

Biosorption of Zn^{+2} on non living biomass of *S. platensis* immobilized on polyurethane foam cubes: Column studies

P Nirguna Babu, Prakash Binnal*, D Jayaprasanna Kumar

Received: 05 July 2014 / Received in revised form: 04 January 2015, Accepted: 20 January 2015, Published online: 07 March 2015
© Biochemical Technology Society 2014-2015

Abstract

In the present study, the non living biomass of cyanobacteria *Spirulina platensis* was used for biosorption of Zn^{+2} in column mode. Polyurethane foam (PUF) cubes were used for immobilizing the biosorbent. A maximum biomass loading of 0.2 g dry *S. platensis* / (g of PUF cubes) could be achieved. The effect of parameters (such as pH of feed solution, flow rate of feed solution to column, bed height and initial concentration of metal ion in feed solution) on uptake capacity of biosorbent was studied. A maximum uptake capacity of 87.3 mg Zn^{+2} / (g *S. platensis*) was observed under optimum conditions. The column was regenerated using 0.1 M HCl and sorption-desorption studies were carried out for four cycles. Both % removal of Zn^{+2} and uptake capacity of biosorbent were found to progressively decrease with increase in the number of cycles. The biomass was characterized by Fourier transform infrared Spectroscopy (FTIR) and Scanning Electronic Microscopic (SEM) images before and after biosorption.

Keywords: *S. platensis*, Polyurethane foam cubes, Column studies

Introduction

There are several reports on biosorption of metal ions using bacteria (Mamba et al. 2009), yeast (Volesky et al. 1993), algae (Amany E.S et al. 2011), and waste materials of food and agricultural industry (Amit B et al. 2010; Sousa F.W et al. 2010) for the removal of heavy metals. *S. platensis*, a member of blue-green algae, is an alternative source of protein for human food and feed purposes. Other than protein, it contains polysaccharides, lipids, and vitamins that contain a variety of functional groups such as carboxyl, hydroxyl, sulphate and other charged groups which are responsible for metal binding (Li et al. 2006).

Recently, biosorption of Cu^{+2} , Pb^{+2} , Cd^{+2} , Ni^{+2} , Zn^{+2} and Co^{+2} by non-living biomass of cyanobacteria *Spirulina platensis* was reported. (Linchuan et al. 2011; Abuzer et al 2011; Livia et al. 2011).

P Nirguna Babu, Prakash Binnal*, D Jayaprasanna Kumar

Department of Chemical Engineering, Siddaganga Institute of Technology, Tumku-572103r, Karnataka, India

*Email: prakashbinnal@yahoo.co.in

However, these studies were restricted to batch kinetics and adsorption isotherms. On the other hand, a packed bed column is more effective process for continuous wastewater treatment, as it makes the best use of the concentration difference which is known to be a driving force for heavy metal biosorption and allows more efficient utilization of biosorbent capacity and results in better quality of the effluent (Vimala et al. 2011). Several reports are also available in literature regarding biosorption of heavy metal ions using non-living algae biomass in column mode (Vijayaraghavan et al. 2005; Vilar et al. 2008; Volesky et al. 1994; Alpana et al. 2012; Xin et al. 2011).

The main requirement of an industrial adsorption system is that the immobilized matrix utilized in a fixed bed must offer as low a pressure drop as possible. Moreover, it should possess a porous structure, high mechanical strength, resistance to organic solvents and microbial attack. Polyurethane foam satisfies all these conditions and hence can be used in an industrial application. Hence, the present study was aimed at testing the efficacy of non living cells of *S. platensis* immobilized on polyurethane foam (PUF) in removing $Zn(II)$ ions from aqueous solutions in a continuous operation. The effect of parameters such as pH of feed solution, flow rate of feed solution to the column, initial concentration of Zn^{+2} in feed solution and bed height of biosorbent on column performance was investigated.

Materials and methods

Preparation of biosorbent

An original strain of *Spirulina platensis* was provided by Spirulina Foundation®, Tumkur, Karnataka, India. The cyanobacteria was cultured at pH 10 and 26°C in modified Zarrouk liquid medium (Xin et al. 2011) containing (g/L): $NaHCO_3$ (13.61), Na_2CO_3 (4.03), K_2HPO_4 (0.5), $NaNO_3$ (1.25), NH_4Cl (0.82), K_2SO_4 (1), $NaCl$ (1), $MgSO_4 \cdot 7H_2O$ (0.2), $CaCl_2 \cdot 2H_2O$ (0.04). 500 ml conical flasks containing 300 ml media were placed in an enclosed wooden illumination chamber which is fitted with 18 cool, white fluorescent tubelights (Philips, Trulite). The light intensity in this chamber could be controlled by switching on required number of tubelights and measured using digital lux meter (Model-LX

101, Taiwan). Cultures were grown at a light intensity of 4 klux and aerated continuously by an aquarium pump. Cell growth rate was measured gravimetrically. After the stationary phase (10 days), the cells were harvested by centrifugation at 10,000 rpm for 10 min. The pellet obtained was washed twice with distilled water, centrifuged, dried at 80 °C for 24 h and ground to obtain a powdered biomass.

Immobilization of biosorbent

The PUF sheet (having a density of 2300 kg/m³) was purchased locally and cut into cubes having a size of 0.5 cm × 0.5 cm × 0.5 cm. 10 g of these cubes were added to 300 ml of aqueous algal suspension containing 10 g dry biomass *S. platensis*. The flasks were agitated in a rotary shaker at 120 rpm for 1 h. The cubes were separated and added to 150 ml distilled water and gently agitated at 20 rpm in rotary shaker to remove greenish pigment. This step was repeated until all color was removed. The cubes were then dried in an oven at 80 °C for 12 h to remove traces of moisture.

