

Research Article

Biosorption potential of the red alga, *Gracilaria verrucosa* for the removal of Zn²⁺ ions from aqueous media: Equilibrium, kinetic and thermodynamic studies

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Abstract

The aim of this study is to explore the potential of red alga, *G. verrucosa* as biosorbent to remove zinc (II) from aqueous solution. Experiments are carried out as a function of solution pH, biosorbent dosage, contact time and temperature. The equilibrium data were analyzed using the Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models. The maximum biosorption capacity of *G. verrucosa* biomass for Zn (II) was found to be 96.1 mg/g at pH 5, biomass concentration 4 g/L, contact time 60 min, and temperature 20 °C. The mean free energy E (9.62 kJ/mol) got from the D-R isotherm indicated a chemical ion-exchange mechanism. Kinetic studies showed that pseudo-second order described the biosorption experimental data better than the pseudo-first order kinetic model. Thermodynamic parameters showed that the biosorption of Zn (II) onto *G. verrucosa* biomass was feasible, spontaneous and exothermic under examined conditions. FTIR analysis demonstrates that carboxyl and hydroxyl groups were involved in the biosorption of the metal ions.

Keywords: Red alga, biosorption, kinetic model, Thermodynamic parameters, FTIR analysis, Desorption

1. Introduction

Rapid industrialization to meet the requirements of population has resulted in ecosystem contamination due to heavy metals like zinc. The effluents of industrial operations such as metal plating, electroplating, galvanizing plants, manufacture of batteries, textile, tannery operations, pigment and chemical manufacturing are major sources of zinc contaminants for surface waters (Weng, C.H., & Huang, C.P. 2004; Arias F & Sen T.K. 2009). Although zinc is an essential element for human health as it participates in metabolism, stimulates the enzymes and plays an important role in the functioning of immunologic system, it becomes toxic for humans at intake levels of 100-500 mg day⁻¹ (USDHHS, 1993). The World Health Organization recommends the maximum acceptable concentration of zinc in drinking water as of 5.0 mg l⁻¹ (Bhattacharya, A.K. *et al* 2006). Therefore, the elimination of this metal from water and wastewaters is important to protect public health. The main techniques that have been used on zinc content reduction from industrial waste are chemical precipitation, ion exchange, membrane filtration, electrolytic methods, reverse osmosis, and solvent extraction (Abuk, A.C. *et al* 2006; Zouboulis, A.I. *et al* 2004). These conventional techniques can reduce metal ions, but they do not appear to be highly effective due to the limitations in the pH

range as well as the high material and operational costs (Tewari, N. *et al* 2005). Hence, there is a crucial need for the development of a method that is highly selective, more efficient, easy to operate and hence cost effective. Biosorption could be a good alternative technology.

Biosorption in natural or uncontrolled situations typically involves a combination of active and passive transport mechanisms starting with the diffusion of the metal ion to the surface of the microbial cell. Once the metal ion has diffused to the cell surface, it will bind to sites on the cell surface which exhibit some chemical affinity for the metal. These steps contain a number of passive accumulation processes and may include adsorption, ion exchange, coordination, complexation, chelation and microprecipitation. Generally, such metal ion adsorption is fast, reversible, and not a limiting factor in bioremoval kinetics when dealing with dispersed cells. Biosorption is often followed by a slower metal binding process in which additional metal ion is bound, often irreversibly. This slow phase of metal uptake can be due to a number of mechanisms, including covalent bonding, surface precipitation, redox reactions, crystallization on the cell surface or, most often, diffusion into the cell interior and binding to proteins and other intracellular sites (Al-Asheh, S. *et al* 2003; Gundogdu, A. *et al* 2009; Witek-Krowiak, A. 2011; Das, N. 2010).

Among the different biological substrates studied, algal biomass has received much attention due to the cost saving, low sensitivity to environmental and impurity

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factors, the possible contaminant recovery from the biomaterial and its elevated adsorption capacity, higher than activated carbon and comparable to those of synthetic ion exchange resins. Biosorption in algae has mainly been attributed to the cell wall structure containing functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals via both electrostatic attraction, ion exchange and complexation (Freitas, O.M *et al* 2008; Zafar, M.N *et al* 2007). The red alga *Gracilaria verrucosa* is very abundant in seaside areas and lagoons and information about biosorption with it, is still scanty.

