# Seaweeds for the remediation of wastewaters contaminated with zinc(II) ions

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## Abstract

Eleven different species of marine macroalgae were screened at different pH conditions on the basis of zinc(II) biosorption potential. Among the seaweeds, a green alga, *Ulva reticulata*, exhibited a highest uptake of 36.1 mg/g at pH 5.5 and 100 mg/l initial zinc(II) concentration. Further experiments were conducted to evaluate the zinc(II) biosorption potential of *U. reticulata*. Sorption isotherm data obtained at different pH (5–6) and temperature (25–35 °C) conditions were fitted well with Sips model followed by Freundlich, Redlich–Peterson and Langmuir models. A maximum zinc(II) biosorption capacity of 135.5 mg/g was observed at optimum conditions of 5.5 (pH) and 30 °C (temperature), according to the Langmuir model. It was observed from the kinetic data that the zinc(II) biosorption process using *U. reticulata* follows pseudo-second-order kinetics. Various thermodynamic parameters, such as $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ were calculated and they indicated that the present system was a spontaneous and an endothermic process. The influence of the co-ions ($Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$) along with zinc(II) present in the wastewater was also studied. Desorption of zinc(II) ions from the zinc(II)-loaded biomass were examined using 0.1 M $CaCl_2$ at different pH conditions in three sorption–desorption cycles. A fixed-bed column (2 cm i.d. and 35 cm height) was employed to evaluate the continuous biosorption performance of *U. reticulata*. The column experiments at different bed heights and flow rates revealed that the maximum zinc(II) uptake was obtained at the highest bed height (25 cm) and the lowest flow rate (5 ml/min). Column data were fitted well with Thomas, Yoon–Nelson and modified dose–response models. The column regeneration studies were carried out for three sorption–desorption cycles. A loss of sorption performance was observed during regeneration cycles indicated by a shortened breakthrough time and a decreased zinc(II) uptake.
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## 1. Introduction

Seaweeds are biological resources, present in many parts of world oceans. They are available largely in shallow coastal waters wherever there is a substratum on which they can grow and flourish. Seaweeds are the only source for the production of agar, alginate and carrageenan. Apart from these, in recent years, seaweeds are extensively used for metal biosorption [1,2]. The metal biosorption potentials of various brown, green and red seaweeds were evaluated by many investigators [3,4]. In general, brown seaweeds always performed well irrespective of metal ions employed. This is due to the presence of alginate, which is present in a gel form in their cell walls [1,5]. On the other hand, green algae usually comprised of xylans and mannans; whereas red algae contains sulfate esters of xylans and galactans in their cell walls [1,6].

Biosorption is often carried out in batch and column mode of operations. The sorption capacity obtained from a batch experiment is useful in providing the fundamental information regarding effectiveness of metal-biosorbent system [7]. However, this data may not be useful to most treatment systems because batch operations are not likely to be employed in industries. Hence, there is a need to perform column biosorption experiments. Packed and fluidized bed column can be used for this purpose. Packed column possess inherent advantages, such as efficient utilization of the sorbent, better quality of effluent, possible sorbent regeneration and easy scale-up procedure. Therefore, many investigators preferred packed column to perform column biosorption [8–11].

Zinc, one of the important heavy metals widely used in electroplating industries, is the model solute used in the present

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study. Zinc is an essential element for enzyme activators in humans, but it is toxic at levels of 100–500 mg/day and it is a known carcinogen [1]. Therefore, this study aimed to investigate the removal of zinc(II) from aqueous solution using seaweeds. Initially, 11 different seaweeds were screened for their zinc(II) biosorption potential. The best performed seaweed was investigated in detail in batch and continuous mode of operation.

## 2. Materials and methods

### 2.1. Materials

The raw biomass of brown algae (*Turbinaria conoides*, *Turbinaria ornata* and *Sargassum polycystium*), red algae (*Gracilaria corticata*, *Gracilaria crassa*, *Gracilaria edulis* and *Hypnea valentiae*) and green algae (*Ulva lactuca*, *Ulva reticulata*, *Codium tomentosum* and *Chaetomorpha antennina*) were collected from Mandapam (Tamil Nadu, India). The biomass was washed with copious quantities of distilled water to remove extraneous materials and dried at 60 °C overnight. The dried biomass was grounded to particle sizes in the range of 0.7–1 mm and subsequently used for biosorption experiments.

### 2.2. Batch experiments

Stock zinc(II) solutions for all experiments were prepared by dissolving its corresponding sulfate salt in distilled water. Batch sorption experiments were performed by contacting 0.2 g of biomass with 100 ml of zinc(II) solution in the concentration range of 250–1500 mg/l at desired pH and temperature in 250 ml Erlenmeyer flasks kept on a rotary shaker at 150 rpm. After 12 h, the algal biomass was separated from the zinc(II) solution by centrifugation at 3000 rpm for 10 min. The zinc(II) concentration in the supernatant was determined using Flame Atomic Absorption Spectrophotometer (AAS 6VARIO; Analytik Jena, Germany). The instrument was calibrated before each use with standard zinc(II) solutions. The samples were diluted, whenever necessary, with distilled water to improve accurate estimation. Batch desorption experiments were carried out by contacting the zinc(II)-loaded biomass with known volume of elutant at 150 rpm for 3 h. The elutants used were 0.1 M CaCl$_2$ at different pH conditions, adjusted using 0.1 M HCl. After elution, the biomass was washed extensively with distilled water, filtered and finally dried overnight at 60 °C [12]. Zinc(II) uptake ($Q$) was calculated using:

$$Q = \frac{V(C_0 - C_{eq})}{M} \qquad (1)$$

where $V$ is the solution volume (l), $M$ the amount of biomass (g), $C_0$ and $C_{eq}$ are the initial and equilibrium concentration of zinc(II) solution (mg/l), respectively.