Batch adsorption studies

Stock solutions of Zinc were prepared by dissolving calculated quantities of Zinc sulphate in 100 ml distilled water. The initial pH of solution was adjusted to a specified value in an experiment by addition of 0.1 M HCl or 0.1 M NaOH. Sorption experiments were conducted in 250 ml Erlenmeyer flasks. Desired quantity of biosorbent was added to feed solution and the flasks were agitated at 80 rpm in rotary shaker incubator for 5 hr. This time was assumed to be sufficient to ensure establishment of equilibrium. The solution was then filtered using Whatman 42 filter paper to separate the biomass. The filtrate was analyzed for residual Zn⁺² concentration using Atomic Absorption Spectrophotometer (Model : GBC Avanta, Australia).

$$q_e = \frac{(C_o - C_e)V}{M}$$

where, C_o and C_e (mg/L) represent concentrations of Zn⁺² present initially and at equilibrium in the solution respectively, V is the volume of solution (L), and M is the mass of adsorbent (g).

Kinetics of sorption and adsorption isotherms

The pseudo first order and second order kinetic models were used to study the sorption kinetics. In order to obtain the data of concentration of Zn⁺² v/s time, samples of solution were withdrawn at regular intervals of time (10, 20, 30, 60, 120, 180, 240 and 300 min) during biosorption and analyzed for Zn⁺². The amount of Zn⁺² (in mg) adsorbed per g of adsorbent at any time t (q_t) is calculated as,

$$q_t = \frac{(C_o - C_t)V}{M}$$

where C_t is the concentration of Zn⁺² in feed solution (ppm) at time t . Freundlich and Langmuir models were used to analyze the equilibrium data. The constants of both isotherms were used to predict the potential of *S. platensis* as a biosorbent.

Column studies

Column experiments were conducted in an acrylic column with an inner diameter of 2.54 cm and height 45 cm. It was packed with known quantity of PUF cubes. A wire mesh was provided at the bottom of column to support the packing material. Saline bottle (1 L) was used as feed tank for Zinc sulphate solution (Figure 1).

The feed solution of known pH and initial Zn⁺² concentrations was circulated through the column from top. Using the regulator provided on the tubing line attached to bottle, the low flow rates used in the experiment (3, 5, 10, 15 ml/min) could be accurately controlled. A distributor plate attached at the top of column provided uniform flow of fluid over packing and avoided channelling. Samples were collected from the exit of column at regular time intervals and analyzed for residual Zn⁺² concentration using Atomic Absorption Spectrophotometer (Model : GBC Avanta, Australia). All experiments were done in duplicate. Blank tests were also conducted at the same experimental conditions in order to determine interference of PUF cubes on Zn⁺² adsorption. However, no adsorption of Zn⁺² on PUF cubes was observed in our studies.

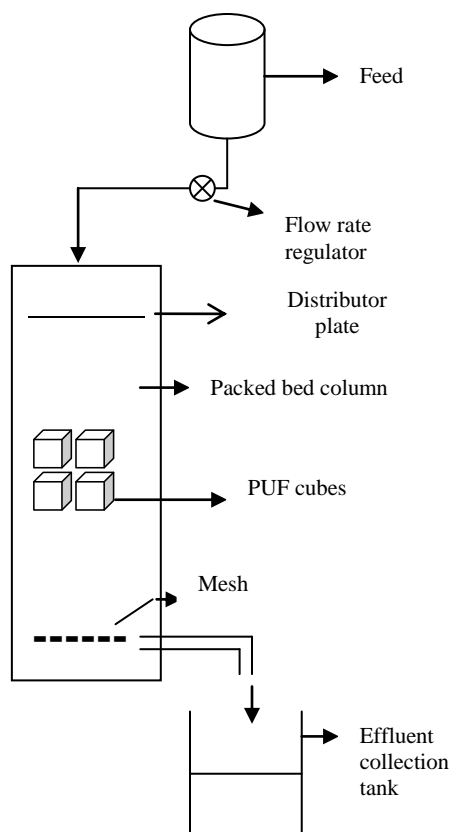


Figure 1: Experimental set up

The total quantity of metal ions adsorbed in the column (m_{ad}) is calculated from the area over the breakthrough curve (Effluent metal ion concentration vs. time) multiplied by flow rate. The uptake capacity (q) of the biomass is then obtained by dividing m_{ad} by biosorbent mass (M). The total amount of the metal ions entering the column (m_{total}) can be calculated from the equation:

$$m_{total} = \frac{C_o F t_e}{1000}$$

where C_o is the initial concentration of metal ion (mg/L), F is the volumetric flow rate (ml/h) and t_e is the exhaustion time (h). Finally, the % metal ion removal was calculated as

$$\text{Total metal removal (\%)} = \frac{m_{ad}}{m_{total}} \times 100$$

The effect of parameters such as pH, bed height, flow rate of feed and initial concentration of Zn^{+2} in feed solution on % Zinc removal and uptake capacity of *S. platensis* was investigated.

Column modeling

Bed depth Service Time model (BDST model)

The analysis of breakthrough curve was done using BDST model. It was proposed by Bohart and Adams (1920). The BDST is a simple model for predicting the relationship between bed height Z , and service time t , in terms of process parameters such as initial metal ion concentration, flow rate and adsorption capacity, and given as (Cooney 1999):

$$t = \frac{N_o Z}{C_o V} - \frac{1}{K_a C_o} \ln \left(\frac{C_o}{C_b} - 1 \right)$$

where C_b is the breakthrough concentration of metal ion, N_o is the sorption capacity of bed (mg/L), V is the velocity of fluid through column ($cm \cdot h^{-1}$), K_a is the rate constant ($L \cdot mg^{-1} \cdot h^{-1}$), Z is the depth of adsorbent (cm). The above equation can be rewritten as,

$$t = mZ - n$$

where, m and n represent slope and intercept of straight line of BDST model. By plotting t against Z at a particular breakthrough percentage from experimental data, N_o can be evaluated from the slope of the graph and K_a from the intercept.

