant (1/min) (7):
Psedo second order model
The assumption of monolayer sorbate attached to the sorbent surface in this model, energy of sorption is the same for each sorbent and there is no interaction between sorbed species. This model described as:

$$q_t = \frac{t}{\left(\frac{1}{k_2q_e^2}+\frac{t}{q_e}\right)} \qquad (6)$$

Where *k_2* is the pseudo second order rate constant (g/mg min) (1).
RESULTS AND DISCUSSION
Effect of immobilization
As show in **Fig.2** removal of copper by immobilized and blank alginate shows that immobilized algal bead give a good index in metal removal and can protect the biomass from lose facilitate handling of algae. Also show that immobilization enhance removal process by contribute with metal removal by alginate (1).
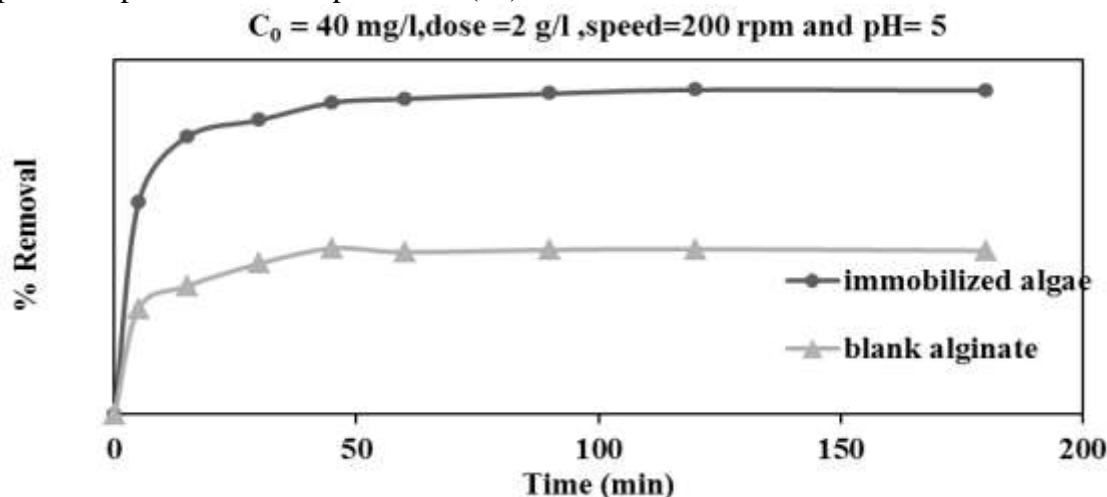

Figure.2 Efficiency of blank alginate and immobilized algal in the removal of copper ions