### 2.3. Sorption models

The equilibrium data were analyzed using four of the most commonly used isotherms equations, such as Langmuir, Fre-

undlich, Redlich–Peterson and Sips isotherm expressions:

$$\text{Langmuir model}: Q = \frac{Q_{\max} b C_{eq}}{1 + b C_{eq}} \tag{2}$$

$$\text{Freundlich model}: Q = K_F C_{eq}^{1/n} \tag{3}$$

$$\text{Redlich–Peterson model}: Q = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta_{RP}}} \tag{4}$$

$$\text{Sips model}: Q = \frac{K_S C_{eq}^{\beta_S}}{1 + a_S C_{eq}^{\beta_S}} \tag{5}$$

where $Q_{\max}$ is the maximum metal uptake (mg/g), $b$ the Langmuir equilibrium constant (l/mg), $K_F$ the Freundlich constant (l/g), $n$ the Freundlich constant, $K_{RP}$ the Redlich–Peterson isotherm constant (l/g), $a_{RP}$ the Redlich–Peterson isotherm constant (l/mg), $\beta_{RP}$ the Redlich–Peterson model exponent, $K_S$ the Sips model isotherm constant (l/g), $a_S$ the Sips model constant (l/mg) and $\beta_S$ is the Sips model exponent. All the model parameters were evaluated by non-linear regression using MATLAB® software.

## 2.4. Column experiments

Continuous flow sorption experiments were conducted in a glass column of 2 cm i.d. and 35 cm height [11]. A known quantity of biomass was placed in the column to yield a desired bed height. Zinc(II) solution having an initial concentration of 100 mg/l was pumped upward through the column at a desired flow rate by a peristaltic pump (pp40, Miclins). Samples were collected from the exit of the column at different intervals and analyzed for zinc(II) concentration. Operation of the column was stopped when the effluent zinc(II) concentration exceeded a value of 99.5 mg/l or higher. All the experiments were carried out in duplicates, and the deviations were within 5%.

The total quantity of metal mass biosorbed in the column ($m_{ad}$) is calculated from the area above the breakthrough curve (outlet metal concentration versus time) multiplied by the flow rate. Dividing the metal mass ($m_{ad}$) by the biosorbent mass ($M$) leads to the uptake capacity ($Q$) of the biomass. The total amount of metal ions sent to the column can be calculated from the following equation:

$$m_{total} = \frac{C_0 F t_e}{1000} \tag{6}$$

where $C_0$ is the inlet metal ion concentration (mg/l), $F$ the volumetric flow rate (ml/min) and $t_e$ is the exhaustion time (h). The mass transfer zone ($\Delta t$) can be calculated from the difference between column exhaustion time ($t_e$) and column breakthrough time ($t_b$). The slope of the breakthrough curve from $t_b$ to $t_e$ was represented by $dc/dt$. Total metal removal (%) with respect to flow volume can be calculated from the ratio of metal mass adsorbed ($m_{ad}$) to the total amount of metal ions sent to the column as follows:

$$\text{total metal removal } (\%) = \frac{m_{ad}}{m_{total}} \times 100 \tag{7}$$

After the column reached exhaustion, the loaded biomass with metal ions was regenerated using the elutant, 0.1 M CaCl$_2$ (in HCl, pH 3.5). The flow rate was adjusted to 5 ml/min. After elution, distilled water was used to wash the bed until the pH in the wash effluent stabilized near 7.0. Then, the column was fed again with metal solution and biosorption studies were carried out. After bed exhaustion, elutant was fed into the column and regeneration studies were conducted. These cycles of sorption followed by desorption were repeated for three times to evaluate the biomass sorption capacity. The metal mass desorbed ($m_d$) can be calculated from the area below the elution curve multiplied by flow rate. The elution efficiency can be calculated from:

$$E(\%) = \frac{m_d}{m_{ad}} \times 100 \tag{8}$$

## 3. Results and discussion

### 3.1. Screening

Initially, batch screening experiments were conducted to identify potent seaweed for zinc(II) biosorption. Fig. 1 shows the performance of 11 seaweeds on the basis of zinc(II) uptake at different pH conditions. Zinc(II) biosorption performances of all seaweeds were markedly affected by pH variations. There were significant differences between maximum zinc(II) uptake values for all seaweeds examined; this was not only observed between different algae divisions, but also between different species of same genus. Also optimum pH for zinc(II) biosorption varied with seaweeds examined. Less zinc(II) uptake at low pH values may be due to hydrogen ion competition and sorbate lyophobic behavior [2]. Since the solubility of many metal complexes in solution decreases with increasing pH, the sorption increases with increasing pH. Based on the zinc(II) uptake values, both species of *Ulva* performed better compared to all other seaweeds, with *U. reticulata* and *U. lactuca* exhibited 36.1 and 34.7 mg/g, respectively, at pH 5.5. Also, it is worth noting that the red seaweed *H. valentiae* exhibited 27.5 mg/g at pH 5.5. However, other red seaweeds, i.e. three species of *Gracilaria* exhibited relatively lower zinc(II) uptake. It is interesting to observe that brown seaweeds not performed very well compared to some of the green and red seaweeds. The highest uptake among the brown algae used was 22.2 mg/g by *T. conoides* at pH 5.5. Hence, the result summarizes that *U. reticulata* performed better for zinc(II) removal from aqueous solution and it was further examined in detail.

