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Removal of Zn^{+2} ions from aqueous solution using *Anabaena variabilis*: Equilibrium and Kinetic studies

Gaur, N.* **and Dhankhar, R.**

Ecology Laboratory, Department of Bio-Sciences, M.D. University, Rohtak - 124001
(Haryana) India

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ABSTRACT: Zinc ions are present in different types of industrial effluents, being responsible for environmental pollution. Biosorption is a process in which solids of natural origin are employed for binding heavy metals. It is a promising alternative method to treat heavy metal wastes mainly because of high metal binding capacity. The effect of some important parameters on sorption capacity of cyanobacterial biosorbent for zinc uptake was studied. The optimum conditions pH, time, initial ion concentration, adsorbent dose; were found to be 8, 90 mins, 100 ppm and 1gm/100mL respectively. Immobilization of biomass was done in calcium alginate and agar matrices for reuse of biosorbent. Freundlich and Langmuir isotherms were applied to equilibrium data of zincions biosorption and Freundlich isotherm was found to fit the data. The maximum adsorption capacity was 71.42 mg/g for *A. variabilis*. The value of value of K_f and n were ranged from 0.4458 to 2.797 and 0.7726 to 2.797 for the cyanobacterial biosorbents. 0.1 M EDTA was used as an eluant and the biosorbent was reused up to five biosorption desorption cycles and percentage desorption of zinc ions was 93 to 84 from first to fifth cycle for the cyanobacterial biosorbents. Fourier transform infra-red analysis of algae with and without biosorption revealed the presence of carboxyl, hydroxyl, amino, amide and imine groups, which were responsible for biosorption of Zn^{+2} ions. The rate law for a pseudo-second-order model fits the experimental data with a very high correlation coefficient and it was greater than 0.9771.

Key words: Zn^{+2} ions, *Anabaena variabilis*, Immobilization, Fourier transform infra-red, Isotherms, Biosorption, Pseudo second order

INTRODUCTION

The increased circulation of toxic metals through the soils, water, air and their inevitable transfer to the human food chain remains an important environmental issue which entails known and unknown health risks. The annual total toxicity of all the heavy metals mobilized, infact exceeds the combined total toxicity of all the radioactive and organic waste generated each year as measured by the quantity of water needed to dilute such waste to drinking water. Each year million of tones of new trace metals are produced from mines and subsequently redistributed in biosphere (Nriagu and Pacyna, 1988). Owing to economic pressure and industrialization, the threat of metal pollution is slowly becoming a reality in developing countries, thus necessitating the monitoring of exposure levels and remedial measures before its too late. Fortunately, some awareness about seriousness of the problem is now discernible.

Of all the forms of water pollution, heavy metal pollution is most hazardous because pollutant is present in mobilized form (Dixit and Tiwari, 2008; Mensi *et al.*, 2008; Murugesan *et al.*, 2008; Akoto *et al.*, 2008; Karbassi, *et al.*, 2008; Abdel-Ghani, 2007). The main techniques utilized for treatment of zinc bearing waste streams include evaporation, adsorption by activated carbon, ion exchange,

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*Corresponding author Email: vikas_bhardwaj@aol.in

membrane processing, solvent extraction, precipitation, reverse osmosis etc. These methods have been found to be limited, because they often involved high capital and operational cost and may also be associated with the generation of toxic secondary waste which further present treatment problem (Ajmal *et al.*, 2000). These processes are sometimes neither effective nor selective and most of them are expensive too. In this respect, the search for a new ecofriendly, economical and effective metal adsorbent is focused on biomaterials such as bacterial and algal biomass (Bailey *et al.,* 1999).

Biosorption utilizes the ability of biological materials to accumulate heavy metals from waste water by physico-chemical pathways of uptake. Use of microorganisms as biosorbents for heavy metals offers a potential alternative to existing method of recovery of these metals from industrial waste water (Grvrilescu, 2004). Biosorption offers the advantage of low operating cost, minimizes the volume of chemical and biological sludge to be disposed, highly efficient in dilute effluent and no nutrient requirements. The mechanism of binding metal ions by inactivated algal biomass may depend on the species and ionic charges of metal ion. The algal organism, the chemical composition of metal ion solution and other environmental factors such as pH, temperature etc. (Rezaee *et al.,* 2006). The use of freshly suspended microbial biomass suffers with disadvantages like small particle size, low mechanical strength and difficulty in sequestering the biomass and effluent. In industrial technical operations, immobilized microbial cell system could also provide additional advantages over freely suspended cells. These include the ease of and reuse of the biomass, easier solid liquid phase separation and minimum clogging in continuous flow system. Natural polymers such as alginate, chitosan, chitin, cellulose derivatives have been mostly used as matrix for immobilization of microbial cells via entrapment technique.