The goal of our study is to assess the zinc (II) biosorption potential of *Gracilaria verrucosa* biomass. For this purpose, biosorption process was characterized under different operating conditions such as initial pH, contact time, and sorbent dosage. Experimental data as functions of temperature and time were evaluated with the pseudo-first-order and the pseudo-second-order kinetic models. The Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherm models were applied to the equilibrium data. The desorption performance and regeneration ability of the biosorbent were studied. IR spectral analysis was also employed to understand the mode of metal- biomass interaction.

2. Materials and Methods

2.1. Materials

The red algae *Gracilaria verrucosa* was collected from the lagoon of Bizerte (North of Tunisia). The biomass were washed with generous amounts of distilled water to remove the surface-adhered particles and then dried in an oven at 60 °C for 48 h to a constant weight. The dried algae biomass were chopped, sieved and the particles with an average of 0.5mm were used for biosorption experiments

2.2. Reagents and equipments

A stock solution of zinc was prepared by dissolving appropriate amount of zinc sulphate ($ZnSO_4 \cdot 7H_2O$) in 1 L of deionized water, and the concentrations of Zn (II) used in this study ($10\text{--}400\text{mg L}^{-1}$) were obtained by dilution of the stock solution. The pH of the solutions was adjusted to the desired value by adding 0.1 M HNO_3 or 0.1M NaOH solutions before mixing the dried biomass with the solution. The metal concentrations were measured using an atomic absorption spectrophotometer (SHIMADZU AA-680, Japan). Transform infrared (FT-IR) spectra of dried unloaded biomass and Cu(II)-loaded biomass prepared as KBr discs were recorded at $400\text{--}4000\text{cm}^{-1}$ wavenumber range using a FT-IR spectrometer (FTS - 135).

2.3. Batch biosorption experiments

The biosorption equilibrium experiments of Zn(II) were performed using a batch process to determine the amount

of metal ion adsorbed by biomass samples under the effect of contact time, biosorbant dosage, pH and temperature of adsorption medium. Necessary amount of the dried biomass was equilibrated in a series of aqueous solutions (25 ml) placed in conical flasks containing different amounts of metal at a constant pH, which was adjusted with 0.1 M HNO_3 or 0.1M NaOH solution at the beginning of each experiment. The flasks were shaken for the desired contact time in an electrically thermostatic reciprocating shaker (Selecta multimatic-55, Spain) at 100 rpm. The experiments were repeated at 293, 303, 313, and 323 K. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and the filtrate was analyzed for metal concentration by using flame AAS. The percent biosorption of metal ion was calculated as follows (Eq.1):

$$\text{Biosorption (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final (or equilibrium) metal concentrations, respectively.

To ensure the accuracy, reliability and reproducibility of the collected data, the measurements were carried out in duplicated and the average values are presented. Throughout the study, the contact time was varied from 5 to 90 min, the pH from 2 to 9, the initial metal concentration from 10 to 400 mg/L, and the biosorbent dosage from 0.1 to 20 g/L.

2.4. Desorption procedure

A sample volume of 25mL, containing 10 mg/L of Zn (II), was transferred into a beaker; 10mL of buffer solution was added. After a fast shaking, 4 g/L of *G.verrucosa* was added and the mixture was shaken again for 60 min at 100 rpm. The system was filtered with blue band filter paper. Then the filter and constituents were washed with distilled water. The sorbed Zn (II) ions from *G.verrucosa* was eluted by using 10mL of 1M HCl and 10mL of 1M HNO_3 . Metal contents of the final solution were determined by AAS. The same procedure was applied to the blank solution. In order to use the biomass for the next experiment, the biomass was washed with excess of 1M acid solution and distilled water, sequentially.

3. Results and discussion

3.1. Effect of pH solution

The metal biosorption depends on the protonation or unprotonation of functional groups (such as, amino, carboxyl and phosphate groups) on the surface of the cell wall. The ionic forms of the metal ions in solution and electrical charge of the cell wall components depend on the solution pH (Deng, L *et al.*, 2007). The biosorption of Zn (II) onto *G.verrucosa* was studied over a pH range of 2–9 and the results are given in Fig. 1.

