ORIGINAL ARTICLE

Adsorptive removal of cadmium ions by *Spirulina platensis* dry biomass

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Abstract   Cadmium is one of the most toxic substances found in aquatic ecosystems. This metal tends to accumulate in photosynthetic plants and fish and is transferred to humans causing many diseases. It has to be removed from our environment to reduce any health risks. Dry biomass of the microalga (cyanobacterium) *Spirulina platensis* was used as biosorbent for the removal of cadmium ions (Cd^{2+}) from aqueous solutions. The effects of different levels of pH (3–9), biomass concentration (0.25–2 g), temperature (18–46 °C), metal concentration (40–200 mg/l) and contact time (30–120 min) were tested. Batch cultures were carried out in triplicate in an orbital shaker at 150 rpm. After centrifuging the biomass, the remaining levels of cadmium ions were measured in the supernatant by Atomic Absorption Spectrometer. Very high levels of removal, reaching up to 87.69% were obtained. The highest percentage of removal was reached at pH 8, 2 g of biosorbent, 26 °C, and 60 mg/l of cadmium concentration after 90 min of contact time. Langmuir and Freundlich isotherm models were applied to describe the adsorption isotherm of the metal ions by *S. platensis*. Langmuir model was found to be in better correlation with experimental data ($R^2 = 0.92$). Results of this study indicated that *S. platensis* is a very good candidate for the removal of heavy metals from aquatic environments. The process is feasible, reliable and eco-friendly.

1. Introduction

Anthropogenic activities are the major cause of heavy metal pollution in aquatic environments. Some of them such as Cu and Zn are required in traces as micronutrients by living organisms, but they become toxic at high concentrations. Other metals like cadmium and lead are very toxic even at low concentrations (Aksu and Acikel, 2000; Kang et al., 2007). The recent wide use of cadmium in industries and disposal of waste containing Cd have led to an increase in the

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residual concentration of cadmium in air, water, soil and food (Landis and Yu, 1998). Cadmium exposure has been associated with many health effects upon both chronic and acute exposure. Due to the toxic effects on human health, this heavy metal needs to be removed before it accumulates in the environment and passes into the human food chain. Chemical precipitation, ion exchange, adsorption on activated carbon and electro dialysis etc. are employed as conventional methods for removal of metal ions from aqueous solutions (Bradl, 2005). There are many disadvantages in the use of these conventional treatment technologies like high cost and partial removal of certain ions (Ahalya et al., 2003).

Biological treatment is poised to be a dependable alternative method to remove the metal ions because it has many desirable advantages such as easy implementation, low cost, minimal use of chemicals, high efficiency and selectivity to remove only the desired metals (Matagi et al., 1998; Chevalier et al., 2000; Mehta and Gaur, 2005). Biological method of treatment is essentially based on the use of microorganisms which efficiently remove toxicants and toxic heavy metals. Biological treatment is done by two different methods which include bioaccumulation (active process) (Churchill et al., 1995; Davis et al., 2003) and biosorption. Biosorption (biological adsorption) is the removal of heavy metals from an aqueous solution by the passive binding of dry biomass (Davis et al., 2003). Biosorption processes depend on the cell wall of non-living biomass (Churchill et al., 1995). Biosorption involves a solid phase (dry biomass) and liquid phase which contains metal ions (Farooq et al., 2010). The higher affinity between the biomass (sorbent) and metal ions (sorbate) makes the latter attracted and bound to the biomass (Das et al., 2008).

Several types of organisms like fungi, bacteria and algae have been used for biosorption processes (Aksu and Donmez, 2006). Among the several microorganisms that are employed for removing heavy metals from aqueous solutions, the microalga (cyanobacterium) Spirulina holds potential for use in biosorption studies.

In recent years, several scientists have employed Spirulina for the removal of different heavy metals from aqueous solutions. For instance, Celekli and Bozkurt (2011) used Spirulina platensis for the adsorption of cadmium and nickel ions. Al-Homaidan et al. (2014) employed the dry biomass of S. platensis for the biosorption of copper ions from aqueous solutions. Water soluble S. platensis extract was used to remove hexavalent chromium ions from industrial waste water (Kwak et al., 2015). Four biomass types with different biochemical compositions of Arthrospira (Spirulina) platensis were utilized for the removal of copper and nickel ions (Markou et al., 2015). All studies recommended using Spirulina biomass as biosorbent for heavy metal removal.

The main objective of this work was to spotlight on the adsorption of cadmium ions (Cd^{2+}) from aqueous solutions by dry biomass of S. platensis and to evaluate the effects of different parameters on the adsorption process.

