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Research Article

Equilibrium and Kinetics Studies by using *Spirulina platensis* as a Biosorbent for the Toxic Metal Ions

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Abstract

The removal of toxic heavy metal ions from wastewaters is of great concern from an environmental point of view. Biosorption is an effective technology using non-living biomass to remove toxic metal ions from aqueous solutions. In this work removal of Lead (Pb) ions and Chromium (Cr) ions from aqueous solutions has been achieved by using low cost, economical, biodegradable and natural material dried biomass of *Spirulina platensis*. The residual concentration of metal ions from the absorption medium was determined by using atomic absorption spectrophotometer (AAS). Lagergren equation describes sorption kinetics of Pb ions and Cr ions. After comparing kinetic data of both metals, it was found that the kinetics follow pseudo-second-order kinetics in the both case of Pb ions and Cr ions. The results from this study indicates that biodegradable *Spirulina platensis* is a good adsorbent for the removal of lead and chromium ions from wastewater.

Keywords: Biosorption, Spirulina sp., toxic metals, kinetic model, wastewater

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Introduction

Biosorption is the process of adsorption by either living microbial biomass or dead microbial biomass and it offers some important advantages such as low cost and high efficiency in removing metal ions and the possibility of recovering the valuable metal ions adsorbed by the biosorbent. Microbial cell wall is provided with amine, carboxylic, thiolic, sulphydrylic and phosphoric functional groups which can bind metal ions and removal from diluted solutions are environmental friendly [1]. However, conventional techniques, such as chemical precipitation, ion-exchange, activated carbon adsorption and membrane separation processes have limitations for the removal of heavy metals from wastewater. They become inefficient and expensive especially when the heavy metal ions concentration is less than 100 ppm [2]. The ability of microorganisms to accumulate metal ions from aqueous solutions has been widely reported [3, 4]. Compared with conventional methods for removing heavy metals from industrial effluents like chemical precipitation, chemical reduction, adsorption, ion exchange, evaporation and membrane processes, the biosorption process offers potential advantages such as low operating cost, minimization of chemical, high efficiency because microorganisms effectively bind hazardous and potentially toxic metal ions [5].

Environmental pollution due to toxic heavy metals include Cd, Hg, Ag, Pb, Sn and Cr, although several nutrient metals, notably Zn, Cu and Ni, also more significant worldwide problem for both human health and aquatic ecosystems, due to their bio magnification in the food chain and continued persistence in the ecosystem [6-9].These metals cannot be degraded once released into the environment. The release of heavy metals from industries into the environment has resulted in many problems for both human health and aquatic ecosystems and Accumulation of trace metals in the food chain has been considered as a major environmental hazard [10]. Heavy metals pollution has emerged as a major concern threatening human health, natural resources and ecosystem [11].

The biological removal of metal ions from industrial wastewaters is a relatively new technology which usually employs biomass as biosorbent can successfully be used for low metal concentrations [12], marine algae which have successfully been used for this purpose are *Scenedesmus abundans*, *Ecklonia radiata*, and *Sargassum fluitansm*, Red algae (*Rhodophyta*), *Cladophora fascicularis* resulted into an effective and economical biosorbent material for the removal of heavy metal ions [13-17]. Various biomasses such as bacteria, yeast, fungi and algae have been widely used for heavy metal removal [18-23].

Lead is one of the toxic heavy metals with a greatest potential hazard to aquatic as well as terrestrial environment. The anthropogenic sources of lead include waste from the factories, leaded petrol, paints and antirust agents [24]. If lead passage through blood vessels, it can disturb bone marrow, liver, reproductive organs and kidneys functions, it can also cause anemia and metabolic disorders [25]. Chelation treatment sometimes leads to fatal outcome due to immediate surge of lead from the deposited site to blood causing severe damages to kidney and brain [26]. Chromium (VI) is known to be more toxic to plants as well as animals, as strong oxidizing agent and a potential carcinogen [27].Cr (III) is generally only toxic to plants at very high concentrations and is less toxic or nontoxic to animals [28]. Strong exposure to Cr (VI) causes cancer in the digestive tract and lungs, epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage.

Spirulina platensis is available in large quantities, worldwide cultivated and its production is about 2000 tons per year [29]. It contains a variety of functional groups like carboxyl, phosphate, hydroxyl, sulphate and other charged groups which can be responsible for the binding with different variety of pollutant material [30]. In this study, *Spirulina platensis* is used to remove lead and chromium ions from aqueous solutions. A kinetic study was carried out for lead and chromium ions removal.

