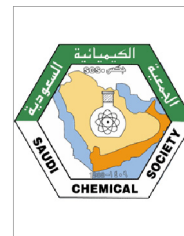




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**SPECIAL ISSUE: ENVIRONMENTAL CHEMISTRY**

# Biosorption of copper ions from aqueous solutions by *Spirulina platensis* biomass

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**Abstract** In this study, the economically important micro-alga (cyanobacterium) *Spirulina platensis* was used as biosorbent for the removal of copper from aqueous solutions. The cyanobacterium was exposed to various concentrations of copper and adsorption of copper by the biomass was evaluated under different conditions that included pH, contact time, temperature, concentration of adsorbate and the concentration of dry biomass. Increased adsorption of copper by the non-living biomass was recorded with gradually increasing pH, and a maximal uptake by the biomass was observed at pH 7. The adsorption of copper was found to increase gradually along with decrease in biomass concentration. Biosorption was found to be at a maximum (90.6%), in a solution containing 100 mg copper/L, at pH 7, with 0.050 g dry biomass and at 37 °C with 90 min of contact time. Analysis of the spectrum obtained with atomic absorption spectrophotometer (AAS), indicated that the adsorbent has a great potential to remove copper from aqueous media contributing to an eco-friendly technology for efficient bioremediation in the natural environment.

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## 1. Introduction

Environmental pollution with heavy metals is one of the most important environmental problems these days. Disposal of wastes containing heavy metals by various industries into environments is the main reason for the problem. Mining and

smelting of minerals and metals, surface finishing industry, energy and fuel production, fertilizer and pesticide industry, electroplating, electrolysis, electro-osmosis, leather work, photography, manufacture of electrical appliances, aerospace and atomic energy installation, etc. are the major source of heavy metal pollutants. Thus, heavy metal pollution has emerged as a major concern threatening human health, natural resources and ecosystem (Alluri et al., 2007). To avoid health hazards, toxic heavy metals must be removed from wastewater before their disposal. Many techniques have been developed to remove heavy metals from contaminated water, including: reverse osmosis, electrophoresis, ultra-ion exchange, chemical precipitation, phytoremediation, etc. However, all these methods have disadvantages such as incomplete metal removal, high reagent and energy requirements, and toxicity which

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requires careful disposal (Ahalya et al., 2003). In this context, safe and cost effective methods, such as microbial biomass application in industrial and waste water treatment have been established.

Copper toxicity may occur from eating food and drinking water, or breathing air enriched with an excess copper. Acute toxicity of copper may cause anemia, intravascular hemolytic, acute liver failure, and acute renal failure with tubular damage, shock, coma and death and mild conditions may result in vomiting, nausea, and diarrhea (Wyllie, 1957; Spitalny et al., 1984; Knobeloch et al., 1994).

These processes may contribute to environmental problems, as large amounts of sediment and sludge that contain toxic compounds are produced and disposed. In addition to high cost and low efficiency for removal of certain metal ions they require the highest level of technical excellence and expertise to solve the problem (Ahalya et al., 2003). Biosorption, one of the several biological treatment processes, is desired for the removal of toxic metals from wastewater since it is based on the metal binding capacity of different biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through the process of uptake via metabolism or physico-chemical pathways (Fourest and Roux, 1992).

Algal biomass is largely employed as a biosorbent material for several reasons. (a) It is available in large quantities, (b) it is largely cultivated worldwide, (c) its processing is relatively cheap and (d) good performance and low cost (Aksu et al., 1998). In this context, the main objective of the present study was to develop a bio-based technology for the removal of toxic copper pollutants from aqueous environments through biosorption using non living biomass of economically important micro alga *Spirulina platensis*.

## 2. Materials and methods

### 2.1. Biosorbent

Biosorbent for the removal of metal ions from aqueous solutions was prepared using the micro alga (cyanobacterium) *S. platensis* (*S. platensis* UTEX LB 2340) which was acquired from the culture collection of algae at The University of Texas at Austin (UTEX). The strain was cultivated using Zarrouk medium (Zarrouk, 1966). Outdoor cultures were carried out according to the methodology described for central Saudi Arabia (Al-Homaidan, 2002). The sun-dried biomass was rinsed with deionized water to remove the residual alkalinity. Later, it was dried in an oven initially at room temperature for 24 h and subsequently at 80 °C for 12 h. The dried biomass was then ground well and passed through a 150–200 mesh sieve to obtain a powder form. Finally the contents were stored in a desiccator at room temperature to be used as a powdered biosorbent (Solisio et al., 2006). Dried algal biomass was used for the studies after rehydration. Re-hydrated biomass was prepared by suspending the prepared dry biomass in 100 ml of deionized water taken in 250-ml-Erlenmeyer flasks. After agitation on a rotary shaker (150 rpm) at ambient temperature for 60 min, the biomass was recovered by filtration through a 0.45 µm membrane filter (Millipore Corporation, U.S.A.) and immediately used in adsorption studies (Cruz et al., 2004).