2. Materials and methods

2.1. The microorganism

The microalga S. platensis was obtained from the culture collection of algae at the University of Texas at Austin, USA, (UTEX NO. LB 2340). It was propagated in the laboratory and in the field according to the methods described by Vonshak (1997) and Al-Homaidan (2002). Harvesting was done by filtration through nylon filters (150–200 mesh). After harvesting, S. platensis was rinsed with deionized water and dried overnight in an oven at 80 °C. The dried biomass was ground well and sieved using a standard metal sieve (100 μm pores) and stored in a desiccator to avoid moisture absorption.

2.2. Preparation of cadmium solution

A Stock solution of cadmium was prepared by dissolving 1.630 g of analar grade cadmium chloride ($CdCl_2$) in deionized water and made up to 1 l in a volumetric flask. Serial dilution was made as required.

2.3. Biosorption studies

The sorption of Cd^{2+} in aqueous solution is affected by different parameters, including the solution pH, biomass dosage, temperature, contact time and Cd^{2+} concentration. The effect of pH on the adsorption of cadmium was studied under different pH regimes (3, 4, 5, 6, 7, 8 and 9). The effect of dry weight of S. platensis biomass on cadmium adsorption was studied by using different dry weights of biomass (0.25, 0.5, 0.75, 1, 1.5 and 2 g) under constant conditions (pH 8, initial Cd concentration 100 mg/l, temperature 26 °C and contact time 60 min). The effect of temperature was examined by incubation at various temperatures (18, 26, 37 and 45 °C), constant conditions of this experiment (pH 8, biomass dosage 2 g, initial Cd concentration 100 mg/l and contact time 60 min). The effect of contact time was examined by incubation for different periods of time (30, 60, 90 and 120 min). This experiment was performed by maintaining other factors at constant conditions (pH 8, biomass dosage 2 g, initial Cd concentration 100 mg/l and temperature 26 °C). The effect of initial concentration of cadmium was studied by varying the initial concentration of cadmium (40, 60, 100, 150 and 200 mg/l), constant conditions of this experiment (pH 8, biomass dosage 2 g, contact time 90 min and temperature 26 °C). All subsequent sorption experiments were carried out under the following parameters: pH: 8, biomass dosage: 2 g, contact time: 90 min, temperature: 26 °C, initial cadmium concentration: 60 mg/l.

The experiments were carried out in triplicate in 250 ml Erlenmeyer flasks containing 100 ml of test solutions in an orbital incubator at 150 rpm. After incubation, the dry biomasses in the solutions were separated by centrifugation at 4000 rpm for 10 min. The supernatants obtained were subjected to vacuum filtration through 0.45 μm Millipore filters and the filtrates were analyzed for residual cadmium using atomic absorption spectrometer (VARIAN, Model AA24OFS) at 283.3 nm.

2.4. Equilibrium isotherms

Langmuir and Freundlich isotherm models were employed to analyze the results obtained for the removal of Cd^{2+} by biosorption in order to have a reasonable description of the equilibrium between the quantity adsorbed (metal ions adsorbed on the biomass surface) and the remaining in solution.

The Langmuir and Freundlich equations have the following forms:

$$\text{Langmuir equation}: q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e}$$

where q_e is the metal ion concentration on the adsorbent (mg/g), $q_{\max}$ is the maximum amount adsorbed (mg/g), K_L is Langmuir adsorption constant (mg/l), and Ce is the equilibrium metal ion concentration in the solution (mg/l).

$$\text{Freundlich equation}: q_e = K_F C_e^{\frac{1}{n}}$$

where q_e is the amount of the adsorbate per unit weight of adsorbent (mg/g), K_F is a constant relating adsorption capacity (Freundlich constants), Ce is the equilibrium metal ion concentration in the solution (mg/l) and $1/n$ is adsorption intensity.

Prior to analysis of the results by the Langmuir and Freundlich isotherms, the amount of cadmium bound to the adsorbents (qe) and the removal percentage of cadmium (R) were calculated as follows:

$$q_e = (C_0 - C_e) \times V/M$$

$$R(\%) = (C_0 - C_e)/C_0 \times 100$$

where C_0 and C_e are the initial and final cadmium concentration (mg/l), respectively, V is the volume of solution (ml), and M is the dry mass of *S. platensis* (g).

2.5. Statistical analysis

The experiments were carried out in triplicate ($n = 3$) and the results are presented as mean ± standard deviations. Data were analyzed using ANOVA statistical test.