Sem-edx results
Fig.3 shows the SEM-EDX result of algae bead before and after Cu (II) ion removal. The SEM result indicate that after adsorption Cu(II)ion was deposit on the surface of beads, EDX show the composition of the surface of the alginate bead before and after copper sorption which indicate that change in light metal on alginate surface which support the theory of ion exchange during the removal process.
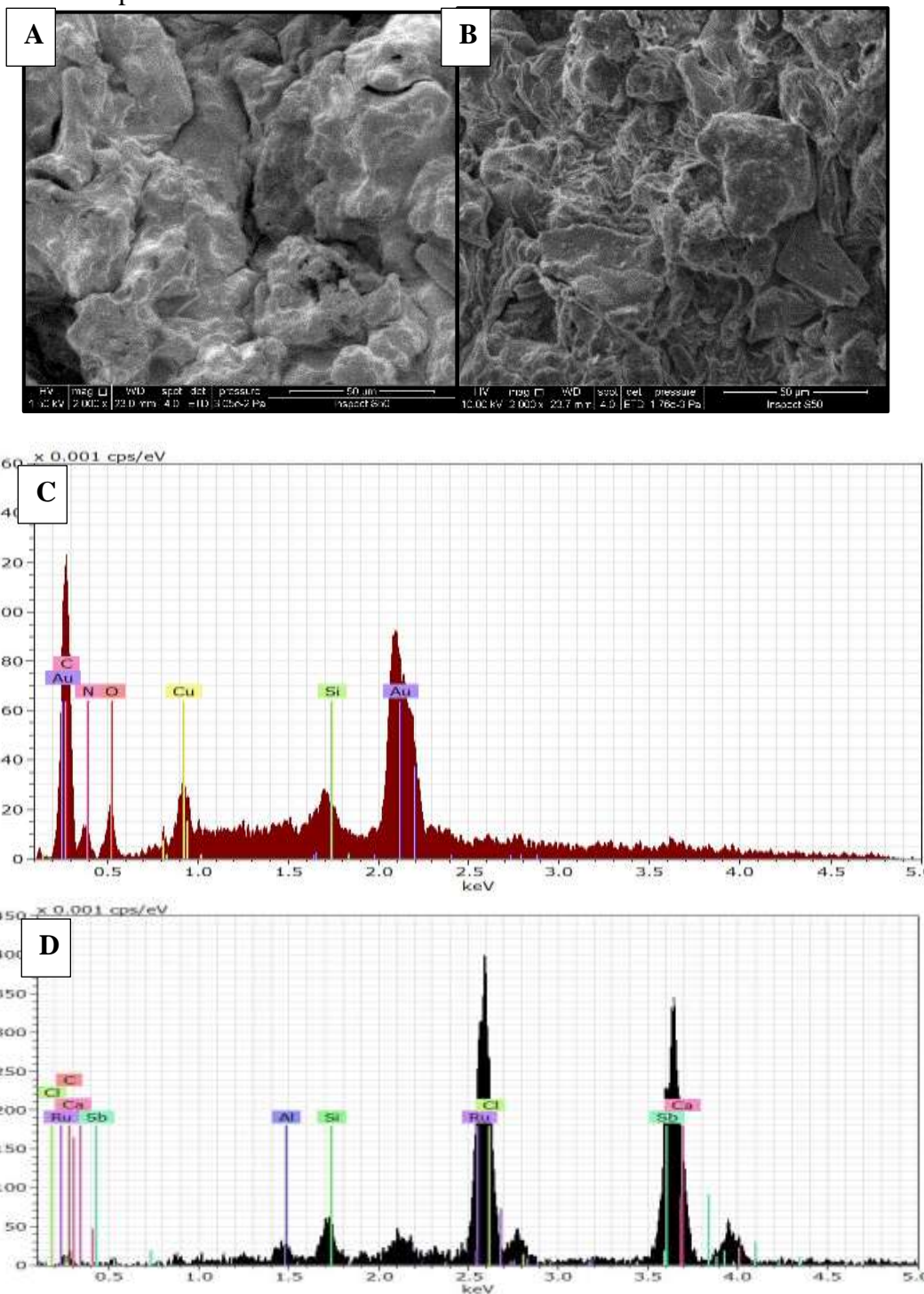
Figure 3 SEM-EDX analysis of immobilized algae A and D before B and C after cu removal

Studied parameters for sorption process
Different paramegers studied to indicate there influence on the removal process these include pH removal time, dose effect and initial metal ions concentration.

PH effect
Biosorption of heavy metal have indicated that pH is one of the important parameter affecting the biosorption process. The effect of pH was studied in a pH range, 2-6; pH was not

exceeded 6 to avoid heavy metal precipitation. Fig.4A show the variation of removal efficiency with different pH value, and the optimum pH was 5 the lowest biosorption values were observed at pH 2.0 for copper ions. because at lower pH, the sorption of heavy metal was less due to the higher concentration of the positively charged hydrogen ions in the solution that compete with metal ions for binding on the active sites on the surface of the sorbet wall (21). As the pH increased (>2-6), 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. At higher pH values (pH > 6) may attributed to that, the amount of OH- ions is increased in the solution, so metal ions react with OH- ions and are precipitated as a metal hydroxide in basic conditions (20).

Dose effect

Different dose of alginate bead (0.05, 0.2, 0.6, 1 and, 2 gm) used to study the effect of dose on sorption process as represented in Fig.4 B. The dosage of a biosorbent strongly influences the extent of biosorption. The uptake capacity increased with decreasing dosage of the biosorbent, which may be due to interference between the binding sites on the biosorbent. Increasing of the sorbent dose more than 1 gm/100 ml the quantity of biosorbed solute per unit weight of biosorbent decreases which may

be due to the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent or the biosorbent surface sites remain unsaturated during the removal process, resulting in low metal uptake (18)(4).