Materials and Methods

Spirulina platensis is easily available in the market in the form of powder, capsules and tablets. All the chemicals used throughout the study were of analytical grade.

Adsorption of metal as a function of the contact time

Kinetic sorption studies for lead and chromium ions were carried out for *Spirulina platensis*, temperature 25 ºC for initial amount 30 mg Chromium and 30 mg lead in 25 mL of double distilled water separately taken into various 50 mL flask. The fixed amount of *Spirulina platensis* (1.0 g) was weighed into the flasks and agitated in an orbital shaker for the different contact time period (10, 20, 30, 40, 50, 60, 70 and 80 minute). After each agitation time, the content of each flask was centrifuged and the residual concentration of metal ions in supernatant solution was analysed using atomic absorption spectrophotometer (ECIL-4141). Blank solutions were also prepared and analysed with AAS.

Adsorption of chromium and lead ions as a function of the contact time

The effect of the contact time in case of was investigated by varying the contact time from 10 to 80 minutes at 25 °C. As a function of contact time, the uptake of chromium metal ions by *Spirulina platensis* was moderate at room temperature, with adsorption attaining a value of 25.26% within 10 minutes and 62.12 % within 30 minute, **Figure 1A**. The maximum uptake was only 94.99% which was attained within 60 minutes and after that it going to slightly decreases up to 80 minutes.

In case of lead, adsorption was very fast attaining a value of 42.99% within 10 minutes and 75.24 % within 20 minutes, Figure 1B. The maximum uptake was only 93.70% which was attained within 30 minutes and after that it going to slightly decreases up to 80 minutes.

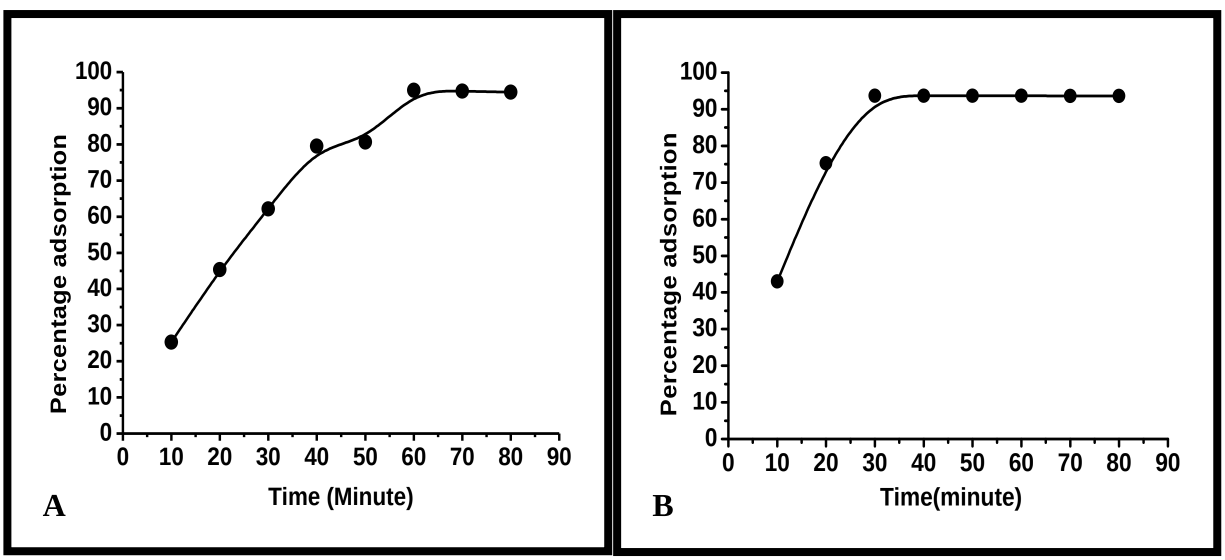

Figure 1 Effect of contact time on the percentage uptake of chromium (A) and lead (B) by *Spirulina platensis*

After each agitation time, the content of each flask was centrifuged and the residual concentration of metal ions in supernatant solution was analysed using atomic absorption spectrophotometer. The percentage absorption of chromium and lead ions from the solution was calculated by the following equation (1).

$$\text{Percentage adsorption of metal} = \{(C_i - C_e) / C_i\} \times 100 \qquad (1)$$

Where C_i is the initial concentration of metal ions in aqueous solution and C_e is the concentration of metal in the supernatant at the equilibrium stage.