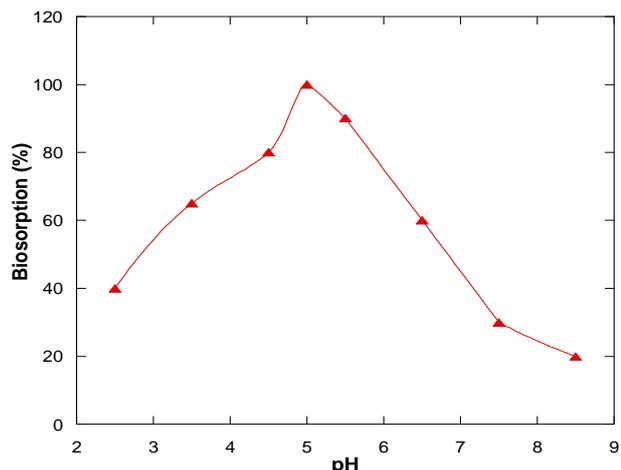


Fig.1. Effect of pH on biosorption of Zn(II) onto *G.verrucosa* (metal concentration:10 mg/L; temperature: 20 °C).

As seen from Fig. 1, the uptake of free ionic zinc (II) depends on pH, increasing with the increase in pH from 2.0 to 5 and then decreasing with increasing pH. At pH values lower than 3.0, zinc (II) removal was inhibited, possibly as a result of the competition between hydrogen and Zn(II) ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligands such as carboxylate groups in *G.verrucosa* alga would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the sorption onto the cell surface (Dursun, 2006). Above pH 5, insoluble Zn (II) hydroxide starts precipitating from the solution, so that adsorption rate was decreased. As a result, the optimum pH for Zn (II) biosorption was found as 5 and the other biosorption experiments were performed at this pH value.

3.2. Effect of biomass dosage

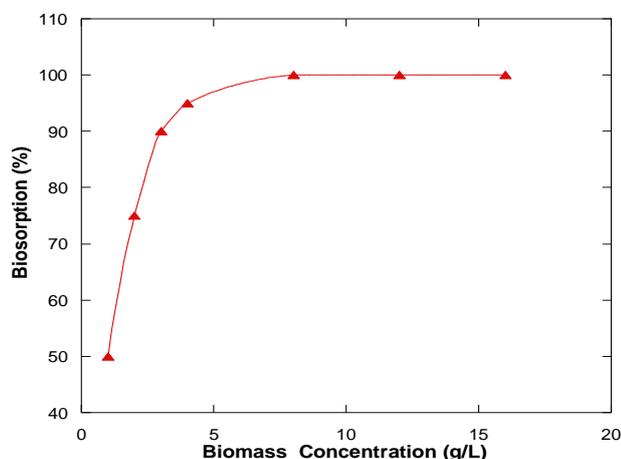


Fig. 2. Effect of biomass dosage on biosorption of Zn (II) by *G.verrucosa* (metal concentration: 10 mg/L; pH: 5; temperature: 20 °C).

The biomass concentration is another important variable during metal uptake. The effect of biosorbent dosage on the removal of Zn (II) is shown in Fig. 2.

As shown in this figure, percentage removal zinc (II) increases with increase in biosorbent dosage from 1 to 4 g/L. There is no significant increase in removal of Zn (II) when biosorbent dosage increases beyond 4 g/L. This suggests that after a certain biosorbent dosage, the maximum biosorption is attained and hence the amount of ions remains constant even with further increase in the surface area of the biosorbent, which in turn increases the number of binding sites. However, at high sorbent dosages the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, resulting in low metal uptake (Gong, R et al. 2005; Prasanna et al., 2007). Therefore, the optimal biomass concentration was selected as 4 g L⁻¹ for the further experiments.

3.3. Effects of contact time and temperature

The rate of sorption is of most important when designing batch adsorption experiments. Consequently, it is important to establish the time dependence of such systems under various process conditions. The experimental runs measuring the effect of contact time on the batch adsorption of metal solution containing 10 mg/L of zinc and initial pH value 5 is shown Fig. 3