### 3.2. Biosorption isotherm

Zinc(II) biosorption isotherms for *U. reticulata* at different conditions of pH (5–6) and temperature (25–35 °C) are presented in Fig. 2. Initial solution pH played a significant role in zinc(II) biosorption, with highest zinc(II) uptake observed at pH 5.5. Temperature affected the zinc(II) biosorption capacity of *U. reticulata*. Among the temperature conditions examined, room temperature (30 °C) favored biosorption. Changing the temperature by ±5 °C from the room temperature resulted in decreased
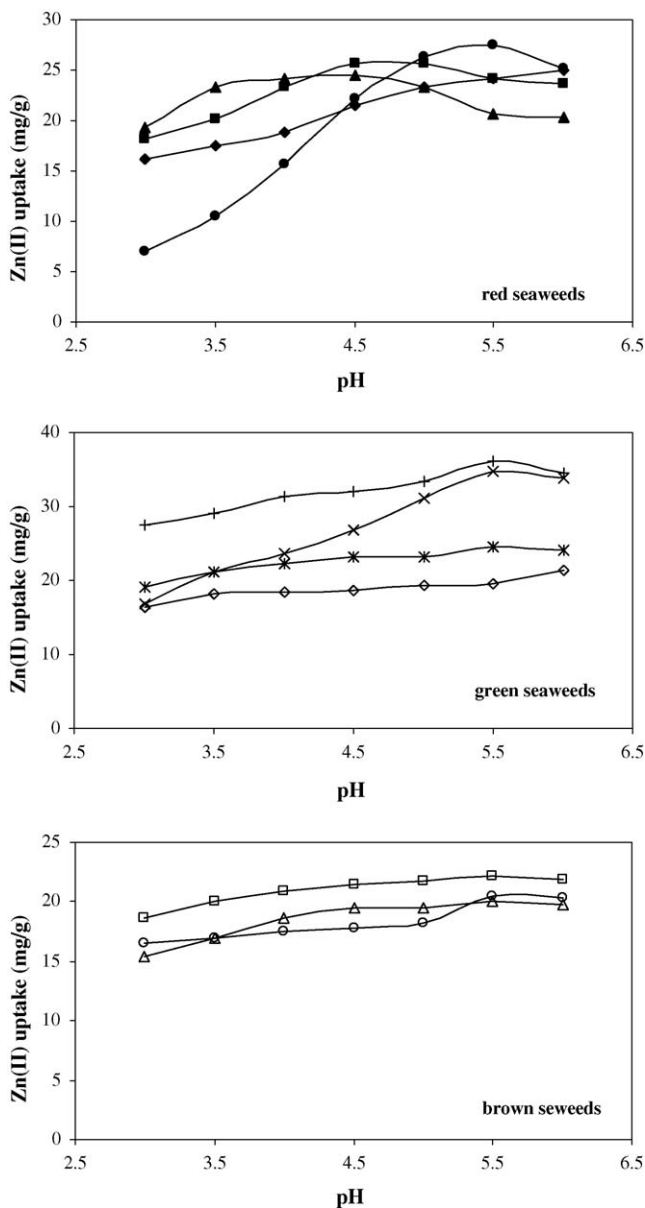
Fig. 1. Effect of initial pH on zinc(II) uptake by green, red and brown seaweeds (initial zinc(II) concentration = 100 mg/l). Seaweeds: (◆) *Gracilaria corticata*; (■) *Gracilaria crassa*; (▲) *Gracilaria edulis*; (●) *Hypnea valentiae*; (×) *Ulva lactuca*; (+) *Ulva reticulata*; (*) *Codium tomentosum*; (◇) *Chaetomorpha antennina*; (□) *Turbinaria conoides*; (△) *Turbinaria ornata*; (○) *Sargassum polycystium*.

zinc(II) biosorption capacity. Thus, from the experimental data, highest zinc(II) uptake capacity of *U. reticulata* was approximately 125.5 mg/g at the optimum conditions of pH 5.5 and 30 °C.

The experimental biosorption isotherms obtained at different conditions were analyzed using Langmuir, Freundlich, Redlich–Peterson and Sips isotherm models. The best-fit model was determined on the basis of non-linear regression correlation coefficient, $R^2$. In general, the equilibrium data were reasonably well represented by all the four isotherm models and the model parameters are presented in Table 1. The Langmuir model served to estimate the maximum metal uptake
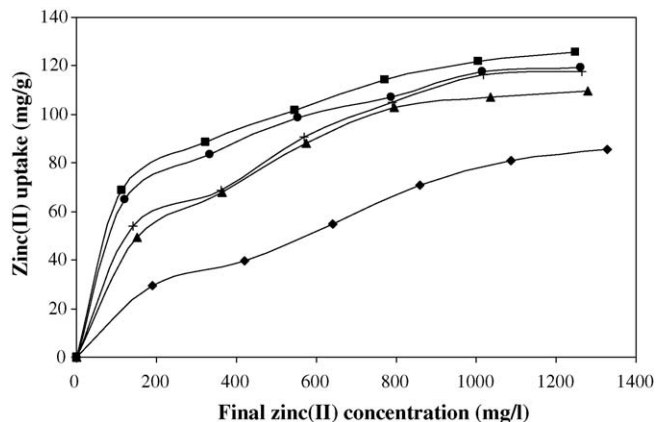


Fig. 2. Zinc(II) biosorption isotherms for *U. reticulata* at different conditions (biomass dosage = 2 g/l, agitation rate = 150 rpm). pH and temperature: (◆) 5 and 30 °C; (■) 5.5 and 30 °C; (▲) 6 and 30 °C; (●) 5.5 and 25 °C; (+) 5.5 and 35 °C.

values where they could not be reached in the experiments. The constant *b* represents affinity between the sorbent and sorbate. Both $Q_{max}$ and *b* were observed maximum at 5.5 (pH) and 30 °C (temperature). High values of *b* are reflected in the steep initial slope of a sorption isotherm, indicating desirable high affinity. Thus, for good biosorbents in general, high $Q_{max}$ and a steep initial isotherm slope (i.e. high *b*) are desirable [6]. The Freundlich model constant ($K_F$), which denotes the binding capacity, was observed maximum at 5.5 and 30 °C. The Redlich–Peterson model, which incorporated the features of the Langmuir and Freundlich isotherms, reasonably described the zinc(II) isotherm data. The isotherm constant $K_{RP}$ and exponent $\beta_{RP}$ was observed maximum at 5.5 and 30 °C. In contrary, a reverse trend was observed with $a_{RP}$, which was lowest at this condition. On the basis of correlation coefficient, the Sips model better described the zinc(II) sorption isotherm data compared to other models examined (Table 1). Similar to Redlich–Peterson model constants, the same trend was observed for Sips model constants.

