Chemical Engineering Journal 144 (2008) 181–187

Chemical Engineering Journal

www.elsevier.com/locate/cej

# Biosorption of zinc onto *Syzygium cumini* L.: Equilibrium and kinetic studies

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Received 2 June 2006; received in revised form 16 October 2006; accepted 15 January 2008

**Abstract**

The biosorption of zinc ions from aqueous solution by *Syzygium cumini* L. was studied in a batch adsorption system as a function of pH, contact time, zinc ion concentration, adsorbent dosage and adsorbent size. The biosorption capacities and rates of zinc ions onto *S. cumini* L. were evaluated. The Langmuir and Freundlich adsorption models were applied to describe the isotherms and isotherm constants. Biosorption isothermal data could be well interpreted by the Langmuir model followed by Freundlich model with maximum adsorption capacity of 35.84 mg/g of zinc ion on *S. cumini* L. leaves biomass. The kinetic experimental data was properly correlated with the second-order kinetic model.


*Keywords:* *Syzygium cumini* L.; Biosorption; Adsorption isotherm; Kinetic studies

## 1. Introduction

The high degree of industrialization and urbanization has resulted in environmental pollution [1–3]. The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentrations [4–6]. Heavy metals pollute the environment from various industries such as metal plating, electroplating, mining, ceramic, batteries and pigment manufacturing [7,8].

Heavy metals such as lead, mercury, arsenic, copper, zinc and cadmium are highly toxic when adsorbed into the body [9]. Zinc is one of the most important metals often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants and not biodegradable and travels through the food chain via bioaccumulation. Therefore, there is significant interest regarding zinc removal from wastewaters [10] and its toxicity for humans at levels of 100–500 mg/day [11]. World Health Organization (WHO) recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg/l [6].

Removal of toxic heavy metals from industrial wastewater has been practiced for several decades, the conventional physico-chemical removal methods, such as chemical precipitation, electroplating, membrane separation, evaporation or resin ionic exchange, are usually expensive and sometimes, not effective. Therefore, there is a need for some alternative technique, which is efficient and cost-effective. Biosorption, based on living or non-living microorganisms or plants, could be such an alternative method of treatment. Kuyucak indicated that the cost of biomass production played an important role in determining the overall cost of a biosorption process [12]. Therefore, low-cost biomass becomes a crucial factor when considering practical application of biosorption.

The present work investigates the potential use of untreated *Syzygium cumini* L. biomass as metal sorbent for zinc from aqueous solution. *S. cumini* L. was chosen as a biosorbent because of the relative lack of information about its sorption ability. Environmental parameters affecting the biosorption process such as pH, contact time, metal ion concentration, adsorbent dosage

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1385-8947/$ – see front matter 
doi:10.1016/j.cej.2008.01.019

and adsorbent size were evaluated. The equilibrium adsorption data were evaluated by Langmuir and Freundlich isotherm models. The kinetic experimental data were correlated by first- and second-order kinetic models.

## 2. Materials and methods

### 2.1. Preparation of biosorbent

The green *S. cumini* L. leaves were collected from Andhra University College of Engineering campus of Visakhapatnam, Andhra Pradesh, India. Leaves were washed with deionized water several times to remove dirt particles. Then the dried leaves were powdered using domestic grinder and the powder was sieved for the average particle size of 75–212 μm, which were used as biosorbent without any pretreatment for zinc adsorption.

### 2.2. Chemical

Analytical grades of $ZnSO_4{\cdot}7H_2O$, HCl and NaOH were purchased from Merck (Mumbai, Maharastra, India). Zinc ions were prepared by dissolving its corresponding nitrate salt in distilled water. The pH of solutions was adjusted with 0.1 N HCl and NaOH.

All the experiments were repeated five 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 the apparatus used.

### 2.3. Biosorption experiments

Biosorption experiments were performed in a rotary shaker at 180 rpm using 250 mL Erlenmeyer flasks containing 30 mL of different zinc concentrations. After 1 h of contact (according to the preliminary sorption dynamics tests), with 0.1 g *S. cumini* L. leaves biomass, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The metal content in the supernatant was determined using atomic absorption spectrophotometer (GBC Avanta Ver 1.32, Australia) after filtering the adsorbent with Whatman filter paper. The amount of metal adsorbed by *S. cumini* L. leaves was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$Q = (C_0 - C_f)\frac{V}{M} \quad (1)$$

where $Q$ is the metal uptake (mg/g); $C_0$ and $C_f$ are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; $V$ is the solution volume (mL); $M$ is the mass of biosorbent (g). The pH of the solution was adjusted by using 0.1 N HCl and 0.1 N NaOH.