3. Results and discussion

3.1. Effects of pH, biosorbent dose, temperature, contact time and initial cadmium concentration on cadmium adsorption

Hydrogen ion concentration is a major factor that affects the adsorption of heavy metals from aqueous solutions. In the present study, the results (Fig. 1) showed that the acidic conditions did not support Cd^{2+} adsorption. At low pH there are many H^+ in the solution, and the higher concentration of H^+ competes with Cd^{2+} for binding to the negatively charged active sites on the biomass surface. This competition between H^+ and Cd^{2+} makes these active sites not available for Cd^{2+} (Sari and Tuzen, 2008a). Similar results were also reported in the literature for adsorption of Cd^{2+} at low pH values (Sari and Tuzen, 2008b; Rathinam et al., 2010). Also it was reported that cadmium was hardly removed by *S. platensis* at pH 3.0 (Rangsayatorn et al., 2004). When the pH value was increased from pH 3.0 to pH 8.0, there was an increase in Cd^{2+} adsorption which could be attributed to the increase in electrostatic attraction between positively charged Cd^{2+} ions and negatively charged binding sites of functional groups present on the cell surface such as carboxylate, phosphate and amino groups (Adhiya et al., 2002). The maximum adsorption efficiency (78%) observed at pH 8.0 is in agreement with an earlier study in which the maximum adsorption efficiency of Cd^{2+} with *S. platensis* was at pH 8.0 (Solisio et al., 2008). However there was a decrease in the uptake of Cd at
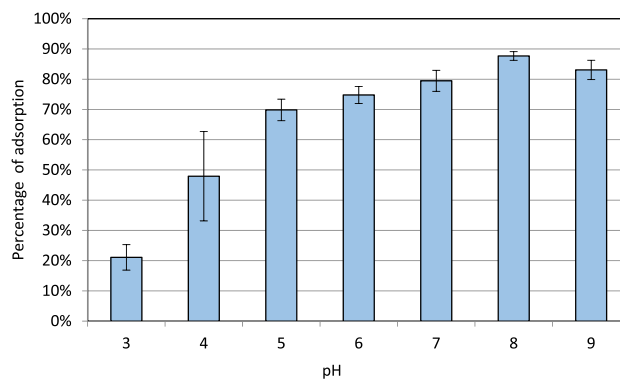

Figure 1 Effect of pH on Cd^{2+} removal by *S. platensis* biomass (biomass dose: 2 g; temperature: 26 °C; contact time: 90 min; cadmium concentration: 60 mg/l).

alkaline pH 9.0 which could be attributed to the formation of a metal complex such as Cd-OH which might have competed with functional binding sites for metal ions and reduced the availability of Cd adsorption (Rao et al., 2005; Kumar et al., 2006).

Biomass dosage in the solution is an important parameter effecting metal adsorption. Results showed that Cd^{2+} removal efficiency increases with increase in the amount of biomass dose from 0.25 g to 2 g, although there was no significant difference between the adsorption at 1.75 and 2 g (Fig. 2). This increase could be attributed to the overall increase in surface area of the biosorbent, which in turn increased the number of available binding sites for adsorption. Similar studies were reported earlier in which it has been reported that 2 g of *S. platensis* was sufficient to get excellent metal removal (up to 98%) when the initial concentration of Cd^{2+} was 100 mg/l (Solisio et al., 2008).

Temperature is a crucial parameter in the adsorption process. In the present study it was noted that the cadmium adsorption from aqueous solution by dry weight of *S. platensis* biomass was influenced by variation in temperature and it was found that 26 °C was ideal for maximal adsorption of Cd^{2+} onto the dry biomass of *S. platensis* (Fig. 3). Higher temperatures did not favor adsorption of metal ions. This decrease in adsorption is probably due to an increase in tendency to desorb Cd^{2+} from the biomass surface to the solution (Sari
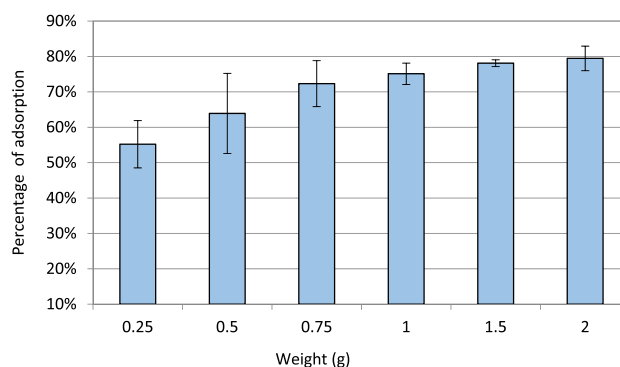