### 2.2. Preparation of stock solution of copper

A stock solution of 1000 ppm copper solution was prepared by dissolving 2.51 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 1 L of deionized distilled water. Various concentrations of test solutions were prepared by appropriate dilution of the stock solution. The initial pH of each solution was then adjusted to the required value with different concentrations of HCl and NaOH solutions before mixing the biosorbent suspension.

### 2.3. Biosorption studies

Batch mode adsorption studies were carried out to investigate the effect of different parameters such as biomass, contact time, temperature, and initial concentration of copper, and pH on the rate of adsorption of copper by biomass. Solution containing adsorbate and adsorbent was taken in 250 mL capacity flasks and agitated at 150 rpm in an environmental shaker (Spain, Model Comecta, s.a) at predetermined time intervals. The adsorbate was then decanted and separated from the adsorbent after centrifugation (6000 rpm, for 30 min) followed by filtration using 0.45 µm membrane filters (Millipore Corporation, U.S.A.).

### 2.4. Effects of biomass dose

The effect of dose (concentration) of adsorbent biomass on adsorption of copper was studied using different biomass concentrations [1.5, 1, 0.75, 0.5, 0.25, 0.2, 0.150, 0.100, 0.050, 0.025, 0.02 g (dry weight)/L] and with 100 mg/L of copper. The equilibrium time and the pH of the test solution were kept constant.

### 2.5. Effects of contact time

Impact of contact time on adsorption of copper by biomass was determined at varying periods of incubation time (30, 60, 90, 120, 150 and 180 min), with an initial concentration of copper 100 mg/L in an environmental shaker (Spain, Model Comecta, s.a). After incubation for specified contact time, the supernatant was analyzed for residual metal concentration in the solution. The pH and the adsorbent concentration of the biomass were kept constant, unless otherwise specified.

### 2.6. Effects of temperature

Effect of incubation temperature on biosorption of copper was carried out at different incubation temperatures (20, 26, 37, 45, 55 and 60 °C) with an initial concentration of copper 100 mg/L in an environmental shaker (Spain, Model Comecta, s.a). The pH, concentration of adsorbent biomass, and contact time were kept constant throughout the study unless otherwise mentioned.

### 2.7. Effects of pH

To determine the effect of pH on adsorption of copper by algal biomass test solutions containing initial concentration of 100 mL of copper with different pH levels (2, 3, 4, 5, 6, 7, 8, 9, and 10) were prepared by adjusting the pH to desired initial

pH value using 1 N HCl or 1 N NaOH before mixing the adsorbent. pH measurements were done using pH meter (Mettler–Toledo GmbH, Switzerland). The equilibrium time, temperature and biomass concentrations were maintained constant throughout the study unless otherwise mentioned.

### 2.8. Effects of initial concentration of copper

The impact of initial concentration of copper in test solution on adsorption by biomass was studied at different initial concentrations (10, 40, 50, 60, 100, 150 and 200 mg/L) in 100 mL aliquots of test solution prepared using stock solution of copper. The equilibrium time, temperature, pH and biomass concentration were maintained constant throughout the study unless otherwise specified.

### 2.9. Heavy metal analysis

After adsorption, the adsorbates – loaded adsorbent were separated from the solution by centrifugation at 6000 rpm for 30 min and then all the samples were filtered immediately through 0.45 µm membrane filters (Millipore Corporation, U.S.A.) to remove biomass. Copper concentrations in test solutions were analyzed by flame atomic adsorption spectrometer (AAS), model AA240FS (Varian, Milan, Italy). Copper concentrations were expressed in mg/L in liquid and the difference between the initial and the residual concentrations was assumed to be adsorbed by *S. platensis* cells (Zhou et al., 1998).