Sorption time

While contact time between the beads and the polluted solution Cu (II) ion, removal percentage increased significantly, Fig 4C shows that there, was a rapid biosorption rate at the initial stage, and then gradually slowed down until equilibrium is established. The slower in the biosorption was likely due to the decrease in biosorption sites on the sorbent surface of. (10)

Initial concentration

An increase in the initial metal concentration also increase the biosorption capacity as it provides a driving force that overcome the mass transfer resistance between the biosorbent and the metal in the solution. In addition, the number of collisions between metal ions and biosorbent increases with increasing initial metal concentration, and thus the biosorption process enhances. The reduction in metal removal efficiency associated with increasing metal concentration might be to the insufficient binding sites for adsorption, and that the binding site of the sorbent was saturated (10) as showed in Fig.4D
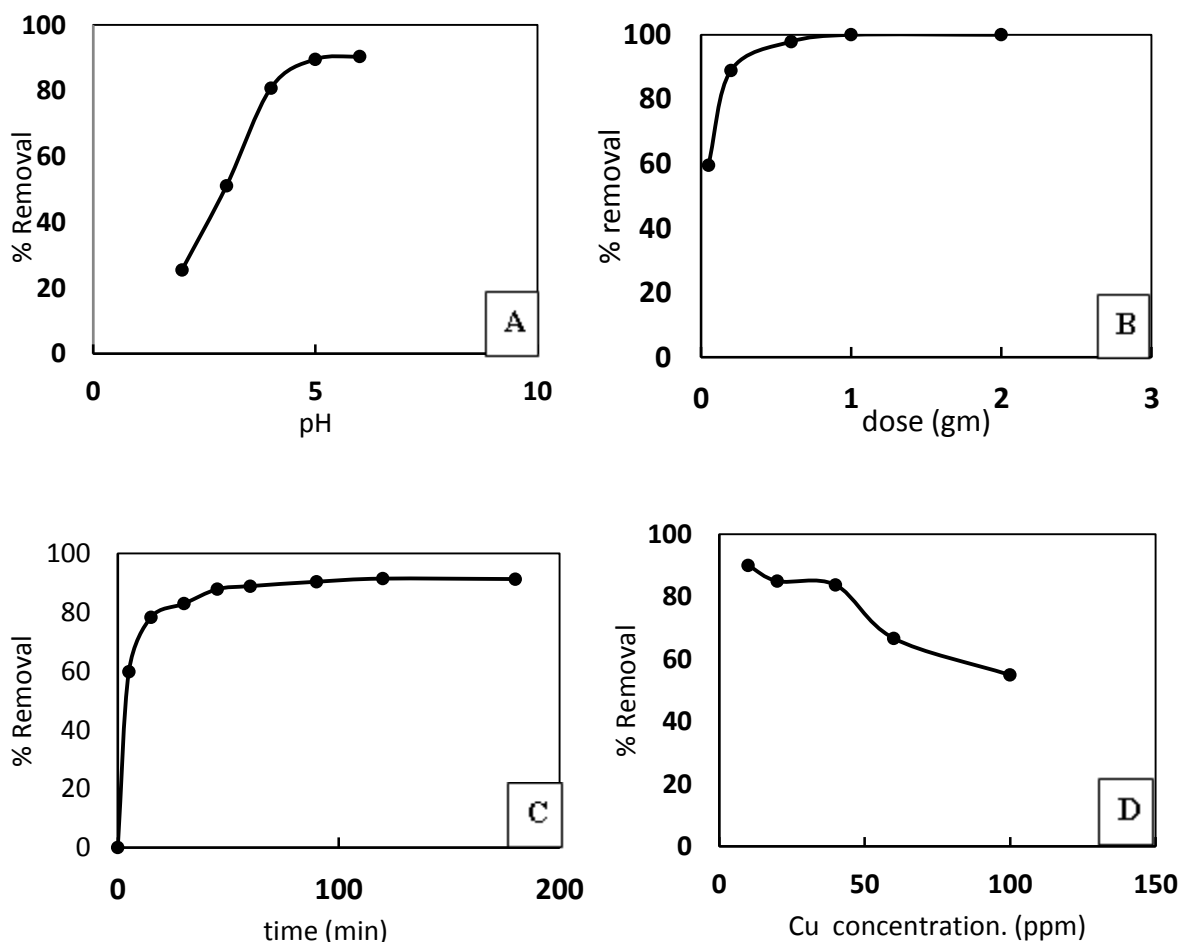
Figure 4. Effect of (A) pH (B) biosorbent dose (c).contact time and (d) initial metal conc

Equilibrium and kinetic studies
Isotherm models
From the previous described results the relationships between the sorbed quantity (q_e, mg/g) and the equilibrium concentration (C_e) for Cu(II) ion in the solution indicate the interaction between the metal and the immobilized algal bead, the results modeled using each of Freundlich and Langmuir models. These models were fitted with measured sorption data of changing initial concentration and all the constants of models determined by using nonlinear regression method in the Microsoft Excel (2016) (15). The values of the calculated parameters, and the correlation coefficients (R^2) are listed in **Table 1** and the models are represented in **Fig.5A.** From the table the high correlation coefficients were found for the two models with the Langmuir little higher than Freundlich, Langmuir model suggested that homogeneous surface of the sorbent where all the sorption sites assumed to have an equal sorbate affinity and the sorption occurs

uniformly on sorbent active sites. (13)(17). On the other hand, the Freundlich isotherm which is based on sorption on heterogeneous surface from the result it is clear that the values of Freundlich affinity constants are greater than 1 and this certify occurrence of the favorable sorption (9).