Figure 2 Effect of *S. platensis* biomass concentration on Cd^{2+} adsorption (pH: 8; temperature: 26 °C; contact time: 90 min; cadmium concentration: 60 mg/l).
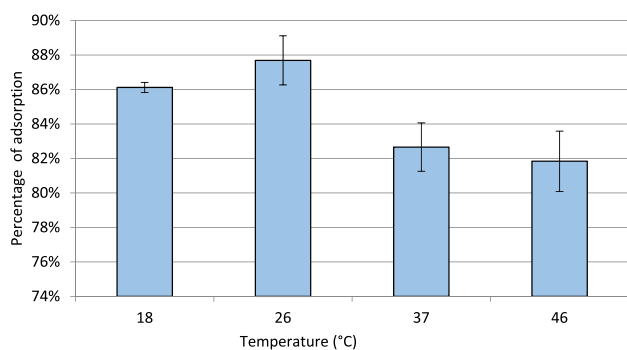
Figure 3 Effect of temperatures on Cd^{2+} adsorption by *S. platensis* biomass (pH: 8; biomass dose: 2 g; contact time: 90 min; cadmium concentration: 60 mg/l).

et al., 2007). Desorption of Cd^{2+} into the solution suggests that the major force (i.e. electrostatic interaction) between cadmium ions and active binding sites might be weakened by elevated temperature. Similar behavior has been reported earlier where it was shown that the uptake of Cd^{2+} ions by the red alga *Mastocarpus stellatus* decreased with increase in temperature (Herrero et al., 2008).

The rate of adsorption with respect to various contact times was studied toward determination of optimal contact time. The results obtained indicated that maximal adsorption (92.05%) was noted after 90 min (Fig. 4). Similar results were reported in a previous study where it was shown that the optimum time to achieve maximum adsorption of Cd^{2+} ions onto *Saccharomyces cerevisiae* was 90 min (Hamza et al., 2010). It was noted that the rate of adsorption was very rapid during the first 30 min ($>80\%$). This is probably due to the fact that initially all sites on the surface of the sorbent were vacant with more functional groups on the biomass surface and available for binding and cadmium adsorption (Saif et al., 2012). At 120 min there was a decrease in the rate of adsorption which may be due to the possible release of the adsorbed cadmium to the solution. Where, through the adsorption process, the sorbent reaches the saturation state and then the adsorbed metal tends to desorb back into the solution (Sari and Tuzen, 2008b).

The initial concentration of cadmium in the solution directly influences the rate of adsorption. The results obtained
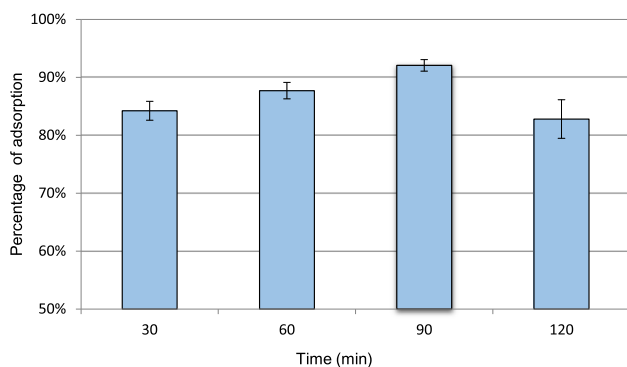
indicated that the initial concentration of cadmium in the aqueous solution influenced the rate of adsorption by *S. platensis* biomass. It was observed that there was an increase in the percentage of cadmium adsorption with increased cadmium concentration from 40 mg/l to 60 mg/l and a maximum cadmium adsorption (96.77%) was observed with a concentration of 60 mg/l (Fig. 5). This could be attributed to the possible higher interaction between metal ions and the binding sites on the biosorbent surface and saturation of all binding sites with metal ions. Therefore, it was inferred that increased level of cadmium concentration in the solution is responsible for the increase in the percentage of cadmium removal until the saturation of the biomass is attained (Saleem and Bhatti, 2011).

3.2. Adsorption isotherm of cadmium

An adsorption isotherm is characterized by certain constants whose values express the surface properties and affinity of the sorbent. The adsorption isotherm was obtained at constant factors: solution pH: 8, biomass dose: 2 g, temperature: 26 °C, contact time: 90 min and cadmium initial concentrations: 60 mg/l.