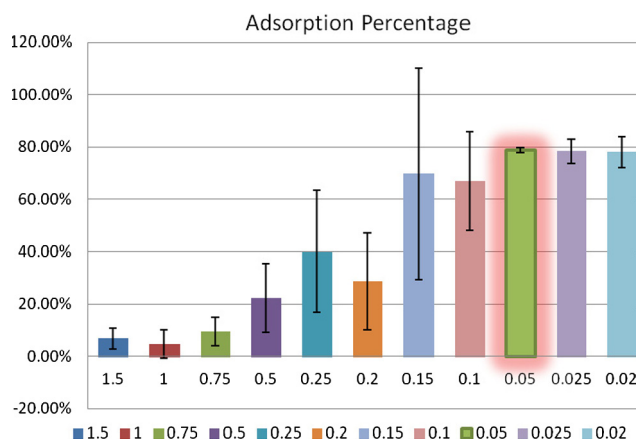
### 2.10. Confirmation test for all the optimal conditions for sorption

Experiments were conducted in the sequential order used for the determination of optimal level of parameters and the best result from each experiment was applied for the subsequent and rest of the experiments followed in the sequence. After determination of optimal levels that supported maximal sorption, the same optimal conditions were chosen for all experiments and repeated three cycles to confirm the obtained results. All the tests were carried out in quadruplicate and the standard deviations and percentage errors between data and mean values were statistically treated.

## 3. Results and discussion

### 3.1. Effect of biomass concentration on adsorption of copper

Results presented in Fig. 1 indicate that the optimum dose of biomass for maximal removal of copper ions was found to be 0.050 g/100 mL with a removal efficiency of 78.82%. It was observed that the metal removal efficiency of the algal biomass was a function of biomass concentration and the percent removal of copper (adsorption) declined along with the increase in biomass concentration from 0.05 g/100 mL. Further it was also noted that maximal adsorption of copper was possible even with low biomass concentrations of 0.025 g/100 mL and 0.020 g/100 mL which effected 78.3% and 77.95%, respectively. Therefore, the optimum biomass dosage was selected as 0.05 g/L for further experiments. pH 7.0 was found to be the ideal condition for effecting maximal adsorption of metal during these experiments. The biomass concentration is an important

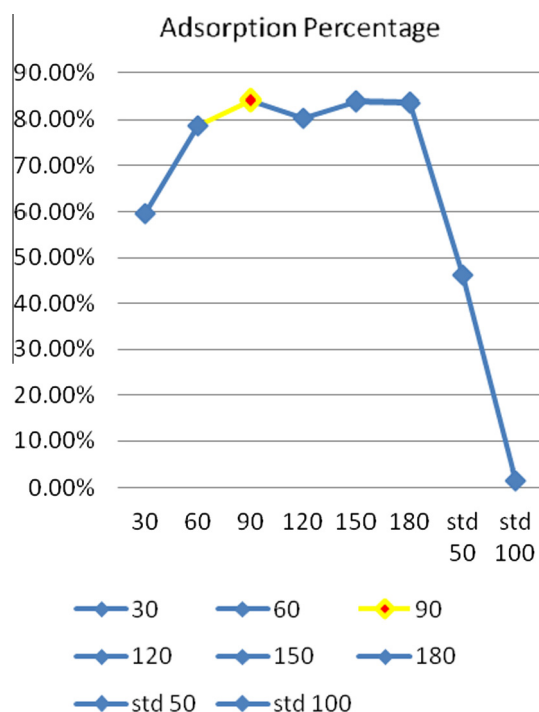


**Figure 1** Effect of biomass concentration on adsorption of copper by non-living biomass of *S. platensis* from solution with stable pH 7.0, 26 °C, 90 min. contact time and 100 mg/L of initial concentration of copper.

variable during metal uptake. At a given equilibrium concentration, the biomass takes up more metal ions at lower cell densities than at higher cell densities (Mehta and Gaur, 2001). It has been suggested that electrostatic interaction between cells can be a significant factor in the relationship between biomass concentration and metal sorption. In this regard, at a given metal concentration, the lower the biomass concentration in suspension, the higher will be the metal/biosorbent ratio and the metal retained by a sorbent unit, unless the biomass reaches saturation, suggesting that high biomass concentrations can exert a shell effect protecting the active sites from being occupied by the metal. Thus, a smaller amount of metal uptake per biomass unit is enabled (Rome and Gadd, 1987). In the present study it was noted that the amount of adsorbent significantly influenced the extent of copper biosorption.