Biotechnological exploitation of biosorption technology for removal of heavy metals depends on the efficiency of regeneration of biosorbents after metal desorption. Therefore; non destructive recovery by mild and cheap desorbing agent is desirable for regeneration of biomass for use in multiple reuse cycles. The deposited metals are washed out (desorbed) and the biosorbent is regenerated for another cycle. The desorption should result in

- ➢ high concentration metal effluent
- ➢ undiminished metal uptake on reuse
- ➢ least physico-chemical damage to biosorbents

Many types of yeast, fungi, algae, bacteria and some aquatic plants have been reported to have the capacity to concentrate metals from dilute aqueous solutions and to accumulate them inside the cell structure (Kapoor and Viraghavan, 1995; Volesky and Holan, 1995; Modak and Natarajan, 1996). Among different biological substrates studied, algal biomass received much attention due to cost saving, low sensitivity to environmental and impurity factors, possible contaminant recovery from biomaterial and its elevated adsorption capacity, comparable to those of synthetic ion exchange resin, cheap availabity, high surface area and high uptake capacity. Mehta and Gaur (2005) critically reviewed the biosorption of metal ions with the algae but little work has been done exclusively with cyanobacteria as metal binding biosorbents.

Hence, the present study emphasizes on the development of cyanobacterial biosorbents from *Anabaena variabilis* for Zn^{2+} biosorption and desorption of heavy metals in batch process by free and immobilized biosorbents and the identification of functional groups responsible for binding of metal ion. The present work reports the spectral study, biosorption equilibrium and kinetics study of Zn^{2+} ions by free and immobilized *Anabaena variabilis*. In biosorption equilibrium, effect of variable initial metal ion concentration, biosorbent dose, sorption time and pH were analyzed. A range of equilibrium adsorption isotherms (Langmuir and Freundlich) were obtained quantitatively to describe the Zn^{2+} ions uptake in aqueous solution. The kinetic studies were carried out by conducting batch experiments.

MATERIALS & METHODS

The cyanobacterium *A. variabilis* was obtained from the National Facility from Blue Green Algae Division, IARI, New Delhi, India. The axenic culture was grown in the Fogg's media

Table 1. Composition of Fogg's media

Chemicals	Concentration (g/L)
KH2PO4	0.2
$MgSO_4.\ 7H_2O$	0.2
$CaCl_2$	0.1
A5	1mL
Fe-EDTA	1mL
pH	7

and composition is shown in Table 1. The cultures were maintained in the culture room illuminated with cool day light 3000 lux under 16 h light /8 h dark cycle at 24 ± 1°C. For preparing biosorbent, exponentially grown cells of *A. variabilis* (22 days) were harvested by centrifuging at 4000 rpm for 10 minutes. The biomass was then washed twice with deionized water and dried at 60°C in oven for 24 h. The dried biomass was ground and sieved through 200 µm screen.

All the chemicals used in the study were of analytical grade and supplied by Qualligenes Fine Chemicals (Bombay) India. The stock metal solution of Zn^{2+} ions were prepared by dissolving appropriate quantities of pure analytical grade metal salts in deionized water. The stock solution was diluted with deionized water to obtain working solution of desirable concentrations. All the experiments were repeated three times and the average values have been reported. Also, blank experiments were conducted to ensure that no adsorption was taking place on the walls of apparatus used.

Immobilization of *A. variabilis* was carried out according to method known in literature (Srinath *et al.*, 2003). Ca alginate and Agar beads were prepared with biomass and then were used for the evaluation of biosorption of Zn^{+2} ions. For each immobilization process, 0.02 g of biomass was entrapped in 1 gm of matrix. The preparations were obtained as follows:

The immobilization of biomass via entrapment was carried out as follows. 2% (w/v) sodium alginate was dissolved in hot distilled water with constant stirring. At room temperature, biosorbent was added under stirring condition for even dispersal. The slurry solution was dripped through the nozzle drop wise into 0.05 M $CaCl_2$. As a result, spherical beads were formed immediately due to phase inversion process as the alginate was cross linked with Ca^{+2} ions. The beads (3.2 ± 0.1 mm) were moderately agitated in deionized water for 24 hrs at 4°C. The curing procedure hardened the beads and resulted in the formation of a micro porous structure. Finally, the beads were stored at 4°C in ultra pure double distilled water until for further use.

The agar beads were prepared by dissolving it in distilled water at 90°C. The biomass was added at room temperature and evenly dispersed by stirring. Spherical beads were obtained on drop wise addition of slurry into a hydrophobic liquid phase (Sun flower oil) over distilled water. The beads were collected and then washed with 0.001% Triton X 100 to eliminate the residual oil phase.

Standard stock solution of Zn^{2+} ions (1000 ± 2 mg/L) was diluted to the concentration to be investigated for metal biosorption. The pH of the metal solution was adjusted with the help of 0.01M HCl or 0.01M NaOH as desired in the experiments. Fresh dilutions were used each time. Biosorption capacity of cyanobacterial biosorbent, both free and immobilized in Ca alginate and agar matrix was determined by 100 mL metal solution of known concentration (20-400 mg/L to cyanobacterial biosorbents (0.2-2 gm) in 250 mL shaking flask. The metal ion solution incubated with biosorbent was shaken at shaker at 100 rpm in tightly stoppered flask. Free biosorbent was removed from metal solution by centrifugation at 3500 rpm for 5 minutes where as immobilized biosorbents were separated by simple decantation. The filtrate was analyzed for residual Zn^{+2} ions with the help of Atomic Absorption Spectrophotometer (Perkin Elemer 280). The batch experiments were carried out as function of pH, biosorbent dose, time, and initial ion concentration of metal ions. All experiments were conducted in triplicate and mean values were used. The quantitative estimation was done by Freundlich and Langmuir isotherms.