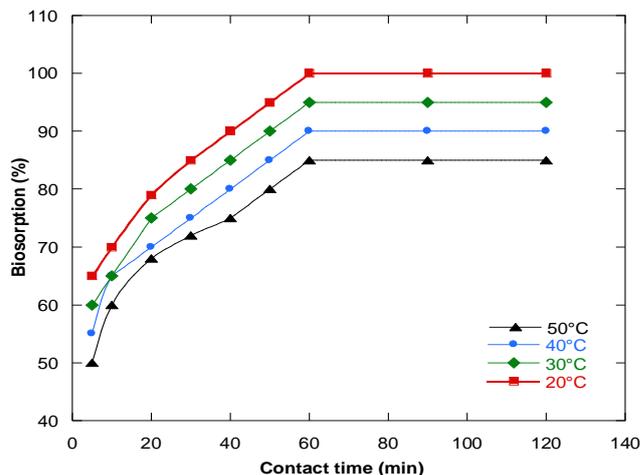


Fig. 3. Effect of contact time and temperature on biosorption of Zn (II) by *G.verrucosa* (metal concentration: 10 mg/L; biomass dosage: 4 g/L; pH: 5)

According to this figure, the biosorption yield of Zn (II) increases with rise in contact time up to 60 min at 20–50 °C. After this time there was no considerable increase. Therefore, the optimum contact time was selected as 60 min for further experiments. On the other hand, the biosorption percentage decreased from 98% to 81% as temperature was increased from 20 to 50 °C for the equilibrium time, 60 min. This result indicated the exothermic nature of Zn (II) biosorption onto *G.verrucosa* biomass. A decrease in the biosorption of Zn (II) ions with the rise in temperature may be due to either the damage of

active binding sites in the biomass or increasing tendency to desorb metal ions from the interface to the solution (Meena, A.K et al, 2005; Dekhil, A.B et al 2011). The optimum temperature was selected as 20 °C for further biosorption experiments

3.4. Biosorption isotherms

For optimization of the biosorption process design, it is necessary to obtain the appropriate correlation for the equilibrium curve. In this study, the equilibrium data were evaluated by three isotherms models, which are namely the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were analyzed. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent (Langmuir, I. 1918). This model can be written in linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \tag{2}$$

where q_e is the equilibrium metal ion concentration on the biosorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_{max} is the monolayer biosorption capacity of the biosorbent (mg/g), and b is the Langmuir biosorption constant (L/mg) relating the free energy of adsorption. The values of q_{max} and Langmuir constant b were calculated from the slope and intercept of the linear plot of C_e/q_e vs C_e (Fig. 4).

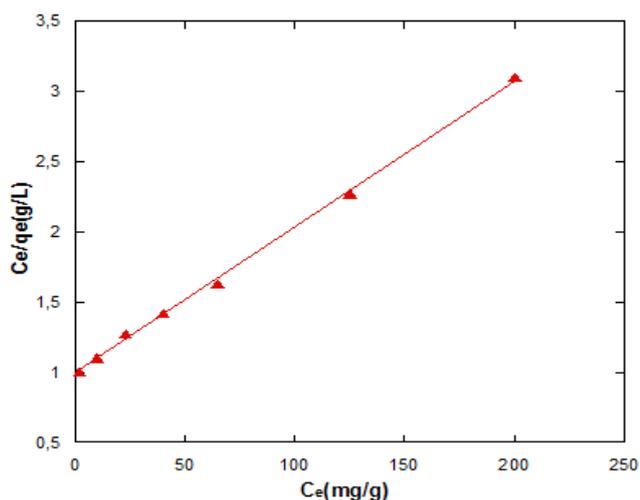


Fig.4. Langmuir isotherm plots for biosorption of Zn (II) onto *G.verrucosa* (biomass dosage: 4 g/L; contact time: 60 min; pH: 5; temperature: 20°C).

As seen from the figure, the value of correlation coefficient ($R^2 = 0.999$) shows that the biosorption of copper ions onto *G.verrucosa* biomass fitted well the Langmuir model indicates the formation of monolayer coverage of heavy metal ions on the outer surface of biosorbent. The maximum biosorption capacity (q_m) and Langmuir constant (b) were found to be 96.1 mg/g and 10.5×10^{-3} , respectively.

The Freundlich isotherm model is employed to describe the adsorption on heterogeneous surface and is not restricted to the formation of monolayer. The linear

form of the Freundlich adsorption isotherm can be defined by the following equation (Freundlich, H. 1939):

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{3}$$

Where k_f a constant is related to the biosorption capacity and $1/n$ is an empirical parameter related to the biosorption intensity of the adsorbent. The Freundlich isotherm constants k_f and $1/n$ were calculated from the slopes and intercepts of the linear plot of $\log q_e$ versus $\log C_e$.