### 3.2. Effect of contact time on adsorption of copper

Data presented in Fig. 2 evidence that adsorption of copper by microalgal biomass increased with an increase in contact time up to 90 min and remained stable until 180 min. Maximum adsorption was recorded within the first 90 min. It was inferred that the contact time influenced the biosorption of Cu by biosorbent from aqueous solutions since it was noted that the rate of copper biosorption by the nonliving cells was very rapid, reaching almost 84.1% within 90 min of contact time. Further, it was also observed that the level of biosorption of copper remained in the range of 80.39–84.1% during the next 90 min of incubation indicating a saturation point of adsorption. Earlier studies have indicated that the process of biosorption became slow during the later stage because during the initial stage of Cu biosorption a large number of unmanned surface sites were available for biosorption compared to that in the later stages, when the rest of the site surface vacancies were probably inaccessible or deeper in the cell membranes (Kumar et al., 2006a, b; Amarasinghe and Williams, 2007; Zafar et al., 2007). As a result it becomes mandatory to determine the optimal contact time for achieving maximal adsorption of metal at the earliest possible time of incubation by the biomass toward having efficient biosorption and consequent metal removal. Results of

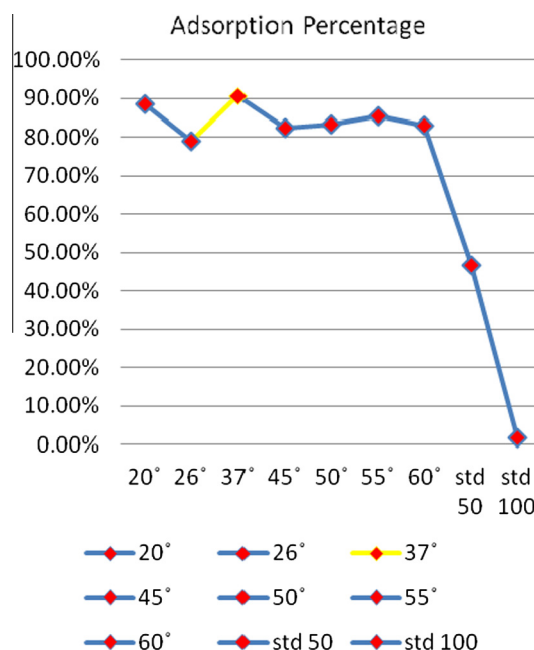


**Figure 2** Effect of contact time on adsorption of copper by non-living biomass of *S. platensis* (0.05 g/L, pH 7.0, 26 °C, and 100 mg/L of initial concentration of copper (expressed as percent adsorption)).

the present study indicated efficiency of *S. platensis* biomass for rapid metal uptake in short periods of contact time.

### 3.3. Effect of temperature on adsorption of copper

Temperature has a vital effect on adsorption process as it can influence the process by an increase or decrease in the amount of adsorption. The effect of temperature on the removal of Cu was investigated as a function of contact time. The kinetic energy of Cu particles increased with increasing temperature of the solution. Results obtained during the course of the present study demonstrated the effect of temperature (20–60 °C) on the biosorption of Cu by the non living biomass of *S. platensis* (Fig. 3). It was found that metal uptake increased gradually with an increase in temperature and the rate of copper biosorption by the nonliving cells was rapid reaching a maximum of 90.61% at 37 °C temperature, indicating that the removal of the copper from aqueous to adsorbent is rapid at ambient temperatures compared to higher temperatures (45–60 °C) where adsorption was in the range of 82.3–85% and at 26 °C (78.8%). In fact about 88% of adsorption of copper was recorded at 20 °C indicating the efficiency of biomass for enhanced uptake of copper. Broadly speaking the biomass was capable of taking up copper at levels above 78% at all temperatures studied indicating that variation in incubation temperature did not influence significantly the process of biosorption, since the observed difference in percent removal was not much. Temperature plays a crucial role in biosorption of metal ions since under certain range it affects (positive/negative) the biosorption of metal ions (Khambhaty et al., 2009). As the collision frequency between adsorbent and Cu particles increased at 37 °C, the Cu particles could have been electro statically