The kinetic study carried out by conducting batch biosorption experiments using cyanobacterial biosorbent, both free and immobilized in Ca alginate and agar matrix and was determined by taking 100 mL metal solution of known concentration (100 mg/L) to cyanobacterial biosorbents (1gm) in 250mL shaking flask , samples were taken out at different time period to analyze the Zn^{2+} ions concentration. The reusability of bio-sorbent is directly related to the application potential of biosorption technology in waste water treatment. *A. variabilis* as biosorbent was reused in three biosorption desorption cycles to determine reusability. For this purpose, immobilized biomass was contacted with 100 mL of 100 ppm of Zn^{2+} ions solution for biosorption and 0. 1M EDTA was used as eluant in desorption cycle in 250 mL flask shaken on orbital shaker for 30 minutes at 100 rpm for achieving sorption desorption equilibrium. The initial and final concentration of the solution was recorded for each cycle before and after sorption. The cyanobacterial biosorbents were washed with deionized water and transferred for the next biosorption cycle.

To obtain a qualitatively and preliminary analysis of main chemical groups present on the cell wall and its content, an infra red (IR) analysis in solid phase was performed on biosorbents. The FTIR spectrum of biosorbents was obtained from sophisticated analytical instrumentation facility, Punjab University. Infrared spectra of free biosorbents before and after biosorption were recorded on Nicolt Model 6000. FTIR spectrometer equipped with a liquid nitrogen cool detector .The samples were prepared using KBr disc. The spectrum was recorded in the range of 400 to 4000 cm^{-1}. The technique was used to elucidate the chemical characteristics relevant to metal ion sorption by the cyanobacterial biomass.

RESULTS & DISCUSSION

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the biomass cell wall, therefore pH is an important parameter for the biosorption of metal ions from aqueous solution (King *et al.*, 2006). The specific and non specific uptake of metal ions by the cell is a pH dependent phenomenon (Zhou, 1999). The maximum percentage removal of Zn^{2+} ions at pH 8 for *A. variabilis, A. variabilis* embedded in Ca alginate, *A. variabilis* embedded in agar matrix was 85.1, 82.3 and 81.1 % respectively. The Zn^{+2} ions uptake pattern by free and immobilized forms of *A. variabilis* biosorbent showed similar pattern of regular increase in %age removal with increasing pH in the range of 2 to 8 reaching maximum at pH 8.0 (Srivastava *et al.*, 1994). The pH dependence of metal adsorption can largely be related to type and ionic state of functional groups present in biosorbent and also on metal chemistry in the solution. The positive charged hydrogen ion may also compete with metal ions for binding on the ligands on the cell wall (Kaewsarn, 2002).

At lower pH, the higher concentration of the hydrogen ion effectively leads to fewer ligands being available for the binding of metal ions. Increased pH (i.e. fewer H^+ ions) results in more ligands being available for metal ion binding and hence biosorption is enhanced. An increase in pH means a lower quantity of protons, which caused a decrease in the competition between proton and heavy metal ion. Hence an increase in the sorption capacity (or removal efficiency) for Zn^{+2} ions could be observed.

The role of contact time on biosorption of Zn^{+2} ions by free and immobilized cyanobacterial biosorbent was studied. In all three types of biosorbents, metal uptake was increased rapidly up to 90 minutes and remained constant after that. Based on these results, equilibrium time of 90 minutes was chosen for further experiments. Adsorption got slow down in later stages because initially a large number of vacant surface sites were present and after that it may be difficult to occupy binding sites due to repulsive forces between the solute molecules of the solid and bulk phase. The diminishing removal with increasing time may be due to intraparticle diffusion process dominating over adsorption.The biosorption process is actually a surface interaction with very rapid uptake of ions by microbial surface. The percentage removal was 84.3, 82.1 and 80.1 for *A. variabilis*, Ca alginate immobilized *A. variabilis* and agar immobilized *A. variabilis* respectively.

The phenomenon of increase in percent Zn^{+2} ions adsorption with increase in adsorbent dose up to certain level and beyond that a less or more constant removal may be explained with increase in adsorbent dose. More and more adsorbent surface become available for the solutes to adsorb and increase the rate of adsorption. However, very slow increase in removal beyond optimum dose may be attributed to the attainment of equilibrium between adsorbate and adsorbent at operating conditions as adsorbent dose was increased. There was less increase in adsorption capacity and as a result, unit adsorption decreased significantly with increase in mass of adsorbent per unit volume. The reason may be attributed to the fact that high biomass concentration could make a screen effect on the outer layers protecting the binding sites from metal ions and there by lowering the specific metal uptake at higher biomass loading (Mehrotra *et al.,* 1999). Optimum dose for removal of Zn^{+2} ions was found to be same i.e. 1gm/100 mL for all the biosorbents, but percentage removal is maximum, 94.7% for *A. variabilis* embedded in Ca alginate matrix.