## 3.3. Biosorption kinetics

The prediction of batch biosorption kinetics is necessary for the design of industrial sorption columns. Fig. 3 shows the plot of zinc(II) uptake versus contact time at different initial zinc(II) concentrations at pH 5.5 and temperature 30 °C. It was observed that the zinc(II) uptake increased with increasing contact time at all initial zinc(II) ion concentrations. Further the uptake increased with increase in initial zinc(II) ion concentration. It was also observed that zinc(II) uptake was rapid for the initial 2 h and thereafter it proceeds at a slower rate and finally attains saturation. The higher sorption rate at the initial period (2 h) may be due to an increased number of vacant sites available at the initial stage, which results in an increased concentration gradient between sorbate in the solution and sorbate in the biosorbent surface. As time increases, this concentration gradient was reduced due to the sorption of zinc(II) ions onto vacant sites, leading to a decrease in sorption rate at later stages.

Table 1
Langmuir, Freundlich, Redlich–Peterson and Sips model parameters at different pH conditions

| pH | Temperature (°C) | Langmuir model | | | Freundlich model | | | Redlich–Peterson model | | | | Sips model | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $Q_{max}$ (mg/g) | $b$ (l/mg) | $R^2$ | $K_F$ (l/g) | $n$ | $R^2$ | $K_{RP}$ (l/g) | $a_{RP}$ (l/mg) | $\beta_{RP}$ | $R^2$ | $K_S$ (l/g) | $a_S$ (l/mg) | $\beta_S$ | $R^2$ |
| 5 | 30 | 124.9 | 0.001 | 0.961 | 19.58 | 4.93 | 0.962 | 0.696 | 0.212 | 0.53 | 0.976 | 2.39 | 0.012 | 0.50 | 0.979 |
| 5.5 | 30 | 135.5 | 0.009 | 0.922 | 22.94 | 4.19 | 0.975 | 1.449 | 0.022 | 0.90 | 0.972 | 4.98 | 0.011 | 0.68 | 0.995 |
| 6 | 30 | 131.2 | 0.004 | 0.919 | 22.88 | 4.56 | 0.963 | 1.222 | 0.077 | 0.71 | 0.973 | 4.36 | 0.012 | 0.51 | 0.974 |
| 5.5 | 25 | 125.0 | 0.008 | 0.933 | 18.04 | 3.75 | 0.986 | 1.446 | 0.028 | 0.87 | 0.986 | 4.93 | 0.034 | 0.66 | 0.992 |
| 5.5 | 35 | 134.6 | 0.005 | 0.912 | 17.86 | 3.91 | 0.973 | 1.153 | 0.040 | 0.79 | 0.967 | 4.18 | 0.019 | 0.57 | 0.973 |
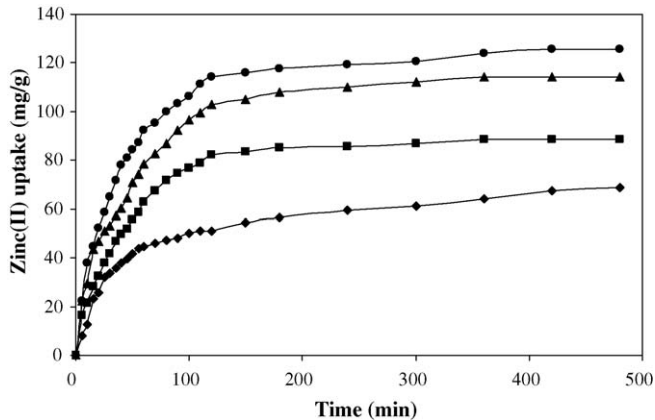


Fig. 3. Effect of initial concentration on the sorption of zinc(II) onto *U. reticulata* (biomass dosage = 2 g/l; pH 5.5; temperature = 30 °C; agitation rate = 150 rpm). Initial zinc(II) concentration: (♦) 250 mg/l; (■) 500 mg/l; (▲) 1000 mg/l; (●) 1500 mg/l.

The experimental biosorption kinetic data were modeled using pseudo-first- and pseudo-second-order kinetics. The linearized form of pseudo-first- and pseudo-second-order models [13] are shown below as Eqs. (9) and (10), respectively:

$$\log(Q_e - Q_t) = \log(Q_e) - \frac{K_1}{2.303}t \tag{9}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e}t \tag{10}$$

where $Q_e$ is the amount of zinc(II) sorbed at equilibrium (mg/g), $Q_t$ is the amount of zinc(II) sorbed at time $t$ (mg/g) and $K_1$ is the first-order equilibrium rate constant (min$^{-1}$) and $K_2$ is the second-order equilibrium rate constant (g/mg min).

Initially, the validity of the two models was checked by studying the kinetics under different initial metal concentrations. The rate constants, predicted equilibrium uptakes and the corresponding correlation coefficients for all concentrations tested have been calculated and summarized in Table 2. In the case of pseudo-first-order model, correlation coefficients were found to

be above 0.923, but the calculated $Q_e$ is not equal to experimental $Q_e$, suggesting the insufficiency of pseudo-first-order model to fit the kinetic data for the initial concentrations examined. The reason for these differences in the $Q_e$ values is that there is a time lag, possibly due to a boundary layer or external resistance controlling at the beginning of the sorption process [14,15].