Characterization of biosorbent

Scanning electron microscope

Scanning electron microscopic (SEM) (SU-1500, Hitachi) studies were conducted for the detection of surface characteristics of the biosorbent. The SEM images of PUF cubes, PUF cubes immobilized with *Spirulina platensis* and immobilized PUF cubes loaded with Zinc ions were recorded.

Fourier transform infrared spectroscopy analysis

The surface functional groups of the adsorbents were identified using Fourier Transform Infrared spectrophotometer. Fourier transform infrared (FTIR) spectra were obtained using a spectroscope (Thermo Electron, Model: Nicolet 5700_{FT-IR}) at resolution 1 cm^{-1} . Pressed potassium bromide (KBr) pellets at a sample/KBr weight ratio of 1:100 were scanned and recorded between 4000 and 400 cm^{-1} .

Results and discussions

Characterization of biosorbent

Scanning electron microscope

The SEM images of PUF cubes, PUF cubes immobilized with *Spirulina platensis* and immobilized PUF loaded with Zn^{+2} ions are shown in Figure 2, 3 and 4 respectively. It can be observed that the structure of biosorbent changed significantly after Zn^{+2} uptake, as is evident by the increase in roughness of surface and appearance of blackish spots on the surface.

Fourier transform infrared spectroscopy analysis

FTIR spectrum of biosorbent showed that its surface contains several functional groups which are responsible for adsorption of Zn^{+2} . FTIR Spectrum of *S. platensis* before and after biosorption is shown in Fig. 5. It is clear that there was a sharp decrease in areas of peaks at 3270.68 , 2925.06 , 1645.96 , 1643.13 and 1031.20 cm^{-1} after biosorption. The peak at 3270.68 cm^{-1} can be attributed to $-OH$ and $-NH$ groups (Robert et al. 2008). The asymmetrical stretching of methylene groups gives rise to a peak at 2925.06 cm^{-1} (Doshi et al. 2007) Remarkable variations in the band intensity was observed at peaks of 1643.13 and 1031.20 cm^{-1} .

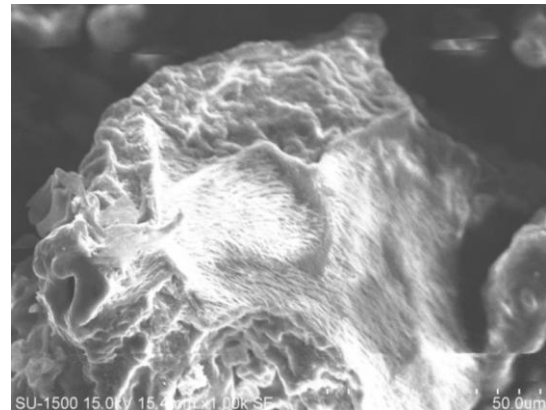


Figure 2. SEM image of PUF alone

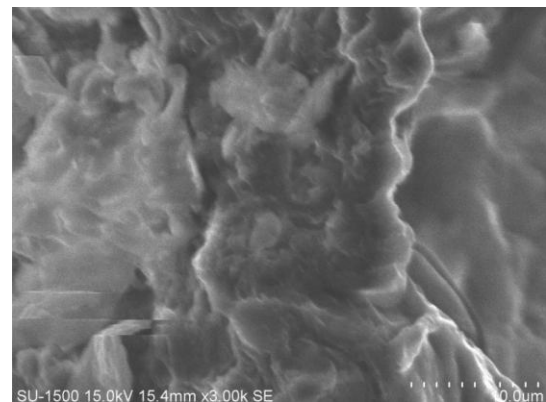


Figure 3. SEM image of PUF immobilized with *S. platensis*

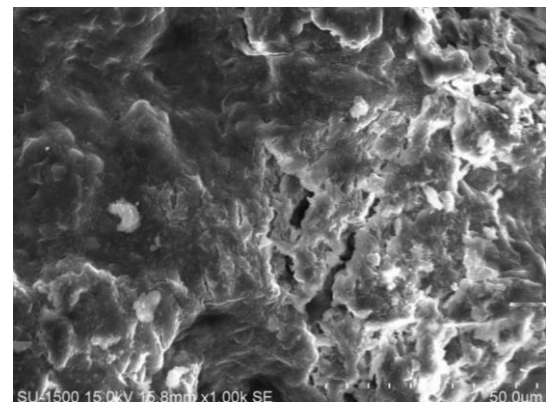


Figure 4. SEM image of PUF immobilized with PUF loaded with Zn^{+2} ions

The peak at 1643.13 cm^{-1} is attributable to C=C stretching of vinyl groups, while that at 1031.20 cm^{-1} is because of C-O stretching of alcoholic groups (Doshi et al. 2007). The sorption peaks appearing in the region of $1280\text{--}1430\text{ cm}^{-1}$ could be attributed to presence of -CH bending vibrations (Doshi et al. 2007). Similar observations were made by Xue Fei et al (2007) who reported that -NH and -OH stretching ($3200\text{--}3600\text{ cm}^{-1}$), -CO stretching coupled with NH deformation ($1650\text{--}1660\text{ cm}^{-1}$) and CO stretching from hydroxyl group (1053 cm^{-1}) were responsible for Zn^{+2} adsorption. S.T.Ramesh et al (2012) reported that -OH and CO_3^{-2} ions were responsible for Zn^{+2} on hydroxyapatite. Devlina Das et al (2012) reported that -NH, -COOH and C=O groups are responsible for biosorption of Zn^{+2} on *Candida rugosa* and *Cryptococcus laurentii*. Some of these observations are in agreement with present studies. -NH and -OH groups are common functional groups among *S. platensis* and other biosorbents. However, in our study, the biosorbent did not possess -COOH and CO_3^{-2} groups. Thus, the variation of FTIR spectra of loaded and unloaded biosorbent confirmed that functional groups played a significant role in the biosorption of Zn^{+2} on biosorbent surface.