The bio-sorption of free and immobilized *A. variabilis* was evaluated by conducting experiments at varying metal ion concentrations (20-400 mg/L). The maximum attainable biosorption was found to be 97.3, 94.6 and 94.0 % for *A. variabilis*, *A. variabilis* embedded in Ca alginate and *A. variabilis* embedded in agar respectively. Decrease in percentage adsorption with increase in the metal concentration is due to saturation of all the binding sites with metal ions and establishment of equilibrium between adsorbate and biosorbent (Bai and Abraham, 2001).

The zinc ions uptake by free and immobilized *A. variabilis* was evaluated using Langmuir and Freundlich adsorption isotherms for the variation of adsorption with respect to the concentration of adsorbate in the bulk solution at constant temperature. The concentration of free metal adsorbed on per unit free and immobilized cyanobacterial (mg metal/gm dry biosorbent) was determined using following expression:

$$q= V\ (C_o-C_{eq})\ /\ M \qquad (IV)$$

q: is the metal uptake (mg/g) of the algal biosorbent

V : is the metal ion solution in litre

C_o : is the initial metal ion concentration (mg/L)

$C_{eq:}$ is the metal ion concentration at equilibrium (mg/L)

M: is the mass of algal biosorbent

According to Freundlich model of adsorption

$$q_e = K_f\ C_e\ 1\ /\ n \qquad (V)$$

q_e is the metal uptake (mg/gm)

K_f : is the Freundlich constant for adsorption capacity

n : is the Freundlich constant for adsorption intensity

C_e : is the equilibrium concentration (mg/L)

To simplify the derivation of K_f and n, equation (V) can be lineraized in the logarithmic form:

$$\log q_e=\log K_f\ +\ 1/n\ \log C_e \qquad (VI)$$

A better fit Freundlich adsorption model signifies that (a) there may be heterogeneous surface offered by the biosorbent during adsorption process (b) surface energy does not remain constant during the process of adsorption, but varies with the surface coverage. The value of Freundlich constant K_f and n were calculated from intercept and slope of the plot as shown in Fig. (2). The values of K_f and n were calculated and shown in Table (2). According to Kadirvelu and Namasivayam, 2000; n values between 1 to 10 represent beneficial adsorption.

Table 2. Isotherm constant of Zn II on to different cyanobacteria

Isotherm constant	***A variabilis***	**Ca alginate + *A variabilis***	**Agar+ *A variabilis***
Langmuir constant Q0 (mg/g)	71.42	44.44	50.5
b	0.0058	0.0301	0.0142
r2	0.8587	0.7501	0.8063
Freundlich constant Kf (mg/g)	0.4458	2.797	0.7790
n	2.7970	1.643	0.7726
r2	0.7791	0.5464	0.9166

Langmuir equation valid for monolayer sorption on surface with a finite number of sites is given in equation

$$q_e = Q_o\, b\, C_e / 1 + b\, C_e \qquad \text{(VII)}$$

The lineraized form of this equation is

$$1 / q_e = 1 / (Q_o\, b\, C_e) + 1 / Q_o \qquad \text{(VIII)}$$

q_e : is the metal uptake (mg/gm)
Q_o : is the Langmuir constant which is a measure of adsorption capacity (mg/gm)
b : is the Langmuir constant which is a measure of adsorption energy (mg/L)
C_e : is the equilibrium concentration (mg/L)

$1/q_e$ vs. $1/C_e$ gives the straight line with slope $1/Q_o b$; 1/ b as its intercept. The linear plot shows that adsorption obeys Langmuir isotherm as shown in (Fig. 4). (Bera *et al.*, 2006). The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity in contrast to Langmuir model.

Langmuir Isotherm is based on following assumption:

1. Metal ions are chemically adsorbed at a fixed number of well defined sites.
2. Each site can hold anyone ion.
3. All sites are energetically equivalent.
4. There is no interaction between ions.

Whereas, the adsorptive behaviour of metal ion on biosorbent satisfies not only Langmuir adsorption assumption but also Freundlich adsorption isotherm i.e. multilayer formation on surface of the biosorbent with an exponential distribution of site energy. The shapes of the isotherm suggest that there are high energy adsorption sites to favour strong adsorption**.** The maximum adsorption capacity was found to be 71.42 mg/g, 44.44 mg/g and 50.50 mg/g for *A. variabilis*, *A. variabilis* embedded in Ca alginate and *A. variabilis* embedded in agar respectively. Freundlich isotherms were in good agreement for *A. variabilis* embedded in agar matrix as shown in Figs.1 & 2.