Adsorption kinetics

Several kinetic models are available to understand the behavior of the adsorbent of metal on *Spirulina platensis* but in the present study; the adsorption data were analysed using two kinetic models, the pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order model was presented by Lagergren [31]. The Lagergren's first-order reaction model is expressed in linear form as equation (2):

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)t \qquad (2)$$

Where q_e and q_t are the amounts of chromium and lead (mg/g) adsorbed on the *Spirulina platensis* at equilibrium, and at time t, respectively and K_1 is the rate constant (min^{-1}) of the pseudo-first-order adsorption process. The plot of $\log(q_e - q_t)$ versus t would be linear for *Spirulina platensis* with a slope of $-K_1/2.303$ and an intercept of log q_e.

In case of chromium and lead, pseudo–first order reaction model, **Figure 2A,B**, the correlation coefficient was found to be 0.4899 and 0.6267 respectively suggesting that the adsorption process is more favourable for lead as compare to chromium. Parameter of pseudo-first order kinetics for chromium ion and lead ion was listed in **Table 1**. In table 1 lists the equilibrium sorption capacity (q_e), the correlation coefficient, R^2, and the rate constants for the pseudo-first-order (K_1) models for both the metal ions.

Table 1 Parameters of the linear fitted kinetic studied of Pseudo-first-order model for chromium and lead ions on *Spirulina platensis*

Pseudo-first-order model (Cr)			Pseudo- first -order model (Pb)		
K_1 (min^{-1})	q_e (mg/g)	R^2	K_1 (min^{-1})	q_e (mg/g)	R^2
0.05090	15.88546	0.4899	0.09235	05.00495	0.6267

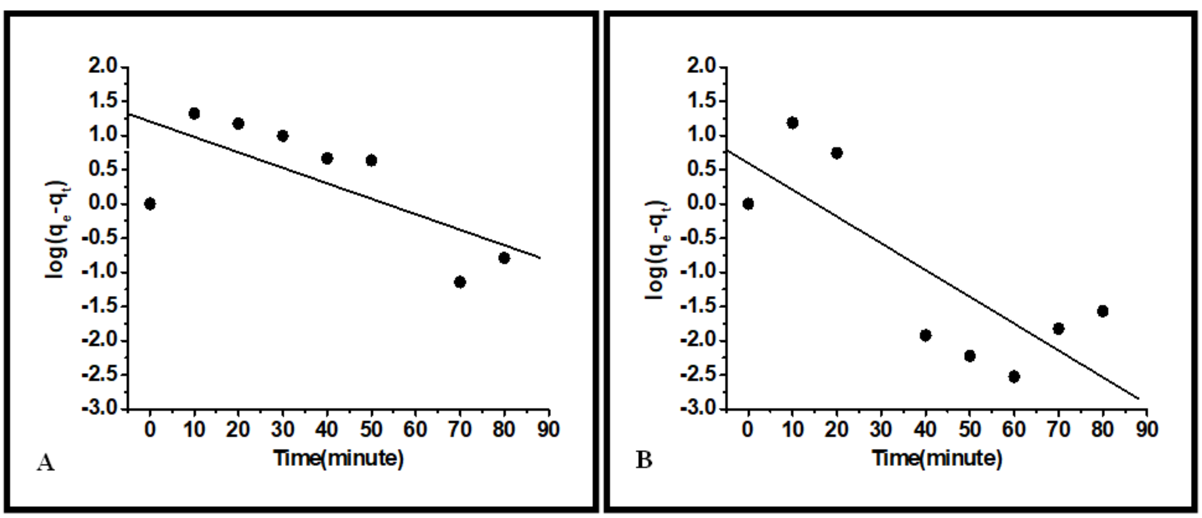

Figure 2 Plots of the application of the pseudo-first-order kinetic model to the data for the adsorption of Chromium (A) and lead (B) ions onto *Spirulina platensis*.