Kinetic parameters
Pseudo first-order and pseudo second-order models used to fit the experimental data using non-liner regression method as shown in **Fig.5B** and the constants of these models listed in **Table 1**. It is clear that the two models are able to explain the relationships between the experimental and predicted values; however, pseudo-second order model for sorption gave a better fit based on the values of R^2. This indicating that the sorption process were chemisorption (1). In addition, the calculated values of sorbed quantity are in a good harmony with the experimental values. In addition, **Fig.5B** shows that the uptake of NH_3-N by ion-exchange resin increased with an increasing of contact time in the first 20

min and, then, the equilibrium reached where this result is consistent with results reported by

(5).

Table 1. Parameters of the isotherm and kinetic models of Cu(II) (initial metal conc.= 10–100 mg/L, , pH =5, biosorbent content=0.2 g/100 mL, and agitation speed 200 rpm)

Isotherm model	Parameters		Kinetic model	Parameters	
Langmuir	q_{max} (mg/g)	27.072	Pseudo-first order	q_e (mg/g)	17.31
	b (L/mg)	0.185		k_1 (min^{-1})	0.38
	R^2	0.978		R^2	0.71
Freundlich	K (mg/g)(L/mg)$^{1/n}$	6.885	Pseudo-second order	q_e (mg/g)	17.78
	n	2.930		k_2 (g/mg min)	0.059
	R^2	0.923		R^2	0.99
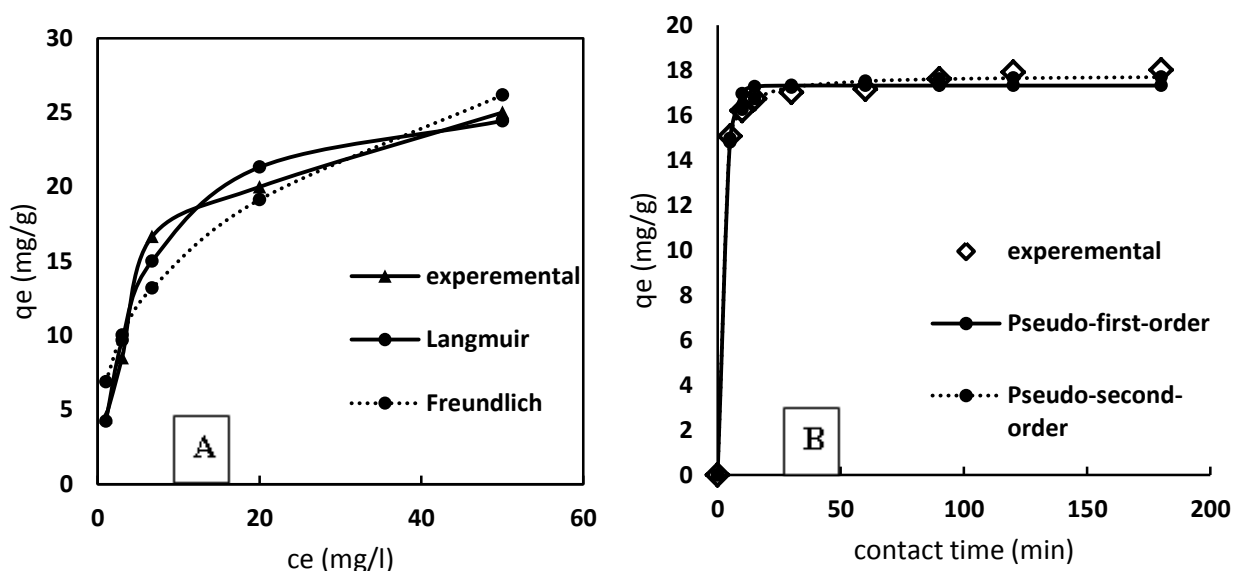
Figure 5. Represents: (A) isotherm model (B) kinetic model

This study shows that immobilized algal biomass give a good choice for copper removal. After studying the effect of different parameter on the removal process isotherm shows that both Langmuir and Freundlich model can be applicable for representing the removal process and from. Pseudo-second order kinetic model has better correlation to present the process of removal according to the model chemisorption is the controlling mechanism in the removal process and from SEM-EDX result also support the theory of chemisorption in the form of ion exchange.

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