The values of k_f and $1/n$ were found to be 1.2 and 0.82, respectively. The $1/n$ values were between 0 and 1, indicating that the biosorption of Zn (II) onto *G.verrucosa* biomass was favourable at studied conditions. However, compared to the R^2 values, 0.981 with that obtained from the Langmuir model, it can be remarkably noted that the Langmuir isotherm model is better fitted the equilibrium data.

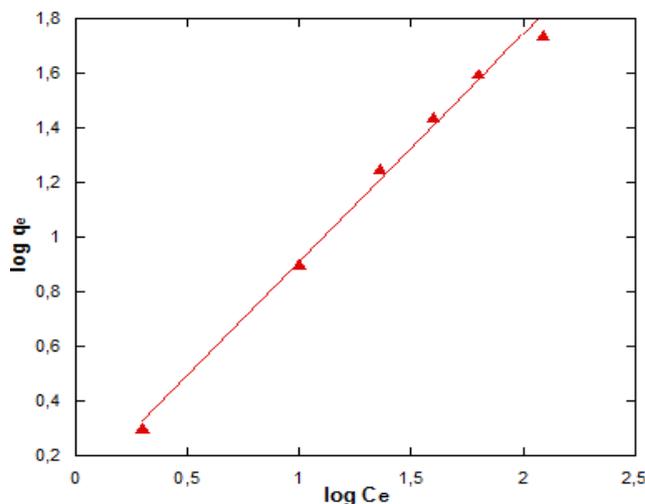


Fig.5. Freundlich isotherm plots for biosorption of Zn (II) onto *G.verrucosa* (biomass dosage: 4 g/L; contact time: 60 min; pH: 5; temperature: 20°C).

The Dubinin-Radushkevich isotherm is more general than Langmuir isotherm since it does not assume a homogeneous surface or constant biosorption potential. It was applied to distinguish between the physical and chemical biosorption of Zn (II) (Malik, U. Ret et al., 2005).

The linear presentation of the D–R isotherm equation (Dubinin, M.M et al., 1947) is expressed by (Eq. 4):

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{4}$$

where q_e is the amount of metal ions adsorbed on per unit weight of adsorbent (mol/L), q_m is the maximum adsorption capacity (mol/g), β is the activity coefficient related to adsorption mean free energy (mol²/J²) and ε is the Polanyi potential [$\varepsilon = RT \ln(1 + \frac{1}{C_e})$].

The D–R isotherm model well fitted the equilibrium data since the R^2 value was found to be 0.998 (Fig. 6). From the intercept of the plots, the q_m value was found to be 4.7×10^{-3} mol/g. The adsorption mean free energy (E , kJ/mol) is as follow:

Table.1 Pseudo-first-order and pseudo-second-order parameters for the biosorption of Zn (II) onto *G.verrucosa* biomass at different temperatures

Température (°C)	$q_{e,exp}$ (mg.g ⁻¹)	pseudo-first-order			pseudo-second-order		
		$k_1(\text{min}^{-1})$	$q_{e,cal}(\text{mg.g}^{-1})$	R^2	$k_2(\text{g.mg}^{-1}.\text{min}^{-1})$	$q_{e,cal}(\text{mg.g}^{-1})$	R^2
20	2.5	5.1×10^{-2}	1.61	0.967	5.9×10^{-2}	2.5	0.996
30	2.37	4.6×10^{-2}	1.55	0.974	5.4×10^{-2}	2.3	0.997
40	2.25	4.1×10^{-2}	1.46	0.972	5.16×10^{-2}	2.2	0.989
50	2.12	3.8×10^{-2}	1.22	0.975	4.7×10^{-2}	2.05	0.998

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

The E (kJ/mol) value gives information about adsorption mechanism, physical or chemical. If it lies between 8 and 16 kJ/mol, the adsorption process takes place chemically and while $E < 8$ kJ/mol, the adsorption process proceeds physically (Dubinin, M.M *et al.*, 1947). The mean adsorption energy was calculated as 9.62 kJ/mol for the adsorption of Cu (II) ions. These results indicated that the adsorption processes of Zn (II) onto *G.verrucosa* biomass may be carried out via chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate (Helfferich, F.1962).