The prediction of adsorption rate gives important information for designing batch adsorption system. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full scale batch process .The adsorption rate with in 60 minutes was observed to be very high and there after the reaction proceed at slower rate till the equilibrium reached at 90 minutes and finally a steady state was observed at equilibrium .The kinetics of the adsorption data was analyzed using pseudo first order and second order kinetic model .The model

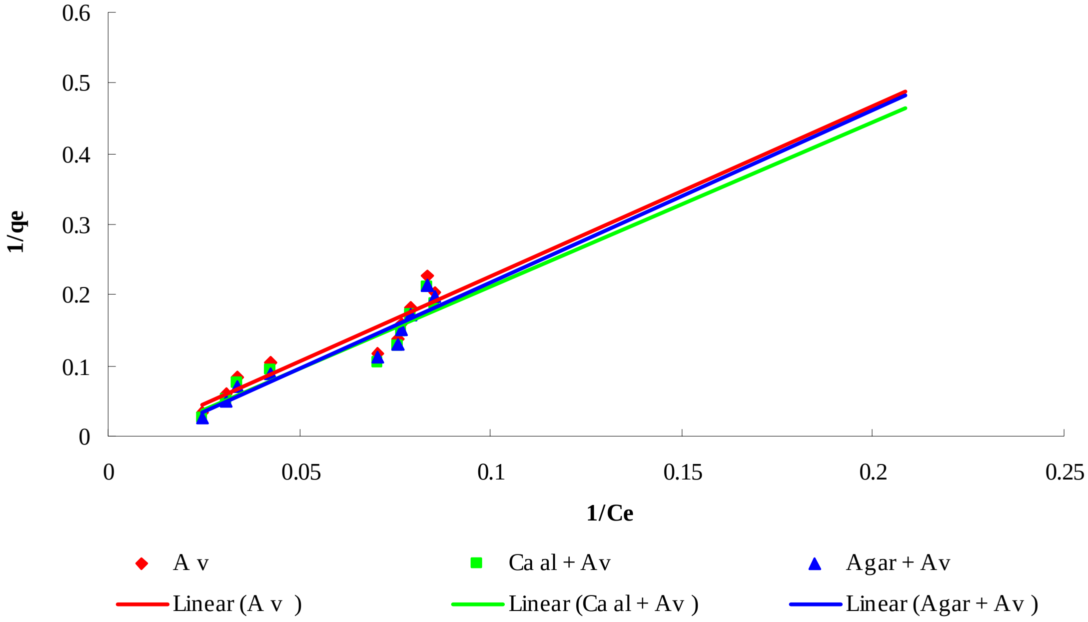

Fig. 1. Langmuir isotherm of adsorption of Zn(II) by cyanobacteria

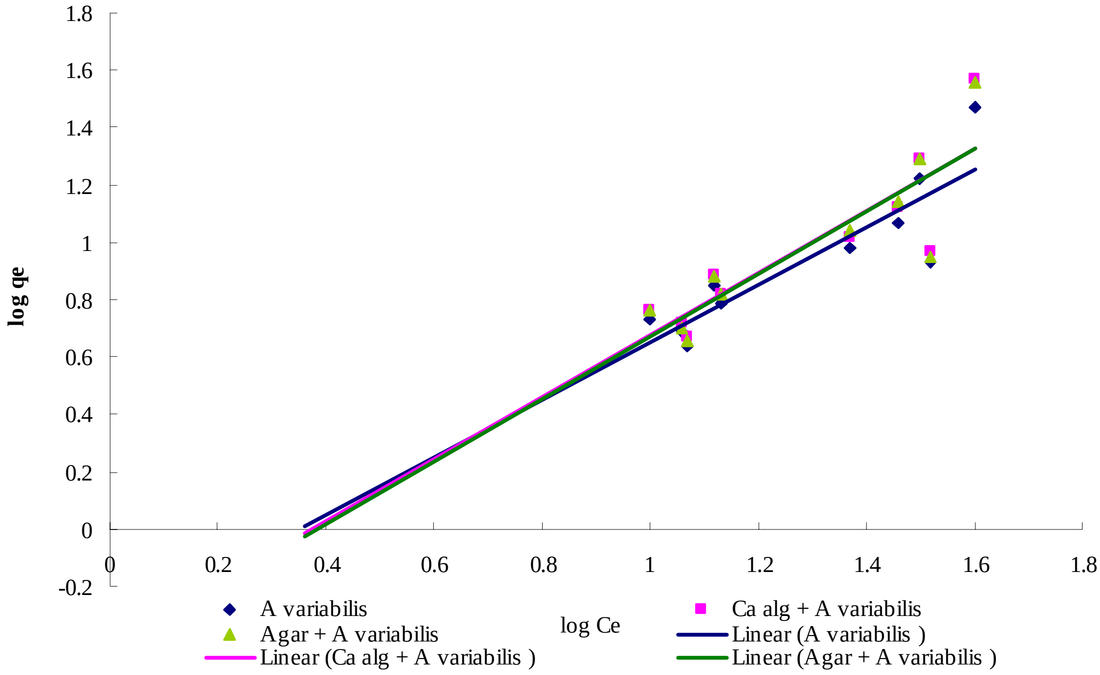

Fig. 2. Freundlich isotherm of adsorption of Zn (II) by cyanobacteria

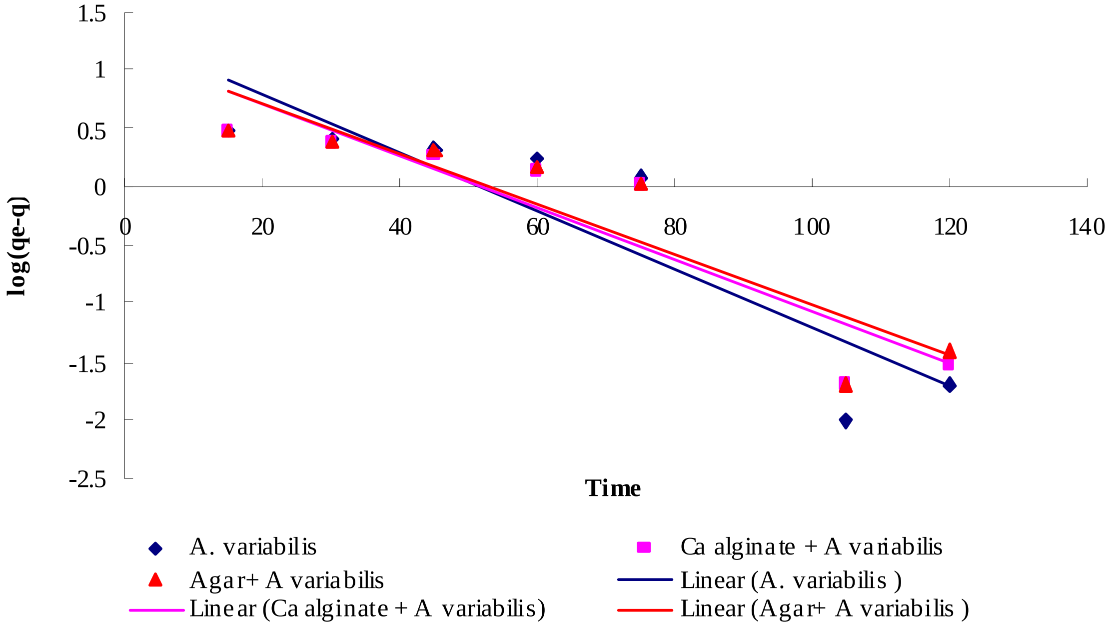

Fig. 3. Pseudo first order kinetic model

correlate solute uptake , which are important in predicting the reactor volume (King *et al.*, 2006). First order equation of Lagergren and Kungliga is generally expressed as follows (Lagergren *et al.*, 1898):

$$dq_t / dt = k_{1ad} (q_e - q_t) \qquad (I)$$

Where

q_e : is the sorption capacity at equilibrium in (mg/g)

q_t : is the sorption capacity (mg/g) at time t

$k_{1ad:}$ is the rate of pseudo first order of reaction (1/min)

After integration and applying the boundary condition, $q_t = 0 - q_t$ at $t = 0 - t$, the integrated form of equation becomes;

$$\log (q - q_t) = \log q - k_{1ad}\, t / 2.303 \qquad \text{(II)}$$

The equation applicable to experimental results generally differs from a true first order equation in two ways:

- The parameters $k_{1ad} (q - q_t)$ does not represent the number of available sites;
- The parameter log (q) is an adjustable parameter which is not found equal to the intercept of a plot of log $(q - q_t)$ against t.

Whereas in the true first order of reaction, log q should be equal to the intercept of plot of log $(q - q_t)$ against t. Pseudo first order rate constant k_{1ad} can be obtained from the slope of plot between log $(q - q_t)$ against time t. Fig.3. shows the Lagergren pseudo first order kinetic plot for adsorption of Zn^{+2} ions. The pseudo first order rate constant K_{1ad} values were calculated