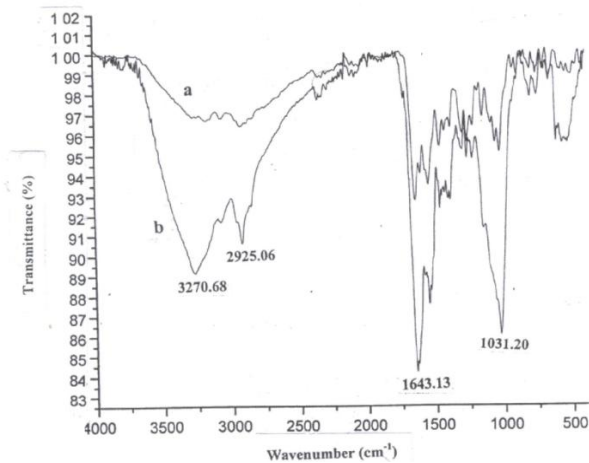


Figure 5. FTIR of *S. platensis* before (a) and after biosorption (b)

Batch studies

Sorption kinetics

The conditions selected for studying the kinetics of sorption of zinc on *S. platensis* were: Initial concentration of $\text{Zn}^{+2} = 100\text{ ppm}$, $\text{pH}=4$, Adsorbent dosage = 3 g/L , contact time= 120 min . In order to understand the sorption kinetics, pseudo first order and pseudo second order kinetic models were applied to experimental data. Fig. 6-7 show the results obtained. It is evident that the kinetics is well described by pseudo second order model as indicated by high value of R^2 (0.99). The constants of model were evaluated as, $k_2=0.0071\text{ g } S. \text{ platensis}/(\text{mg } \text{Zn}^{+2} \cdot \text{min})$ and $q_e = 75.23\text{ mg } \text{Zn}^{+2}/\text{g}$ of *S. platensis*. Figure 7 shows that pseudo first order fails to explain the kinetics of biosorption (low R^2 of 0.91).

Sorption isotherms

Langmuir and Freundlich isotherms were used to fit to the experimental equilibrium data. Figures 8 and 9 show that both isotherms described the biosorption of Zn^{+2} on *S. platensis* satisfactorily. Maximum monolayer sorption capacity of *S. platensis* (q_0) was

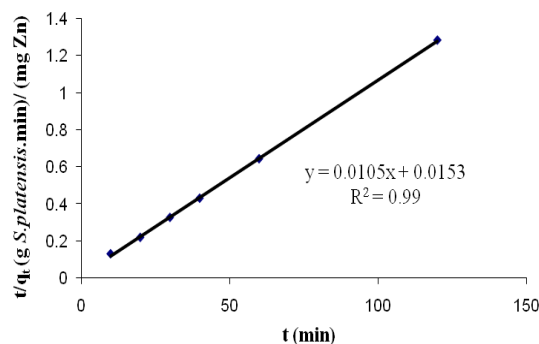


Figure 6. Pseudo second order plot for kinetics of biosorption

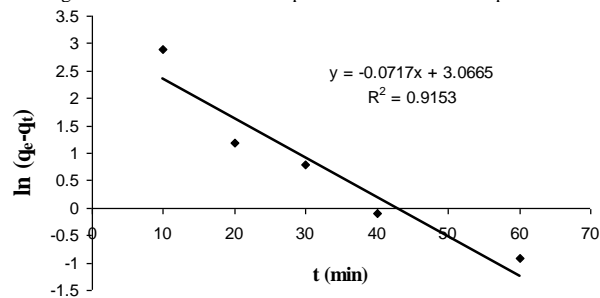


Figure 7. Pseudo first order plot for kinetics of biosorption

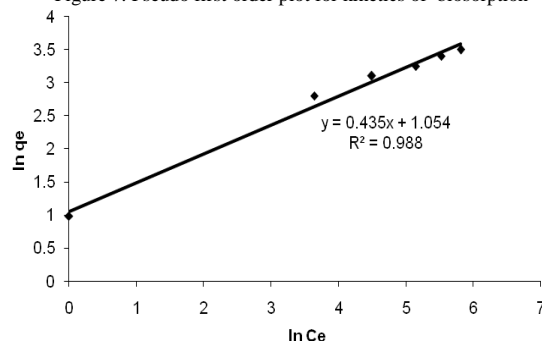


Figure 8. Freundlich adsorption isotherm plot for biosorption

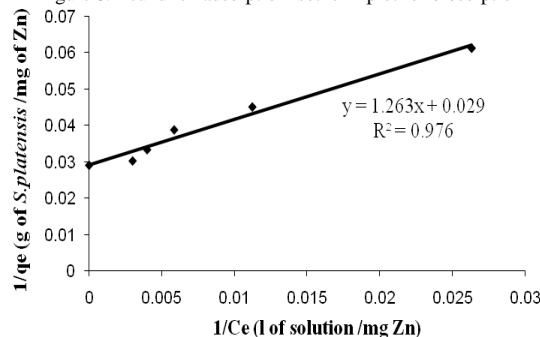


Figure 9. Langmuir adsorption isotherm plot for biosorption

calculated from Langmuir's isotherm as $34.82\text{ mg } \text{Zn}^{+2}/\text{g}$ of *S. platensis*. Another constant of Langmuir isotherm (b) was found to $0.0229\text{ L of solution}/\text{mg of } \text{Zn}^{+2}$. The higher magnitude of Freundlich's constant ($K=4.34\text{ mg of } \text{Zn}^{+2}/\text{g}$ of *S. platensis*) indicated that the uptake of Zn^{+2} by *S. platensis* was easy. Further, the sorption intensity was high as indicated by large magnitude of another constant of Freundlich 'n' (1.98).