The pseudo-second-order model is based on the sorption capacity on the solid phase. Contrary to other well-established models, it predicts the behavior over a whole range of studies and it is in agreement with a chemisorption mechanism being the rate controlling step [14]. This was consistent with the better results obtained with the pseudo-second-order model (Table 2). Correlation coefficients were always greater than 0.997, and the lowest correlation coefficient in this case was better than the first-order model correlation coefficients. The values of predicted equilibrium sorption capacities showed reasonably good agreement with the experimental equilibrium uptake values.

### 3.4. Sorption thermodynamics

Sorption isotherm data obtained for different temperatures were used to calculate the important thermodynamic properties, such as standard Gibbs free energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$) and standard entropy change ($\Delta S°$). The Langmuir constant $b$ (l/mg) was used to calculate the standard Gibbs free energy change ($\Delta G°$) according to the following equation,

$$\Delta G° = -RT \ln b \tag{11}$$

where $R$ is the gas constant (8.314 J/mol K) and $T$ is the absolute temperature (K). Standard enthalpy and entropy change were obtained from the plot of $\Delta G°$ versus $T$ and the equation is as follows,

$$\Delta G° = \Delta H° - T\Delta S° \tag{12}$$

The values of $\Delta G°$ were obtained as −14.7, −15.1 and −15.4 kJ/mol at 25, 30 and 35 °C, respectively. The negative

Table 2
Pseudo-first- and second-order model kinetic parameters at different initial zinc(II) concentrations

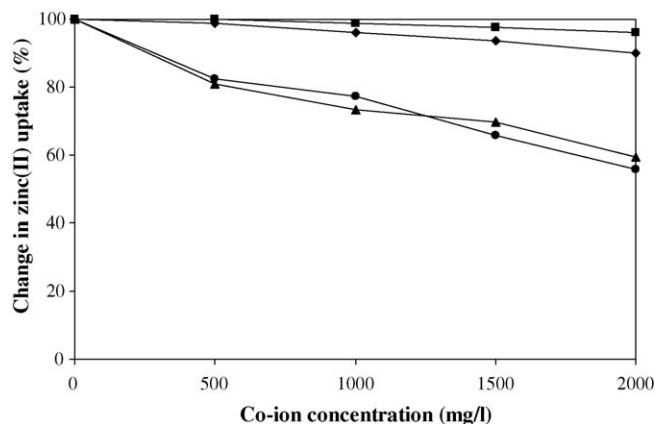| Initial concentration (mg/l) | Experimental $Q_e$ (mg/g) | $K_1$ (min$^{-1}$) | Predicted $Q_e$ (mg/g) | $R^2$ | $K_2$ (g/mg min) | Predicted $Q_e$ (mg/g) | $R^2$ |
|---|---|---|---|---|---|---|---|
| 250 | 68.9 | 0.004 | 46.1 | 0.923 | 0.0003 | 72.5 | 0.997 |
| 500 | 88.4 | 0.014 | 62.6 | 0.941 | 0.0003 | 96.1 | 0.998 |
| 1000 | 114.4 | 0.013 | 83.3 | 0.974 | 0.0002 | 123.4 | 0.998 |
| 1500 | 125.5 | 0.011 | 72.8 | 0.934 | 0.0002 | 133.3 | 0.999 |

Fig. 4. Effect of co-ions on the sorption of zinc(II) onto *U. reticulata* (biomass dosage = 2 g/l; initial zinc(II) concentration = 1500 mg/l; pH 5.5; temperature = 30 °C; agitation rate = 150 rpm). Co-ions: ($\blacklozenge$) Na$^+$; ($\blacksquare$) K$^+$; ($\blacktriangle$) Ca$^{2+}$; ($\bullet$) Mg$^{2+}$.



Fig. 5. Effect of solid-to-liquid ratio on zinc(II) elution efficiency of 0.1 M CaCl$_2$ at different pH conditions. Elutants: ($\blacklozenge$) 0.1 M CaCl$_2$ at pH 3; ($\blacksquare$) 0.1 M CaCl$_2$ at pH 3.5; ($\blacktriangle$) 0.1 M CaCl$_2$ at pH 4.

value of free energy change indicates the feasibility of zinc(II) biosorption process and confirms affinity of biosorbent for the zinc(II) ions. The values of $\Delta H°$ and $\Delta S°$ obtained from the plot of $\Delta G°$ versus $T$ were 4.45 and 0.064 kJ/mol K, respectively. The positive value of enthalpy shows that the zinc(II) biosorption process is endothermic and the positive entropy value indicates the increasing randomness at the solid/liquid interface during the biosorption process [16,17].

### 3.5. Influence of co-ions

Industrial wastewaters usually contain respectable amounts of different cations, which may influence the biosorption of metal ion of interest [18]. Light metal ions, such as Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ are almost common in all industrial effluents. Thus, the influence of these light metal ions on zinc(II) uptake capacity of *U. reticulata* was studied (Fig. 4). The change in zinc(II) uptake was calculated by the ratio of zinc(II) uptake with the presence of co-ions to the zinc(II) uptake without the presence of co-ions. From Fig. 4, it was observed that as the concentration of co-ions increases, the change in zinc(II) uptake (%) decreases. This may be due to the sorption of co-ions onto algal biomass instead of zinc(II) ions. Among the four co-ions investigated, Ca$^{2+}$ and Mg$^{2+}$ ions considerably reduced the zinc(II) uptake capacity of *U. reticulata*. The other two ions, K$^+$ and Na$^+$, were inefficient in competing with zinc(II) ions to occupy the binding sites.