and their corresponding linear regression correlation coefficient r_1^2 were also calculated. The linear regression correlation coefficient r_1^2 was found as 0.806, 0.8457 and 0.8296 for *A. variabilis*, *A. variabilis* embedded in Ca alginate and *A. variabilis* embedded in agar respectively. First order kinetic model cannot be applied due to low regression values.

In many cases the equation (II) cannot be used to describe the kinetics of the adsorption process. In such cases, a pseudo-second order expression may be used. This model reduces to:

$$t / q_t = 1 / k_{2ad}\, q_e^2 + 1(t) / q_e \qquad \text{(III)}$$

k_{2ad} = pseudo-second order rate constant (g mg^{-1} min^{-1})

If pseudo-second order kinetics is applicable, the plot of t/q_t against t of equation (III) should give a linear relationship, from which q and k can be determined from the slope and intercept of the plot as shown in (Fig. 4) and there is no need to know any parameter beforehand. The pseudo-second order rate constant $k_2$ad, the corresponding linear regression correlation coefficient values r_2^2 are given in Table 3. At all initial zinc concentrations, the linear regression correlation coefficient r_2^2 values were higher. The higher r_2^2 values confirm that the adsorption data are well represented by pseudo-second order kinetics and supports the assumption behind the model that the adsorption is due to chemisorption.

In order to compare the feasibility of using algal biosorbent for multiple uses, a set of desorption cycles were carried out. Desorption of adsorbed Zn^{+2} ions from the free and immobilized cyanobacterial biosorbent were studied. In order to show the reusability of the biosorbent, adsorption desorption cycles were repeated five times using same procedure. Percentage desorption was 93 to 85 for *A. variabilis* 91 to 82 for *A. variabilis* immobilized in calcium alginate matrix and 88 to 84 for *A. variabilis* immobilized in agar matrix as shown in Fig. 5. These results showed that the biosorbent can be used repeatedly in case of immobilized biosorbent. The capacity of repeated use for free *A. variabilis* was poor in terms of separation (Dong, 2004).