The adsorption data was also analysed in terms of pseudo-second-order mechanism, described by Y.S. Ho and McKay [32] the linear form of the equation (2) as follows:

$$t/q_t = 1/K_2 q_e^2 + (1/q_e)t \qquad (2)$$

Where K_2 is the rate constant of pseudo-second-order adsorption (g/mg min), $K_2 q_e^2$ is the initial rate of adsorption of metal (mg/g min). The plot of t/q_t against t of equation (2) should give a linear relationship for *Spirulina platensis* with a slope of $1/q_e$ and an intercept of $K_2 q_e^2$.

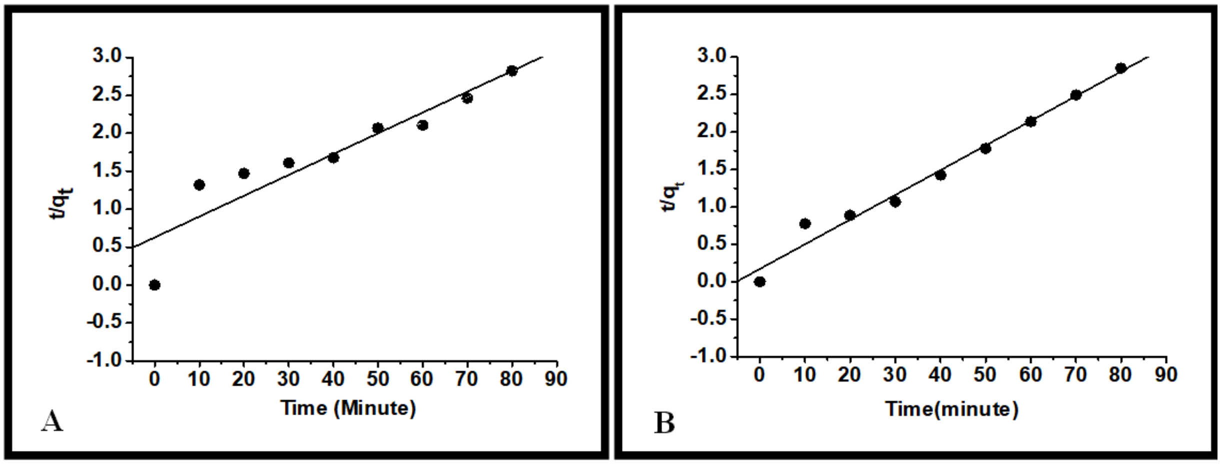

Figure 3 Plots of the application of the pseudo-second-order kinetic model to the data for the adsorption of Chromium (A) and lead (B) ions onto *Spirulina platensis*

Pseudo-second order plot, **Figure 3A,B** for chromium and lead ions shows a linear behaviour with correlation coefficient, R^2 is 0.8620 and 0.9812 respectively, therefore, the kinetic parameters suggest that adsorption process follows pseudo second order kinetic model. In case of lead ions, on the basis of correlation coefficient it is more linear as compare to chromium ions. Parameter of pseudo-second order kinetics model for chromium and lead ions is listed in **Table 2**. Table 2 represents the equilibrium sorption capacity (q_e), the correlation coefficient, R^2, and the rate constants for the pseudo-second order (K_2) models for both the metal ions.

Table 2 Parameters of the linear fitted kinetic studied of Pseudo-second-order model for chromium and lead ions on *Spirulina platensis*

Pseudo-second-order model (Cr)			**Pseudo-second-order model (Pb)**		
K_2 [g/(mg min)]	**q_e (mg/g)**	**R^2**	**K_2 [g/(mg min)]**	**q_e (mg/g)**	**R^2**
0.00119	36.49635	0.8620	0.00626	30.39510	0.9812

The data demonstrate good compliance with pseudo-second-order rate law rather than the pseudo-first-order rate law. This shows that the pseudo-second-order kinetic model show a better explanation of the kinetic adsorption data obtained in the present study. *Spirulina platensis* is electronegative in nature which attracts the positively charged metals ions. This would allow electrostatic interaction between the positively charged metal ions and the *Spirulina platensis* surface.

Conclusions

This study indicated that *Spirulina platensis* is a good adsorbent for removal of chromium and lead ions from aqueous solutions because it contains a variety of functional groups like carboxyl, phosphate, hydroxyl, sulphate and other charged groups which can be responsible for the binding with metal ions. The kinetics of the adsorption of lead ions was rapid in the initial stage as compare to chromium ions. The kinetic data demonstrate good compliance with pseudo-second-order rate law rather than the pseudo-first-order rate law.

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