Column studies

Effect of pH

Initial pH of feed solution is one of the most important parameters affecting biosorption. The behavior of biosorbent is mainly related to the cell wall, which is considered as the primary site of biosorption. The pH of medium affects ionization state of the functional groups on the biomass surface. Also, the Zeta potential of the biomass is a function of pH.

Various experiments were conducted to study the effect of pH on Zn²⁺ removal. Initial set of experiments were conducted from 2-8 to get an approximate optimum. At low pH values, uptake capacity was low (39.2 & 45.5 mg Zn²⁺/g *S. platensis* at pH 2 and 3 respectively. This is attributable to high concentration of H⁺ ions prevailing at low pH, which hinders the adsorption of Zinc ions. However, a sharp increase in uptake was observed in pH range of 3-5 (from 45.5 to 75.2 mg Zn²⁺/g *S. platensis*), approaching a saturation thereafter. At pH 5 and above, there are lower numbers of competing hydrogen ions and more ligands are exposed with negative charges, resulting in zinc sorption. Hence, for further optimization of pH, experiments were conducted in a pH interval of 3-5 (Figure 10). A maximum uptake capacity of 76.85 mg Zn²⁺/g *S. platensis* was observed at pH 4.4. This is because, Zn²⁺ ions, being positively charged, have high affinity for negative charge on the biomass surface. Carboxyl groups (-COOH) are the important groups for metal uptake by biomass surface. Based on typical deprotonation constants for carboxylic (4 < pKa < 6), high metal uptake capacity observed at pH 4.4 can be attributed to deprotonation of carboxylic groups.

The charge on *Spirulina platensis* has been found to decrease with increasing pH and reaches a minimum at pH 4 (corresponding to a zeta potential of :-2.44mv) (Tamer et al. 2009) and is constant up to pH 8. Hence, for all further experimental runs, pH of feed solution was adjusted at 4.4.

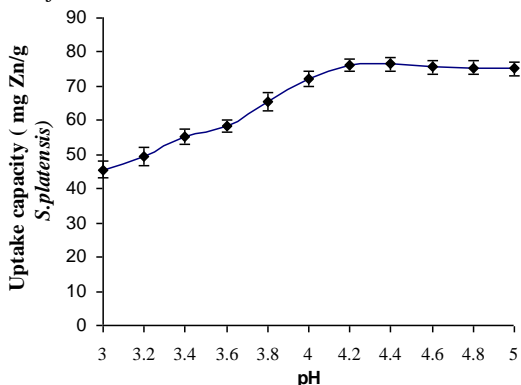


Figure 10: Effect of pH on uptake capacity of Zn²⁺ ions on *S. platensis* (Initial concentration of feed solution=100 mg/L, Flow rate =5 ml/min, Bed height = 10 cm).

Effect of bed height

Various experiments were conducted to study the effect of bed height on the degree of biosorption. The initial concentration of feed solution was maintained at 100 mg/L and flow rate at 5 ml/min. The nature of breakthrough curves is depicted in Figure 11. Four bed heights (10, 15, 20 and 25 cm) were tested. The corresponding mass of biomass were 1.8 g, 2.7 g, 3.6 g and 4.5 g respectively (biomass loading on PUF cubes was found to be 0.2 g *S. platensis* /g of PUF cubes). It can be observed that the breakthrough time, exhaustion

time and % adsorption increased with increasing bed height (Table 1). The increase in bed height resulted in greater adsorption capacity of column. According to the literature (Han et al. 2006), larger bed height is, the greater service time in the column, which increases the superficial area of the adsorbent and the amount of active sites available for binding.

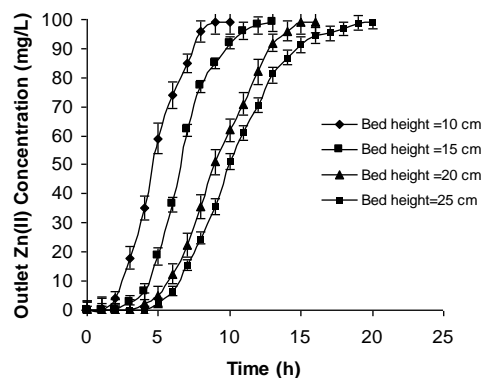


Figure 11: Effect of bed height on Zn²⁺ uptake capacity of *S. platensis* (Initial concentration of feed solution=100 mg/L, Flow rate =5 ml/min, pH of feed solution=4.4)

Table 1-Column data and parameters obtained during biosorption of Zn²⁺ *S. platensis* at different bed heights

Bed height (cm)	t _b (h)	t _e (h)	q (mg Zn adsorbed/g <i>S. platensis</i>)	% removal
10	2.1	9.3	83.44	53.83
15	3.8	13.5	85.25	56.83
20	5.2	16.1	86.3	64.28
25	6.3	18.5	86.9	70.45
30	6.5	17.9	87.3	70.68

In the present study, an uptake of 86.9 mg Zn²⁺/g *S. platensis* and % removal of 70.45 were observed for a bed height of 25 cm. No significant increase in the uptake capacity of biosorbent was observed above 25 cm bed height (A meagre increase in uptake capacity of 0.35% was observed at 30 cm bed height). This can be because, ratio of mass of metal ions adsorbed to mass of adsorbent remains almost constant above certain height of column. A bed height of 25 cm was chosen as optimum for all further runs, as, increasing bed height by 5 cm to achieve an improvement in uptake capacity of 0.35 % is not economical.