The plots of linear Langmuir isotherm model (Fig. 6) and Freundlich isotherm model (Fig. 7) describe the relationship
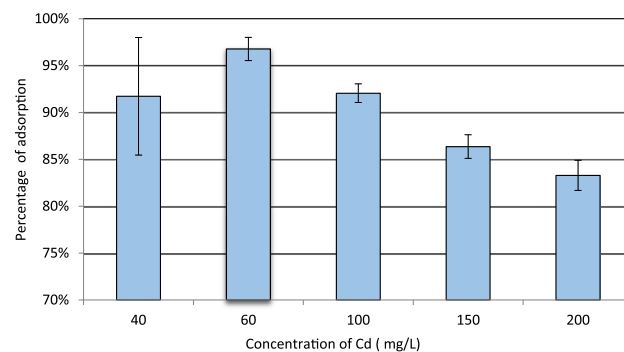

Figure 5 Effect of initial concentration of cadmium on Cd^{2+} biosorption by *S. platensis* biomass (pH: 8; biomass dose: 2 g; temperature: 26 °C; contact time: 90 min).

Figure 4 Effect of contact time on Cd^{2+} removal by *S. platensis* biomass (pH: 8; biomass dose: 2 g; temperature: 26 °C; cadmium concentration: 60 mg/l).
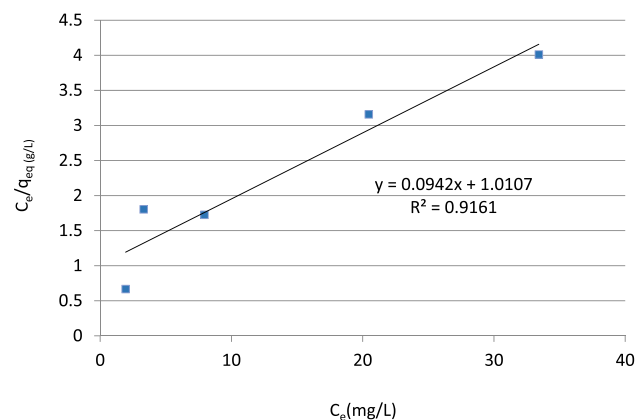

Figure 6 Langmuir isotherm for Cd adsorption by *S. platensis* dry biomass (pH: 8; biomass dose: 2 g; temperature: 26 °C; contact time: 90 min; cadmium concentration: 60 mg/l).

Figure 7 Freundlich isotherm for Cd adsorption by *S. platensis* dry biomass (pH: 8; biomass dose: 2 g; temperature: 26 °C; contact time: 90 min; cadmium concentration: 60 mg/l).
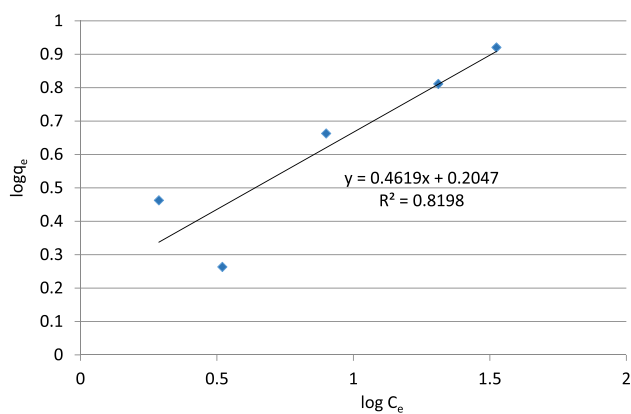
between the adsorbed amounts of Cd^{2+} on *S. platensis* against the concentration of Cd^{2+} ions remaining in the solution. By Comparing the R^2 of Freundlich model (0.819) with that obtained from the Langmuir model (0.916), it can be noted that the Langmuir isotherm model best fitted the equilibrium data. The present results are in conformity with earlier reports on the Langmuir model which gave a better fit than the Freundlich model for the adsorption of Cd^{2+} using different adsorbents such as adsorption isotherm of Cd^{2+} obtained for *S. platensis* biomass (Çelekli and Bozkurt, 2011).

4. Conclusion

Based on the results of our study it is concluded that the adsorption process of Cd^{2+} onto *S. platensis* dry biomass was found to be dependent on various parameters that included solution pH, biomass dosage, temperature, contact time and the initial concentration of Cd^{2+}. Optimal conditions for the removal of cadmium by the algal biomass were pH 8, 2 g of dry biomass, incubation at 26 °C, 90 min of contact time and 60 mg/l of cadmium initial concentration. The experimental data fitted well with Langmuir isotherm model. *S. platensis* dry biomass has immense potential for the removal of cadmium ions from aqueous solution and is equally competent with other well-known algae used in heavy metal removal.

Acknowledgement

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