FTIR spectroscopy has been frequently used to detect vibrational frequency changes in biosorbents. It offers excellent information on the nature of the bonds present and allows identification of different functionalities on the cell surface (Murphy *et al.*, 2007). Numerous chemical groups have been proposed to be responsible for biosorption of metals by algae

Table 3. Kinetics constant of Zn II on to different cyanobacteria

Kinetic constant	***A variabilis***	**Ca alg+ *A variabilis***	**Agar+ *A variabilis***
Pseudo first order			
K1ad	0.0566	0.5043	0.48823
$r1^2$	0.8061	0.8457	0.8296
Pseudo second order			
K^2ad	0.1026	0.1065	0.1078
$r2^2$	0.9771	0.9868	0.9824

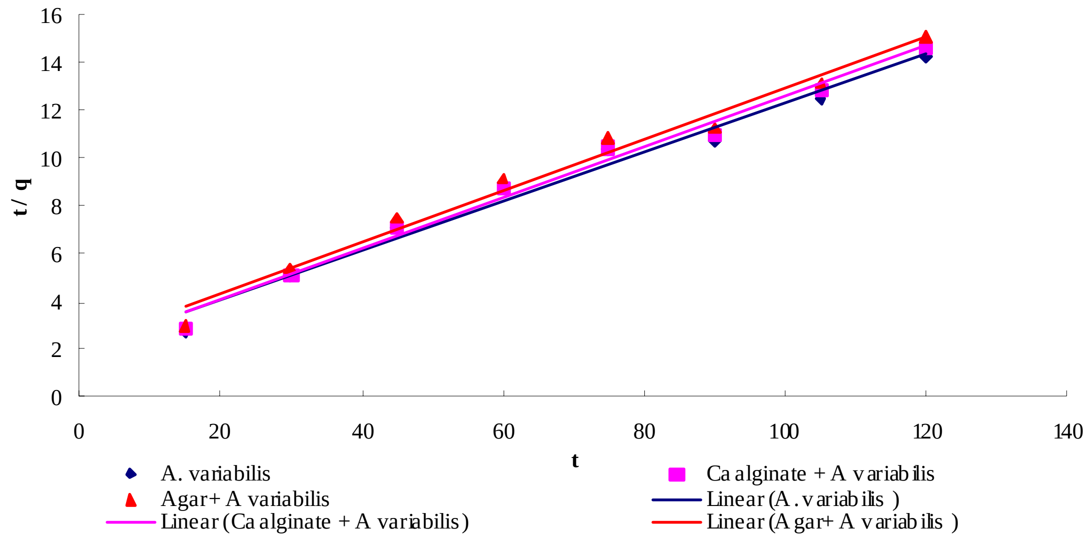

Fig. 4. Pseudo second order kinetic model

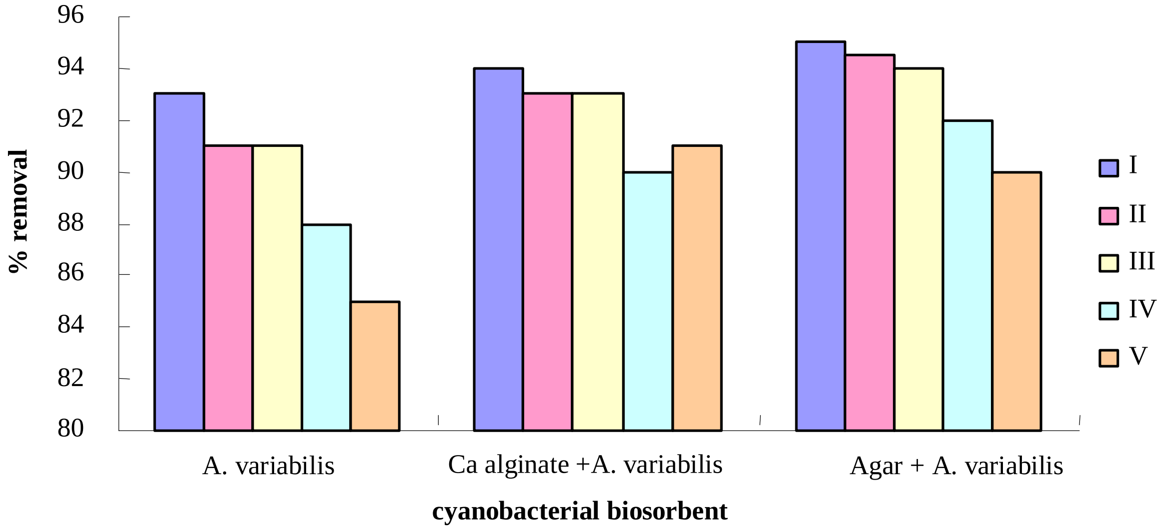

Fig. 5. Desorption cycles of Cyanobacterial biosorbents

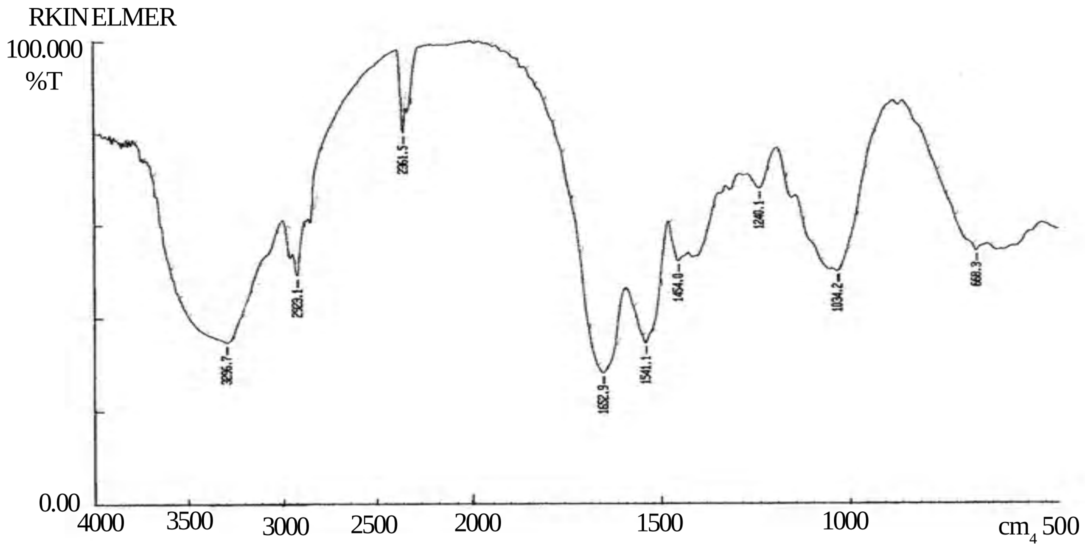

Fig. 6. FTIR of Anabaena

(Smith and Lacher, 2002). Their relative importance in metal sorption may depend on factors such as quantity of sites, their accessibility, chemical state and affinity between site and metal. The FTIR spectrum of *A. variabilis* has been shown in Fig. (6). The bands at 3296 cm^{-1} (broad and sharp) were assigned to bonded –OH, -NH stretching. Band at 2923 cm^{-1} (sharp) can be assigned to asymmetric stretch of aliphatic chains. Sharp peak observed at 2361.5 cm^{-1} was attributed to nitrile (-CN). Peaks observed at 1652.9, 1541.1, 1454, 1240, 1034.2, 668.3 cm^{-1} were attributed to asymmetric C=O stretching from ketone and aldehyde, amide, symmetric C=O, C-O stretch of –COOH and C-O stretch of an alcohol (-OH) respectively. It can be seen that the IR spectra indicated the presence of ionisable functional groups; their ionization leaves vacant sites which can be replaced by metal ions. This gives an indication that these materials can be used as adsorbents for heavy metal removal (Ghani *et al.*, 2007).

CONCLUSION