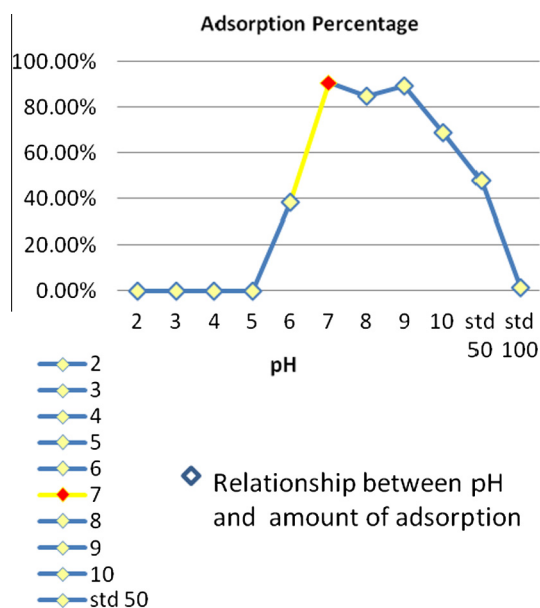
**Figure 3** Effect of temperature on adsorption of copper from solution by non-living biomass of *S. platensis* with stable biomass concentration (0.05 g/L), pH 7.0, 90 min contact time, and 100 mg/L of initial concentration of copper.

adsorbed onto the surface of the adsorbent particles. This indicates that biosorption process of Cu ions is endothermic. Previous studies related to biosorption of heavy metals indicated that the effect of temperature on biosorption depends on metal biosorbent systems. Similar results were observed for copper on different biomaterials (Nuhoglu and Oguz, 2003).

### 3.4. Effect of pH on adsorption of copper

One of the critical factors that influences adsorption of metal ions is pH since it directly affects the metal solubility or the dissociation degree of functional groups located on the surface of sorbent. Thus the adsorption of copper by *S. platensis* was observed in the present study as a function of pH (Fig. 4). Results showed that in all cases, metal uptake by the biomass increased with an increase in pH from 5.0 to pH 7.0 although optimal pH for maximal copper adsorption was found to be 7.0. Further it was noted that adsorption of copper by biomass was affected by acidic pH (pH 2.0–5.0) while pH 7.0 to 9.0 supported the adsorption process. However, highly alkaline pH conditions (pH 10.0) led to a decline in adsorption efficiency. In general, the metal adsorption rate decreases to a large extent with an increase in alkalinity mainly at pH > 6.0–7.0 (Vannela and Verma, 2006). An increase in pH means a lower amount of protons, which causes a decrease in the competition between proton and heavy metal ions. Increased pH is an indication that the ligands are available for metal ion binding and so biosorption is enhanced (Kaewsarn, 2002). Further, the interaction between sorbents and sorbent is affected by the pH of an aqueous medium in two ways: firstly, metal ions can have different forms in different types of pH. Secondly, the surface of the biosorbent composed of biopolymers with many functional groups, affecting the net charge of biosorbent (Maurya et al., 2006). The results of the present study indicated that the





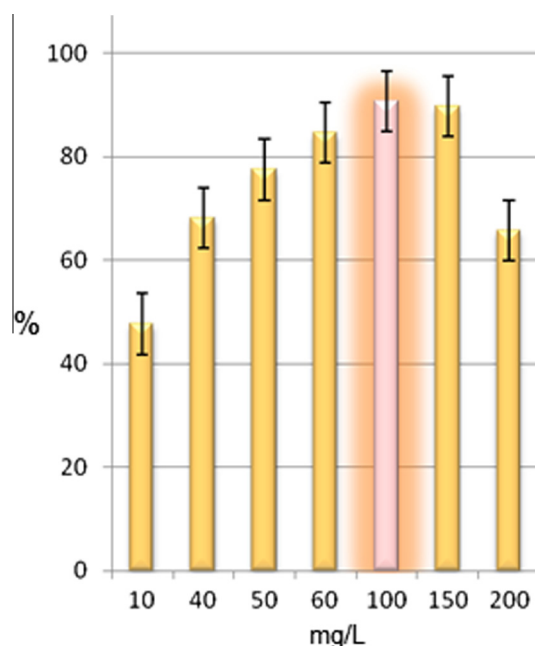
**Figure 4** Effect of pH on adsorption of copper by non-living biomass of *S. platensis* with stable biomass concentration (0.05 g/L), 37 °C, 90 min contact time, and 100 mg/L of initial concentration of copper.

adsorption of copper increased along with an increase in pH of the aqueous solutions. In fact the cell surface of non-living cells becomes more positively charged at low pH values, thereby reducing the attraction between metal ion and functional groups at the cell wall. On the other hand, when the pH increases, the cell surface is more negatively charged and preferably keep the process until reaching a maximum around pH 7 (Volesky and Holan, 1995).