Effect of flow rate

The effect of flow rate of metal solution on the performance of packed bed is shown in Fig. 12. The bed height was maintained at 25 cm, initial concentration of metal ion in feed solution at 100 mg/L and pH at 4.4 during these runs. It is evident that increasing flow rate from 3 ml/min to 15 ml/min decreases the breakthrough and exhaustion times which leads to steeper breakthrough curves and shortening of mass transfer zone. The breakthrough time decreased to 0.8 h and exhaustion time to 7.5 h at a flow rate of 15 ml/min. Thus, at high flow rates, both uptake capacity and % metal ion removal decrease. The results obtained are tabulated in Table 2. The % removal of Zn²⁺ and uptake capacity of adsorbent decreased to 48.33 % and 72.5 mg Zn²⁺/g *S. platensis* respectively at a flow rate of 15 ml/min. The possible reason for this behaviour is that at higher flow rates, the residence time of metal solutions in the column will be not sufficient to establish equilibrium. Thus most of metal

ions leave the column before attaining equilibrium ultimately resulting in poor adsorption rate. The column was found perform best at 3 ml/min. Hence, this flow rate was maintained for further column runs.

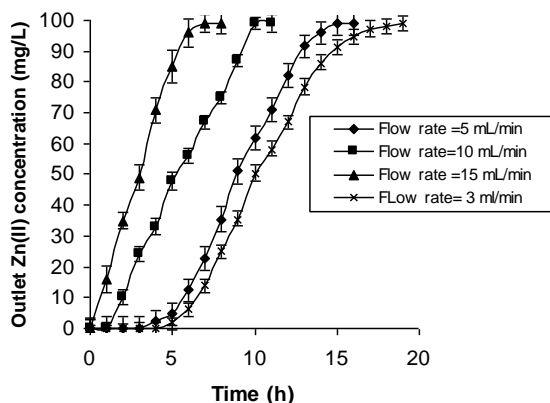


Figure 12: Effect of flow rate on Zn⁺² uptake capacity of *S. platensis* (Initial concentration of feed solution=100 mg/L, Bed height=25 cm, pH of feed solution=4.4)

Table 2-Column data and parameters obtained during biosorption of Zn⁺² *S. platensis* at flow rates of feed solution

Flow rate (ml/min)	t _b (h)	t _e (h)	q (mg Zn adsorbed/g <i>S. platensis</i>)	% removal
3	3.5	18.2	87.3	83.33
5	2.5	16.8	86.9	70.45
10	1.9	10.8	75.5	52.4
15	0.8	7.5	72.5	48.33

Effect of initial concentration of Zinc in feed solution

The effect of increasing the initial metal ion concentration on rate of extraction is depicted in Figure 13. Three different initial concentrations (100, 150 and 200 mg/L) were studied. The flow rate was maintained at 3 ml/min, pH of feed solution at 4.4 and bed height at 25 cm. The results are shown in Table 3. The breakthrough time and exhaustion times decreased to 1.9 and 10.2 h respectively at 200 mg/L. The % extraction decreased from 83.33 to 74.14 %, while, the uptake capacity of biosorbent decreased from 87.3 to 60.5mg Zn⁺²/g *S. platensis*. At higher initial concentration of metal ion, larger number of metal ions enters the column in a given time, resulting in quicker saturation of bed and hence lower breakthrough and exhaustion time. With increasing metal ion concentration, the number of available for adsorption become fewer compared to mass of metal ions. Also, at lower concentrations, the functional groups present in the adsorbent will be sufficient to accommodate the solute ions. But at higher concentrations, the capacity of functional groups to hold metal ions approaches saturation. Hence, the excess ions which could not be bound leave the column unadsorbed. This decreases the uptake capacity of column.

Table 3: Column data and parameters obtained during biosorption of Zn⁺² *S. platensis* at initial concentrations of Zn⁺² in feed solution

Initial concentration of Zn ⁺² (mg/L)	t _b (h)	t _e (h)	q (mg Zn adsorbed/g <i>S. platensis</i>)	% removal
100	3.5	18.2	87.3	83.33
150	2.8	14.5	67.2	77.2
200	1.9	10.2	60.5	74.14

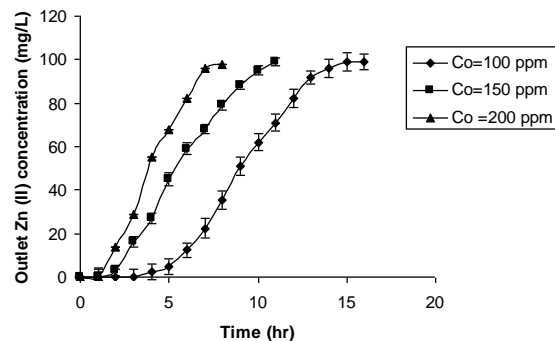


Figure 13: Effect of initial concentration of Zn⁺² on uptake capacity of *S. platensis* (Flow rate= 3 ml/min, Bed height=25 cm, pH of feed solution=4.4)

Regeneration studies

The potential of biosorbent to retain its adsorption capacity over repeated cycles of adsorption-desorption was evaluated. 0.1 M HCl was used an eluent at a flow rate of 3 ml/min. The bed height maintained was 25 cm, pH of feed solution at 4.4 and the initial concentration of Zn in feed solution at 100 mg/L. The eluent was passed through the column and the effluent Zn(II) concentration was recorded at regular intervals. The flow of eluent was stopped when the effluent concentration of Zn(II) reduced to zero. Distilled water was then passed through the column until the effluent pH approached 7. The regenerated bed was reused for next cycle. The experiments were conducted for 4 cycles. The data obtained is depicted in Fig.14 and Table 4. It can be observed that, the breakthrough time and exhaustion times decreased progressively with increase in number of cycles. The uptake capacity of Zn⁺² removal decreased to 45.36, 35.8 and 24.5 mg Zn⁺²/g *S. platensis*, while the % removal decreased to 70.1, 66.29 and 64.47% after second, third and fourth cycles respectively. This loss in the sorption performance of bed is attributable to gradual deterioration of bed with continuous reuse. Because of acidic environment due to use of 0.1 M HCl, the functional sites on biomass surface get deteriorated.