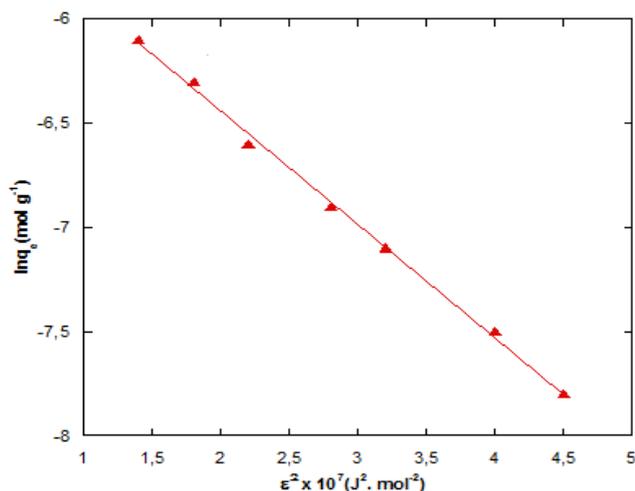


Fig.6. D–R isotherm plots for adsorption of Zn (II) onto *G.verrucosa* (biomass dosage 4 g/L; contact time 60 min; pH 5; temperature 20°C).

3.5. Biosorption kinetics study

Biosorption kinetics depends on the biosorbate–biosorbent interaction and operating condition and examined for their suitability for practical applications in water pollution control. In order to analyze the biosorption kinetics of Zn(II) onto *G.verrucosa*, the pseudo-first-order and pseudo-second-order kinetics model were tested using experimental data. Pseudo-first-order kinetics equation as

expressed by Lagergren (Lagergren, 1898) can be written as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

where q_t and q_e (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the equation (min^{-1}). The values of the rate constant, k_1 , equilibrium adsorption capacity, q_e , and the correlation coefficient, R^2 , were calculated from the plots of $\log(q_e - q_t)$ versus t (figure is not shown) (Table 1).

Kinetic data were further treated with pseudo second-order kinetic model which is given in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \tag{7}$$

where k_2 ($\text{gmg}^{-1} \text{min}^{-1}$) is the rate constant of adsorption, q_2 is maximum adsorption capacity (mg g^{-1}) (Ho and McKay., 2000). The values of k_1 , q_e and k_2 , q_2 were obtained from the slopes and intercepts of plots of $\log(q_e - q_t)$ versus t and t/q_t versus t at different temperatures.

The linear plots of t/q_t versus t for the pseudo-second order model for the biosorption of Zn(II) ions onto *G.verrucosa* biomass at 20–50°C were shown in Fig. 7.

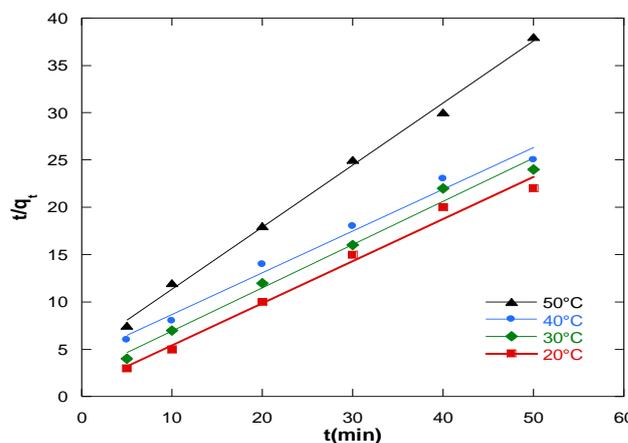


Fig.7. Pseudo-second-order kinetic plots at different temperatures (pH: 5; biosorbent dosage: 4 g/L; contact time: 60 min; temperature:20 °C)

The Pseudo-first-order and pseudo-second-order parameters for the biosorption of Zn(II) onto *G.verrucosa* biomass at different temperatures were given in Table 1.

The data show that the correlation coefficient values (R^2) for pseudo-first-order kinetics are very low in comparison to pseudo-second-order kinetics (Table 1). The values of theoretical biosorption capacity $q_{e(theo)}$ are very near to experimental values $q_{e(exp)}$ for second-order kinetics but for first-order kinetics equation these values are very different. Higher correlation coefficient (R^2) values and similar $q_{e(cal)}$ and $q_{e(exp)}$ values indicate the better applicability of pseudo-second-order kinetics model.