At pH < 3.0, hydrogen ions compete with metal ions for the same adsorption sites on the biosorbent, compromising again metal sorption. Therefore, there is an optimum pH for the sorption of each metal, usually within the range 4.0–6.0, in which the competition of hydrogen ions is minimized, thereby enhancing metal sorption (Gong et al., 2005). In spite of the discrepancies recorded in the literature on the effect of pH on the biosorption it is inferred that pH would alter the process of adsorption of metal ions to cells and it varies with the type of adsorbents (cells) and adsorbates (metal ions) (Chen et al., 2005). Thus in the present study it was observed that acidic pH levels did not support biosorption while neutral pH 7.0 favored maximal biosorption of copper by non-living cells of *S. platensis*, similar to that reported earlier for other species of microorganisms (Volesky and Holan, 1995).

### 3.5. Effects of initial concentration of copper on adsorption of copper

Data presented in Fig. 5 evidence the effect of initial metal ion concentration ranging from 10 to 200 mg/L on the adsorption of copper by algal biomass. Increase in initial copper concentration was found to influence an increase in biosorption of copper by biomass and concentration of 100 mg/L recorded the optimum absorption of copper. The initial metal concentration plays an important role in the process of biosorption. In fact along with an increase in concentration of copper from 10 to 100 mg/L there was a gradual increase in adsorption from



**Figure 5** Effect of initial concentration of copper on adsorption by non-living biomass of *S. platensis* with stable biomass concentration (0.05 g/L), pH 7.0, 37 °C, and 90 min of contact time.

47.65% to 90.61%, almost a double fold increase in percent adsorption was recorded at 100 mg/L. However, further increase in initial concentration of copper above 150 mg/L led to a decline in the percent adsorption of copper indicating saturation of all the binding sites on algal surface beyond a particular concentration. An earlier study reported that percent adsorption decreased with an increase in the metal concentration, due to saturation of all binding sites with metal ions and establishment of equilibrium between adsorbate and biosorbent (Bai and Abraham, 2001). The initial concentration of metals plays an important role in the process of biosorption, probably due to the reason that large amounts of metal ions are available to compete on the binding sites. Thus Cu concentration above 100 mg/L did not increase the biosorption significantly and percent metal removal remained almost constant or showed even a decrease indicating saturation of all the binding sites on algal surface beyond a particular concentration (Ozturk et al., 2004). In the present study a similar decrease in the removal efficiency with increasing Cu concentration up to 200 mg/L was observed. Further it was noted that percent metal removal decreased from 90.6% to 65.7%. The decrease was probably due to the saturation of the sorption sites on the adsorbent, as the concentration of the metal increased. However, higher biosorption yields were observed at lower metal concentrations (Malkoc, 2006). The adsorption capacity (mg of adsorbed metal/g microalgal biomass) was found to increase exponentially along with an increase in the initial metal concentration in the range of 10–200 mg metal/L. An increase in biomass adsorption capacity with the increasing initial metal concentration has been previously reported for both single and mixed metal solutions and was attributed to the higher mass transfer and kinetic energy, thus the probability for collision between metal ions and the biosorbents (Atkinson et al., 1998; Donmez et al., 1999; Lesage et al., 2007).

#### 4. Conclusion

Biosorption is a relatively new process that has been shown to have a considerable potential for the efficient removal of pollutants from aqueous effluents. The present study gives the evidence of the possible benefits of using the dry biomass of *S. platensis* for the removal of heavy metals from aqueous media and the biomass concentration was found to have a significant impact. The dried algal biomass, in the batch experiment, was found to be very efficient in removing copper ions ( $\approx 90.6\%$ ) from aqueous solution containing metal waste, and the maximum removal rate was achieved within 90 min of contact time. The process is strongly affected by several parameters such as: contact time, initial copper concentration and the pH of the solution. This study indicated the scope for developing an appropriate technology for effective designing of a waste water treatment plan. However, further work should be performed in order to have a better understanding of copper biosorption binding mechanism by dried *S. platensis*. It is concluded that this adsorbent has a great potential for removing copper from aqueous solutions as an eco-friendly process.

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