### 3.6. Desorption studies

Reusability of sorbent is of crucial importance in industrial practice for metal removal from wastewater. For this purpose, it is desirable to desorb the sorbed metal ions and to regenerate the biosorbent for another cycle [19]. The elutant must be effective, non-damaging to the biomass, non-polluting and cheap [20]. *U. reticulata* is a soft green alga and exposure to severe acidic and alkaline conditions may deteriorate the biomass. Vijayaraghavan et al. [12] reported that mineral acids performed very well in elut-
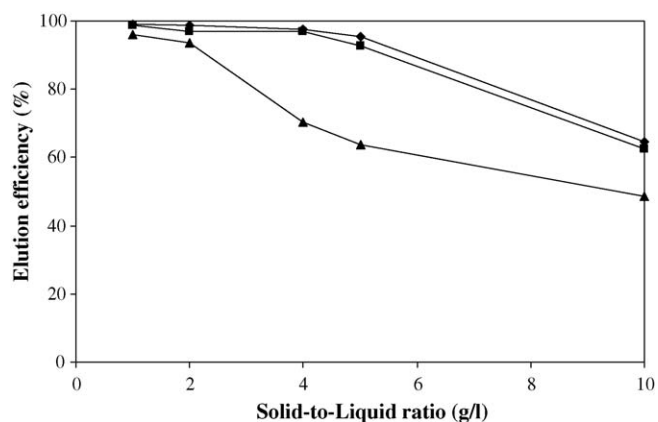
ing copper(II) ions from copper-loaded *U. reticulata*; however, the biomass became more fragile and the weight losses were over 35%. Also, they identified 0.1 M CaCl$_2$ (in HCl, pH 3) as the suitable elutant for desorbing copper from *U. reticulata*. Therefore, in this study, 0.1 M CaCl$_2$ at different pH conditions and solid-to-liquid (S/L) ratios was used to desorb zinc(II) ions from zinc(II)-loaded *U. reticulata*. Elution efficiency was determined by the ratio of the metal mass in the solution after desorption to the metal mass initially bound to the biomass. An important parameter for metal biosorption is the solid-to-liquid ratio defined as the mass of metal-laden biosorbent to the volume of the elutant [20]. Fig. 5 illustrates the effect of pH on the zinc(II) elution efficiency of 0.1 M CaCl$_2$ at different S/L ratios. The elution efficiency of 0.1 M CaCl$_2$ was strictly pH dependent and maximum elution efficiencies were observed in the pH range of 3–3.5. However, the biomass weight loss was observed as 5.5 and 4% at pH 3 and 3.5, respectively. Also, it is worth mentioning that S/L ratio severely affects the elution efficiency of CaCl$_2$. For instance, at pH 3.5, the elution efficiency of 98.7% at 1 g/l S/L ratio was dropped to 62.5% at S/L 10 g/l. However, it is desirable to use the smallest possible eluting volume so as to contain the highest concentration of the metal. At the same time, the volume of the solution should be enough to provide maximum solubility for the metal desorbed. Considering the high elution efficiency and less biomass damage, the solution of 0.1 M CaCl$_2$ (in HCl, pH 3.5) at 4 g/l S/L ratio was identified as the practical elutant for zinc(II) desorption.

Experiments were also conducted to regenerate *U. reticulata* in three sorption–desorption cycles. *U. reticulata* biomass exhibited zinc(II) uptake capacities of 125.5, 121.1 and 112.8 mg/g in first, second and third cycles, respectively. The elutant, 0.1 M CaCl$_2$ (in HCl, pH 3.5), maintained a consistent elution efficiency of around 97% in all the cycles examined. At the end of the third cycle, a biosorbent weight loss of 11.5% was observed. This may be due to the soft nature of the biomass and acidic nature of the elutant. Thus, the batch experiments provided the fundamental information regarding the biosorption potential of *U. reticulata* and its possible application in continuous biosorption.
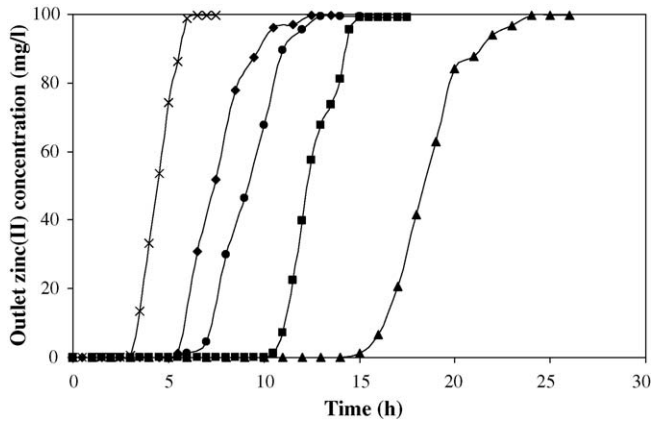
Fig. 6. Breakthrough curves for biosorption of zinc(II) by *U. reticulata* at different bed heights and flow rates (inlet zinc(II) concentration = 100 mg/l; influent pH 5.5). Bed height and flow rate: (♦) 15 cm and 5 ml/min; (■) 20 cm and 5 ml/min; (▲) 25 cm and 5 ml/min; (●) 25 cm and 10 ml/min; (×) 25 cm and 15 ml/min.

## 3.7. Column studies

### 3.7.1. Effect of bed height and flow rate

In column experiments, breakthrough curves were obtained at different bed heights (15–25 cm) and flow rates (5–15 ml/min). In order to yield different bed heights, 3.4, 4.2 and 6.0 g of biomass were added to produce 15, 20 and 25 cm, respectively. Fig. 6 shows the breakthrough curves obtained during zinc(II) biosorption by *U. reticulata* at different conditions. Both breakthrough and exhaustion time increased with increasing bed height, as more binding sites available for sorption, also resulted in a broadened mass transfer zone (Table 3). In contrary increase in flow rate decreased both breakthrough and exhaustion time, this may be due to insufficient residence time of the solute in the column and the diffusion limitations of the solute into the pores of the sorbent at higher flow rates [21]. At 25 cm and 5 ml/min, zinc(II) uptake capacity and removal efficiency were found maximum as 77.7 mg/g and 64.7%, respectively.