3.6. Thermodynamic parameters

Thermodynamic parameters such as Gibbs free energy change ΔG^0 , standard enthalpy change ΔH^0 and standard entropy change ΔS^0 were also found out to give more information about the nature of sorption process (Bursali, E.A et al., 2009). The thermodynamic parameters were calculated by the following equations

$$\ln k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{8}$$

(Van't Hoff equation)

$$\Delta G^0 = -RT \ln k_c \tag{9}$$

where $K_c = (q_e / C_e)$ is the adsorption equilibrium constant, T is absolute temperature (K), R is gas constant. When $\ln K_c$ versus $1/T$ is plotted (Fig.6), ΔH^0 and ΔS^0 values can be computed from slope and intercept of the van't Hoff equation. The calculated parameters were given in Table 2.

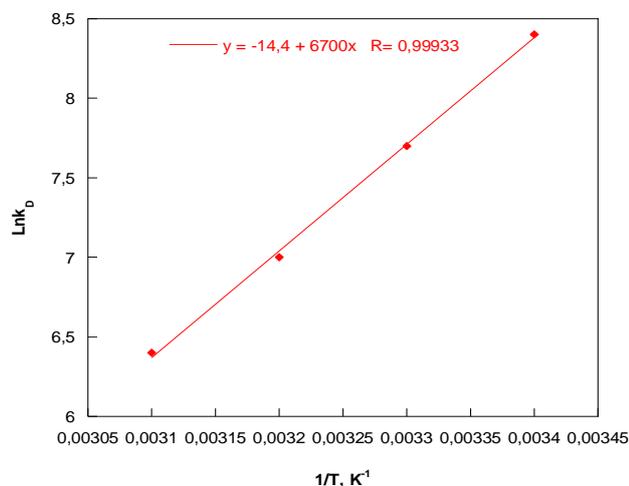


Fig.8. Determination of thermodynamic parameters for biosorption of Zn(II) onto *G.verrucosa* alga

The negative ΔG^0 values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in ΔG^0 value with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures.

Table.2 Thermodynamic parameters for Zn (II) biosorption onto *G.verrucosa* biomass.

T(k)	ΔG^0 (kJmol ⁻¹)	ΔH^0 (kJmol ⁻¹)	ΔS^0 (Jmol ⁻¹ K ⁻¹)
Zn (II)			
293	-20.6	-55.7	-119.72
303	-19.42		
313	-18.22		
323	-17.03		

The negative ΔH^0 is indicator of exothermic nature of the biosorption and also its magnitude gives information on the type of biosorption, which can be either physical or chemical. Therefore, the ΔH^0 values showed that the biosorption processes of Zn(II) ions onto *G.verrucosa* biomass was taken place via chemisorption (Smith.,1998). The negative ΔS^0 value (-70.17 J/mol K) suggests a decrease in the randomness at the solid/solution interface during the biosorption process (Asku and Alper Isoglu, 2005).

3.7. FTIR analysis of biomass

The FTIR spectrum is carried out as a qualitative analysis to determine the main functional groups that are involved in the adsorption process. The FTIR spectrum pattern of the red algae *G.verrucosa* before and after biosorption process is shown in Fig. 9.

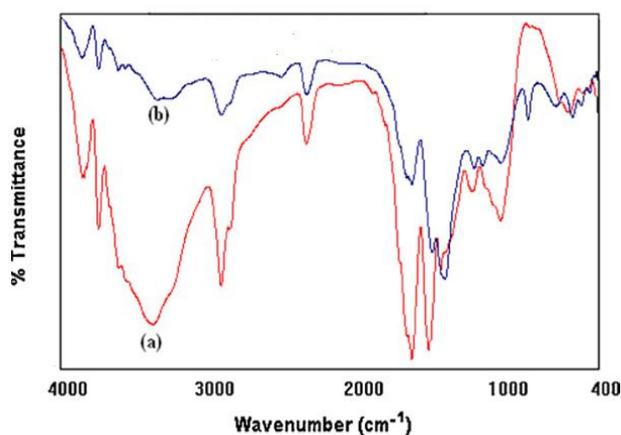


Fig. 9. FT-IR spectrum of *G.verrucosa* : (a) virgin , (b) Zn (II)-loaded biomass.