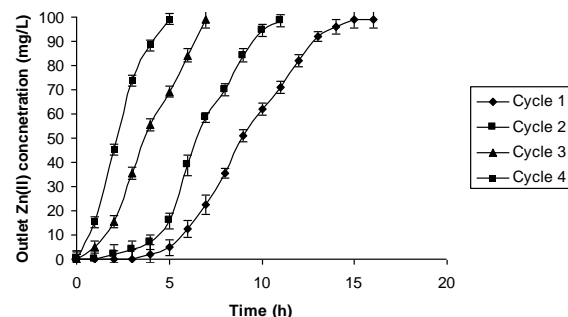


Figure 14: Effect of number of cycles of Zn⁺² on uptake capacity of *S. platensis* (Initial concentration of feed solution=100 mg/L, Flow rate= 3 ml/min, Bed height=25 cm, pH of feed solution=4.4)

Table 4: Column data and parameters obtained during biosorption of Zn⁺² *S. platensis* at different cycles

Cycle No.	t _b (h)	t _e (h)	q (mg Zn adsorbed/g <i>S. platensis</i>)	% removal
1	3.5	18.2	87.3	83.33
2	3.2	16.2	45.36	70.1
3	1.8	13.5	35.8	66.29
4	0.8	9.5	24.5	64.47

Comparison of uptake capacity of *S. platensis* with other biosorbents

The biosorption capacity of *S. platensis* for Zn^{+2} in column mode was compared with other biosorbents used in the literature. The results are depicted in Table 5. As can be observed, the biosorption capacity of *S. platensis* is higher than other biosorbents. This is due to high sorption capacity of *S. platensis* and high porosity of PUF which facilitates faster transport of metal ions to biosorbent surface.

Table 5: Comparison of Zn^{+2} biosorption capacity of *S. platensis* with other biosorbents in column mode

Biosorbent	Biosorption Capacity (mg Zn^{+2} /g biosorbent)	Reference
Crab carapace	76.9	Shuguang Lua et al.
<i>C.rugosa</i> (untreated)	46.7	Devlina D et al
<i>C.rugosa</i> (SDS treated)	50.8	Devlina D et al
<i>C.laurentii</i> (untreated)	40.9	Devlina D et al
<i>C. laurentii</i> (SDS treated)	54.8	Devlina D et al
Chicken feathers	1.73	Ismael A et al
<i>Utricularia reticulata</i>	77.7	Senthilkumar R et al
<i>S. platensis</i>	87.3	This study

Modelling of column data

The plot of service time v/s bed height at a low rate of 3 ml/min showed linear relationship between the two variables. ($R^2 = 0.97$). This indicates, BDST model predicts the column performance satisfactorily. The BDST model parameters were determined as, $N_0 = 5920$ mg/L, and $K_a = 0.093$. N_0 represents the sorption capacity of bed per unit bed volume. The high value obtained in the present study confirms the suitability of *S. platensis* as a biosorbent for Zn(II) in column mode. The magnitude of K_a characterizes the rate of solute transfer from fluid phase to the solid phase. Generally if K_a is large, even a short bed will avoid breakthrough, but as K_a decreases a progressively longer bed is required to avoid breakthrough (Xue F S et al. 2008). The low value obtained in the present study dictates that a short column bed can avoid breakthrough. The BDST model can be used to scale up the process for other flow rates without further experiments.

Conclusion

Non living biomass of *S. platensis* immobilized on polyurethane foam cubes was successfully used for Zn^{+2} biosorption in column mode. The optimum conditions for biosorption were determined as: Flow rate of influent to column = 3 ml/min, pH of feed solution = 4.4, Initial concentration of $Zn^{+2} = 100$ mg/L and bed height of biosorbent = 25 cm.

A maximum uptake capacity of 87.3 mg Zn^{+2} /(g *S. platensis*) was observed under optimum conditions. The column was regenerated using 0.1 M HCl and four adsorption-desorption cycles were conducted. After fourth cycle, the uptake capacity reduced 24.5 mg Zn^{+2} / g *S. platensis* and % removal to 64.47%. A comparison of FTIR and SEM images of biosorbent before and after biosorption confirmed that non living biomass of *S. platensis* can be a suitable biosorbent for Zn^{+2} .

Acknowledgement

The authors thank financial support from VTU Belagavi, under VTU research Grants Scheme-2010-11.