### 3.7.2. Modeling of column data

Various mathematical models can be used to describe fixed bed sorption. Among these the Thomas model is the most widely employed in the literature [9,10,22]. Recently, the Yoon–Nelson model has been used to predict breakthrough curves [10]. Also, Yan et al. [23] proposed a modified dose–response model, which successfully describes the column kinetics of metal biosorption onto immobilized *Mucor rouxii*. Therefore, in this study three models (Thomas, Yoon–Nelson and modified dose–response
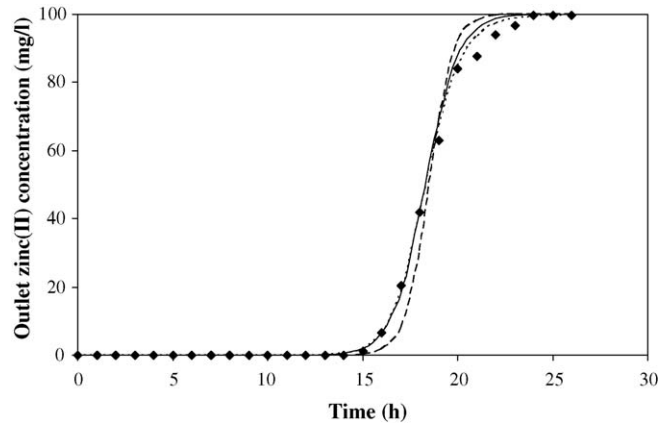


Fig. 7. Application of Thomas (——), Yoon–Nelson (− − − −) and modified dose–response (------) models to experimental column data (♦) at bed height = 25 cm, flow rate = 5 ml/min and initial zinc(II) concentration = 100 mg/l.

models) were used to describe column zinc(II) biosorption by *U. reticulata*.

Thomas model :
$$\frac{C_0}{C} = 1 + \exp\left(\frac{k_{\mathrm{TH}}}{F}(Q_0 M - C_0 V_{\mathrm{eff}})\right) \tag{13}$$

Yoon–Nelson model :
$$\frac{C}{C_0} = \frac{\exp(k_{\mathrm{YN}}t - \tau k_{\mathrm{YN}})}{1 + \exp(k_{\mathrm{YN}}t - \tau k_{\mathrm{YN}})} \tag{14}$$

modified dose–response model :
$$\frac{C}{C_0} = 1 - \frac{1}{1 + (V_{\mathrm{eff}}/b_{\mathrm{mdr}})^{a_{\mathrm{mdr}}}} \tag{15}$$

where $k_{\mathrm{TH}}$ is the Thomas model rate constant (ml/min mg), $Q_0$ the maximum solid-phase concentration of the solute (mg/g), $V_{\mathrm{eff}}$ the volume of metal solution passed into the column, $k_{\mathrm{YN}}$ the Yoon–Nelson model rate constant (min$^{-1}$), $\tau$ the time required for 50% adsorbate breakthrough (min), and $a_{\mathrm{mdr}}$ and $b_{\mathrm{mdr}}$ are the modified dose–response model constants.

All the three models described the column data well at all conditions examined. The model parameters at different bed heights and flow rates are summarized in Table 4. Fig. 7 shows the column data fitted using Thomas, Yoon–Nelson and modified dose–response models. Even though very high correlation coefficients were observed in the case of Thomas model, the model over predicted the zinc(II) uptake values at all conditions examined. For instance, at 25 cm and 5 ml/min the Thomas model predicted 91.4 mg/g zinc(II) uptake compared to experimental determination of 77.7 mg/g. Similarly, Yan et al. [23]

Table 3
Column data and parameters obtained at different flow rates and bed heights

| Bed height (cm) | Flow rate (ml/min) | Uptake (mg/g) | $t_{\mathrm{b}}$ (h) | $t_{\mathrm{e}}$ (h) | $\Delta t$ (h) | d$c$/d$t$ (mg/l h) | Zinc(II) removal (%) |
|---|---|---|---|---|---|---|---|
| 15 | 5 | 60.5 | 5.5 | 13.5 | 8.0 | 13.8 | 50.8 |
| 20 | 5 | 69.4 | 10.5 | 15.5 | 5.0 | 23.1 | 62.7 |
| 25 | 5 | 77.7 | 15.0 | 24.0 | 9.0 | 13.7 | 64.7 |
| 25 | 10 | 61.9 | 6.0 | 13.0 | 7.0 | 16.0 | 47.6 |
| 25 | 15 | 44.4 | 3.0 | 6.5 | 3.5 | 30.9 | 45.6 |

Table 4
Thomas, Yoon–Nelson and modified dose–response model parameters at different bed heights and flow rates

| Bed height (cm) | Flow rate (ml/min) | Thomas model | | | Yoon and Nelson model | | | Modified dose–response model | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $k_{TH}$ | $q_0$ | $R^2$ | $k_{YN}$ | $\tau$ | $R^2$ | $a_{mdr}$ | $b_{mdr}$ | $R^2$ |
| 15 | 5 | 0.012 | 65.0 | 0.996 | 1.42 | 7.4 | 0.994 | 18.79 | 2.39 | 0.952 |
| 20 | 5 | 0.014 | 89.6 | 0.995 | 1.46 | 12.6 | 0.994 | 19.05 | 3.74 | 0.995 |
| 25 | 5 | 0.011 | 91.4 | 0.998 | 1.63 | 18.5 | 0.998 | 19.67 | 5.56 | 0.999 |
| 25 | 10 | 0.012 | 90.2 | 0.996 | 1.42 | 9.1 | 0.991 | 18.96 | 5.49 | 0.974 |
| 25 | 15 | 0.019 | 66.5 | 0.998 | 1.43 | 4.4 | 0.993 | 17.85 | 4.08 | 0.973 |