The broad and strong bands at $3372-3748\text{cm}^{-1}$ were due to bounded hydroxyl ($-\text{OH}$) groups of the algal biomass. The peak at 2349cm^{-1} represents the stretching vibrations of $-\text{NH}_2^+$, NH^+ and $-\text{NH}$ groups of the biomass. The bands peaks at 1544 , 1647 and 1682cm^{-1} may be attributed to asymmetric and symmetric stretching vibration of carboxyl ($-\text{C O}$) groups. The band observed at 1061cm^{-1} was assigned to $\text{C}-\text{O}$ stretching of alcohols and carboxylic acids. Some bands in the fingerprint region could be attributed to the phosphate groups. After zinc sorption, the stretching vibration bands of hydroxyl group were shifted

to the range of 3300–3742 cm^{-1} . The stretching vibration band of amide group was shifted to 2344 cm^{-1} . Asymmetric and symmetric stretching bands of carboxyl groups were shifted from 1544, 1647 and 1682 cm^{-1} to 1509, 1641, and 1685 cm^{-1} , respectively. The band assigned to C–O stretching was also shifted to 1050 cm^{-1} . The results indicated that the ion-exchange between the metal ions and the hydrogen atoms of carboxyl, hydroxyl, and amide groups of the biomass was mainly involved in the biosorption of Zn (II) onto algal biomass.

3.8. Desorption efficiency

Desorption of Zn (II) from *G.verrucosa* was also studied by using HCl and HNO₃ at various concentrations. For these studies, 10 mL of each eluent was used to desorb the Zn (II) ions. Analyte ions were desorbed from *G.verrucosa* with both 1M HCl and 1M HNO₃.

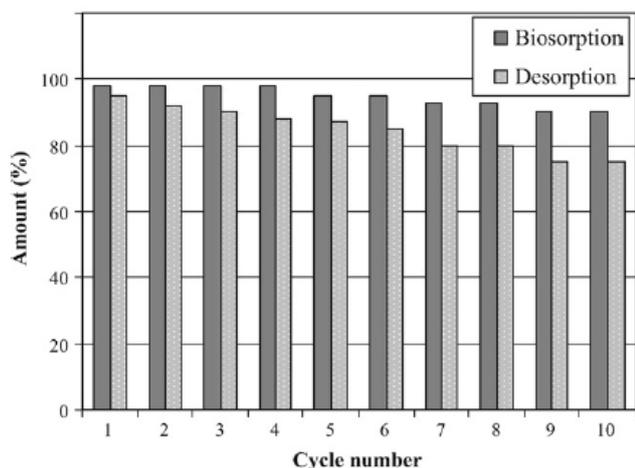


Fig.10. Biosorption–desorption efficiency with cycle number (biomass concentration: 4 g/L; contact time: 60 min; temperature: 20 °C).

The highest recovery was found to be 95% and 80% using 10 mL of 1M HCl and 10 mL of 1M HNO₃, respectively. In addition, as it can be seen from Fig.10, the high stability of *G.verrucosa* permitted 10 times of biosorption–desorption process along the studies with a decrease about 20% in recovery of Zn(II). These results indicate that the *G.verrucosa* biomass offers potential to be used repeatedly for removal of Zn (II) from aqueous solutions.

4. Conclusion

The potential of *G.verrucosa* alga for the removal of Zn(II) ions from aqueous solutions was dependent on biosorption process such as pH, biosorbent dose, contact time, and temperature.

The Langmuir biosorption isotherm was demonstrated to provide the best correlation for the biosorption of zinc (II) ions onto *G.verrucosa*. The maximum biosorption capacity was found to be 96.1 mg of zinc (II)/g of *G.verrucosa*. The calculated mean free energy (9.62 kJ/mol) from the D–R model indicated that the biosorption

of Zn(II) using *G.verrucosa* alga was taken place by chemical ion-exchange. The kinetic results provided the best correlation of the experimental data of biosorption of zinc (II) onto *G.verrucosa* by pseudo second-order equation. The data obtained from thermodynamic studies indicated the feasibility, exothermic and spontaneous nature of the biosorption process at 20–50 °C. The FTIR revealed that functional groups such as amine, hydroxyl and carboxyl groups were responsible for the sorption of the metal ions onto the biomass. The overall results indicated that since the *G.verrucosa* biomass is an easily, locally available, low-cost adsorbent and has a considerable high biosorption capacity, it may be treated as an alternative adsorbent for treatment of wastewater containing zinc (II) ions.

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