References

- Mamba BB, Dlamini NP, Nyembe DW, Mulaba-Bafubiandi A.F (2009) Metal absorption capabilities of clinoptilolite and selected strains of bacteria from mine water. *Physics and Chemistry of the Earth, Parts A/B/C* 34:830-840
- Volesky B, May H, Holan Z.R (1993) Cadmium biosorption by *Saccharomyces cerevisiae*. *Biotechnol. Bioeng* 41:826-829
- Amany ES, Ahmed EN, Azza K (2011) Copper sorption onto dried red algae *Pterocladia capillacea* and its activated carbon. *Chem. Eng. J* 168: 707-71
- Amit B, Minocha AK, Mika S (2010) Adsorptive removal of cobalt from aqueous solution by utilizing lemon peel as biosorbent. *Biochem. Eng. J* 48:181-186
- Sousa FW, Oliveira AG, Ribeiro JP, Rosa MF, Keukeleire D, Nascimento RF (2010) Green coconut shells applied as adsorbent for removal of toxic metal ion using fixed-bed column technology. *J Environ Manage* 91:634-640
- Li ZY, Guo. SY, Li L (2006) Study on the process, thermodynamical isotherm and mechanism of Cr(III) uptake by *Spirulina platensis*. *J. Food Eng.* 75 (2006) 129–136.
- Linchuan F, Chen Z, Peng C, Wenli C, Xingmin R, Ke D, Wei L, Ji D.G, Qiaoyun H (2011) Binding characteristics of copper and cadmium by cyanobacterium *Spirulina platensis*. *J. Hazard. Mater* 190:810-815
- Abuzer C, Huseyin B (2011) Bio-sorption of cadmium and nickel ions using *Spirulina platensis*: Kinetic and equilibrium studies. *Desalination* 275 :141-147
- Livia SF, Mayla SR, Joao C, Monteiro DC, Alessandra L, Elisabetta F, Patrizia P, Attilio C (2011) Adsorption of Ni^{2+} , Zn^{2+} and Pb^{2+} onto dry biomass of *Arthrospira (Spirulina) platensis* and *Chlorella vulgaris*. I. Single metal systems. *Chem. Eng. J* 173: 326
- Vimala R., Charumathi D, Nilanjana D (2011) Packed bed column studies on Cd(II) removal from industrial wastewater by macrofungus *Pleurotus platypus*. *Desalination* 275: 291-296
- Vijayaraghavan K, Jegan J, Palanivelu K, Velan M (2005) Biosorption of copper, cobalt and nickel by marine green alga *Ulva reticulata* in a packed column. *Chemosphere* 60:419–426
- Vilar V.J, Botelho CM, Loureiro JM, Boaventura RA (2008) Biosorption of copper by marine algae *Gelidium* and algal composite material in a packed bed column. *Bioresour. Technol* 99: 5830–5838
- Volesky B, Prasetyo I (1994) Cadmium removal in a biosorption column. *Biotechnol. Bioeng* 43 1010-1015
- Alpana S, Kumar D, Gaur JP (2012) Continuous metal from solution and industrial effluents using *Spirogyra* biomass packed column reactor. *Water research* 46:779-88
- Xin Y, Kumar A, Ashish KS, Sarina JE (2011) Impact of ammonia concentration on *Spirulina platensis* growth in an air lift photobioreactor. *Bioresour. Technol*, 102:3234-3239
- Bohart G, Adams E.Q (1920) Some aspects of the behavior of charcoal with respect to chlorine. *J. Am. Chem. Soc* 42:523–544
- Cooney, D.O (1999) Adsorption Design for Wastewater Treatment. CRC Press, Boca Raton, 137–172
- Doshi H, Ray A, Kothari IL (2007) Biosorption of cadmium by live and dead *Spirulina*: IR spectroscopic, kinetics and SEM studies. *Curr. Microbiol* 54:213-218
- Robert, MS, Francis XW (2008) Spectrometric identification of organic compounds, Wiley India (P) Ltd, New Delhi

- Xue FS, Shu-Guang W, Xian-Wei L, Wen-Xin G, Nan B, Bao-Yu G (2008) Competitive biosorption of zinc(II) and cobalt(II) in single- and binary-metal systems by aerobic granules. *Journal of Colloid and Interface Science* 324:1–8
- Ramesh ST, Rameshbabu N, Gandhimathi R, Nidheesh PV, Srikanth Kumar M (2012) Kinetics and equilibrium studies for the removal of heavy metals in both single and binary systems using hydroxyapatite. *Appl Water Sci* 2:187–197
- Devlina D, Geetanjali B, Lakshmi V, Nilanjana D (2012) Kinetics and equilibrium studies on removal of zinc(II) by untreated and anionic surfactant treated dead biomass of yeast: Batch and column mode. *Biochem. Eng. J* 64: 30–47
- Tamer A, Zerrin K, Sefika U, Dilek Y, Guldem O, Sibel TA (2009) Enhanced biosorption of nickel(II) ions by silica-gel-immobilized waste biomass: Biosorption characteristics in batch and dynamic flow mode. *J. Hazard. Mater* 163: 1134–1141
- Han R, Zou W, Li H, Li Y, Shi J (2006) Copper(II) and lead(II) removal from aqueous solution in fixed-bed columns by manganese oxide coated zeolite. *J. Hazard. Mater* 137:934–942
- Shuguang Lua B, Stuart W, Gibb B, Emma C (2007) Effective removal of zinc ions from aqueous solutions using crab carapace biosorbent. *J. Hazard. Mater* 149:208–217
- Ismael A, Aguayo V, Adrian B P, Virginia HM, Miguel AMM, Hilda ERA (2011) Batch and column studies of Zn⁺² removal from aqueous solution using chicken feathers as sorbents. *Chem. Eng. J* 167:67–76
- Senthilkumar R, Vijayaraghavan K, Thilakavathi M, Iyer P V R, Velan M (2006) Seaweeds for the remediation of wastewaters contaminated with zinc(II) ions. *J. Hazard. Mater* B136 : 791–799
- Necip A, Asim O, Shaobin W (2012) Adsorption of cadmium (II) and zinc (II) on boron enrichment process waste in aqueous solutions: Batch and fixed-bed system studies. *Chem. Eng. J* 192:1–7