Table 5
Sorption and elution process parameters for three sorption–desorption cycles

| Cycle no. | Uptake (mg/g) | $t_b$ (h) | $t_e$ (h) | $\Delta t$ (h) | d$c$/d$t$ (mg/l h) | Zinc(II) removal (%) | Elution efficiency (%) |
|---|---|---|---|---|---|---|---|
| 1 | 77.7 | 15.0 | 24.0 | 9.0 | 12.4 | 64.72 | 99.9 |
| 2 | 75.7 | 14.1 | 23.2 | 9.1 | 11.9 | 60.57 | 99.9 |
| 3 | 49.7 | 9.8 | 21.1 | 11.3 | 10.1 | 55.19 | 99.3 |

reported that Thomas model overestimated $Q_0$ values of cadmium, lead and zinc biosorption by immobilized *M. rouxii*. The time required for 50% sorbate breakthrough ($\tau$) obtained from the Yoon and Nelson model agreed well with the experimental data at all conditions examined. The Yoon–Nelson rate constant ($k_{YN}$) was observed maximum at 25 cm and 5 ml/min. Similarly, the modified dose–response model constants ($a_{mdr}$ and $b_{mdr}$) were observed maximum at 25 cm and 5 ml/min. From the results, it was observed that all the three models were able to describe the column data well with high correlation coefficients.

### 3.7.3. Regeneration

The column regeneration studies were carried out for three sorption–desorption cycles at 5 ml/min. The column was packed with 6.0 g of *U. reticulata* biomass yielding an initial bed height of 25 cm. The breakthrough time, exhaustion time and zinc(II) uptake for all the three cycles are summarized in Table 5. At the end of third cycle, 5.23 g of dry biomass was left in the column indicating a weight loss of 12.8%. A decreased break-

through and exhaustion time was observed as the regeneration cycles progressed, which also resulted in a broadened mass transfer zone. This behavior is primarily due to gradual deterioration of biomass because of continuous usage [24]. The breakthrough curves along with the elution curves for all the three cycles are presented in Fig. 8. It was interesting to note that the loss of sorption performance was not reflected in the first two cycles. However, a considerable decrease in zinc(II) uptake was observed in the third cycle. This observation clearly pointed out that biomass damage and inaccessibility of binding sites in later cycles may be responsible for this result. The uptake also strongly depended on the previous elution step, since prolonged elution may destroy the binding sites or inadequate elution may allow metal ions to remain in the sites.

## 4. Conclusions

Biosorption performances of 11 macro algae were investigated for the removal of zinc(II) from aqueous solution. Results showed that,

- *U. reticulata* has exhibited a maximum zinc(II) uptake compared to other seaweeds examined, at the optimum conditions of pH 5.5 and temperature 30 °C.
- Biosorption isotherms were modeled with the Langmuir, Freundlich, Redlich–Peterson and Sips isotherms. The maximum uptake capacity of *U. reticulata* for zinc(II) biosorption was 135.5 mg/g, according to the Langmuir model.
- Kinetic studies showed that about 90% of the total zinc(II) ion biosorption occurred within 2 h. Pseudo-second-order kinetic equation represented the experimental data well.
- The presence of $Ca^{2+}$ and $Mg^{2+}$ ions was found to have more influence in zinc(II) biosorption, compared to $K^+$ and $Na^+$ ions.
- A solution of 0.1 M $CaCl_2$ (in HCl, pH 3.5) was found to be the best elutant for desorbing the zinc(II) ions from zinc(II)-loaded biomass.
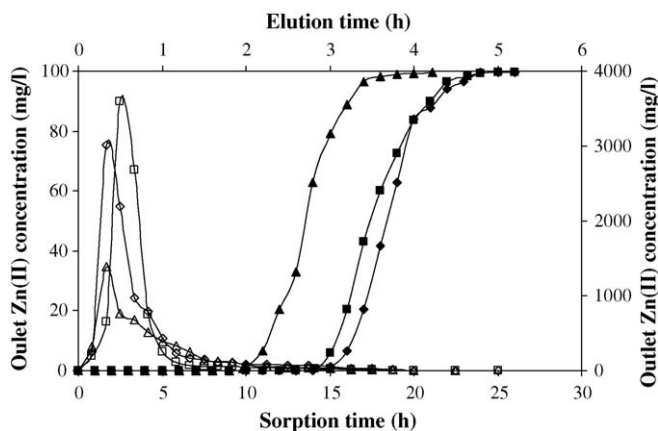


Fig. 8. Sorption and elution breakthrough curves for zinc(II) during regeneration cycles (inlet zinc(II) concentration = 100 mg/l, bed height = 25 cm, flow rate = 5 ml/min, influent pH 5.5). Sorption cycles: (◆) 1 cycle; (■) 2 cycle; (▲) 3 cycle. Elution cycles: (◇) 1 cycle; (□) 2 cycle; (△) 3 cycle.

- Column studies indicated that bed height and flow rate affected the biosorption characteristics of *U. reticulata*, with the highest bed height (25 cm) and the lowest flow rate (5 ml/min) resulted in the highest zinc(II) uptake of 77.7 mg/g.
- Column data obtained at different bed heights and flow rates were described using Thomas, Yoon–Nelson and modified dose–response models.
- *U. reticulata* biomass was regenerated using 0.1 M CaCl$_2$ (in HCl, pH 3.5) and reused for three cycles of zinc(II) biosorption. A slight decrease in zinc(II) biosorption was observed as the cycles proceeded due to gradual deterioration of biomass in repeated cycles.
- The results of our experiments demonstrate that *U. reticulata* has all intrinsic characteristics to be employed for the treatment of zinc(II)-bearing wastewaters.

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