A. variabilis demonstrated a good capacity of Zn^{+2} ions biosorption highlighting its potential for effluent treatment process. Both free and immobilized *A. variabilis* had a strong effect on biosorption capacity and maximum at pH 8. Langmuir Isotherm was in favour of results for free *A. variabilis* and *A. variabilis* embedded in Calcium alginate where as Freundlich isotherm hold in good agreement for and *A. variabilis* embedded in agar matrix. Desorption study showed that 85-95 % Zn^{+2} ions can be desorbed from the biosorbent using 0. 1 M EDTA. FTIR provides qualitative analysis of the functional groups like carboxyl, hydroxyl, amino, amide and imine groups, responsible for absorption of Zn^{+2} ions .The study also indicated that algae biomass can be used to develop high capacity biosorbent materials for the removal and recovery of Zn^{+2} ions from dilute industrial waste water. Pseudo second order chemical reaction for sorption of Zn^{+2} ions was apparent as this kinetic model describes adequately the largest part of the process.

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Nomenclature

b -binding capacity of solute on the sorbent surface (mg/L)
C -initial metal ion concentration (mg/L)
C_e -metal ion concentration at equilibrium (mg/L)
K_f -Freundlich constant for adsorption capacity.
n-Freundlich constant for adsorption intensity.
q-amount of metal adsorbed per unit weight of biosorbent (mg/gm)
q_e -amount of metal adsorbent per unit weight of biosorbent at equilibrium (mg/gm)
Q_o-maximum amount of metal adsorbed per unit weight of biosorbent (mg/gm)
r^2-correlation coefficient
V - reaction volume (litre)
M-mass of biosorbent (gm)
t - time (minute)
K_{1ad} - rate of pseudo first order of reaction (1/min)
q_t - sorption capacity (mg/g) at time t
K_{2ad} - rate of pseudo second order of reaction (g mg^{-1} min^{-1})
r_1^2-correlation coefficient of pseudo first order of reaction
r_2^2-correlation coefficient of pseudo second order of reaction

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