The Langmuir [13] sorption model was chosen for the estimation of maximum zinc sorption by the biosorbent. The Langmuir isotherm can be expressed as,

$$Q = \frac{Q_{max} b C_f}{1 + b C_f} \quad (2)$$

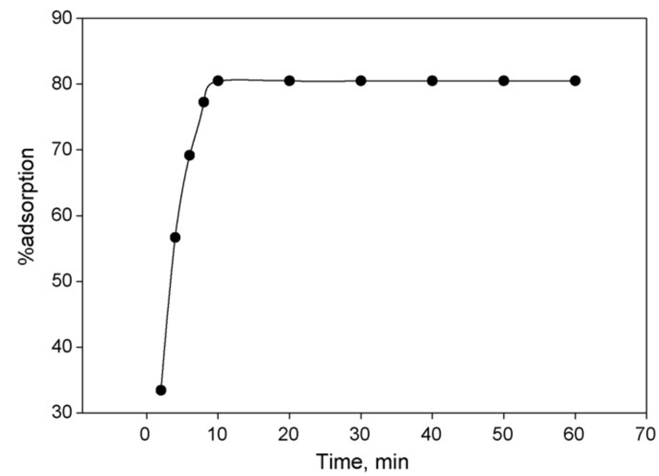


Fig. 1. Effect of contact time on adsorption of zinc by *Syzygium cumini* L. for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentration.

where $Q_{max}$ indicates the monolayer adsorption capacity of adsorbent (mg/g) and the Langmuir constant $b$ (L/mg) is related to the energy of adsorption. For fitting the experimental data, the Langmuir model was linearized as

$$\frac{1}{Q} = \frac{1}{Q_{max}} + \frac{1}{b Q_{max} C_f} \quad (3)$$

The Freundlich [14] model is represented by the equation,

$$Q = K C_f^{1/n} \quad (4)$$

where $K$ (mg/g) is the Freundlich constant related to adsorption capacity of adsorbent and $n$ is the Freundlich exponent related to adsorption intensity (g/L). For fitting the experimental data, the Freundlich model was linearized as follows

$$\ln Q = \ln K + \frac{1}{n} \ln C_f \quad (5)$$

### 2.4. Biosorption kinetics

The kinetic studies were carried out by conducting batch biosorption experiments with different initial zinc concentrations. Samples were taken at different time periods and analyzed for their zinc concentration.

## 3. Results and discussion

### 3.1. The effect of contact time

The data obtained from the biosorption of zinc ions on the *S. cumini* L. showed that a contact time of 10 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. Therefore, the uptake and unadsorbed zinc concentrations at the end of 10 min are given as the equilibrium values ($q_e$, mg/g; $C_{eq}$, mg/L), respectively (Fig. 1) and the other adsorption experiments were conducted at this contact time of 10 min (pH 6).

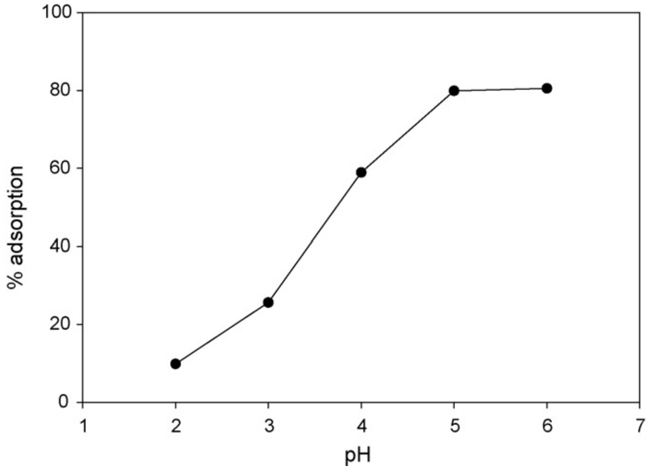


Fig. 2. Effect of pH on zinc adsorption by *S. cumini* L. for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentration.

### 3.2. Effect of pH

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 walls, so pH is an important parameter on biosorption of metal ions from aqueous solutions [15–19].

*S. cumini* L. presents a high content of ionizable groups (carboxyl groups from mannuronic and guluronic acids) on the cell wall polysaccharides, which makes it very liable to the influence of the pH. As shown in Fig. 2, the uptake of zinc increased with the increase in pH from 2.0 to 6.0. Similar results were also reported in literature for different biomass systems [20–22]. At pH values lower than 2.0, zinc removal was inhibited possibly as a result of the competition between hydrogen and zinc 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 *S. cumini* L. would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface.

In this study, these zinc cations at around pH 6 would be expected to interact more strongly with the negatively charged binding sites in the adsorbent. As a result, the optimum pH for zinc adsorption was found as 6 and the other adsorption experiments were performed at this pH value.

### 3.3. Effect of metal ion concentration

Fig. 3 shows the effect of metal ion concentration on the adsorption of zinc by *S. cumini* L. The data shows that the metal uptake increases and the percentage adsorption of zinc decreases with increase in metal ion concentration. This increase (4.83–20.35 mg/g) is a result of increase in the driving force, i.e. concentration gradient. However, the percentage adsorption of zinc ions on *S. cumini* L. was decreased from 80.51 to 67.86%. Though an increase in metal uptake was observed,

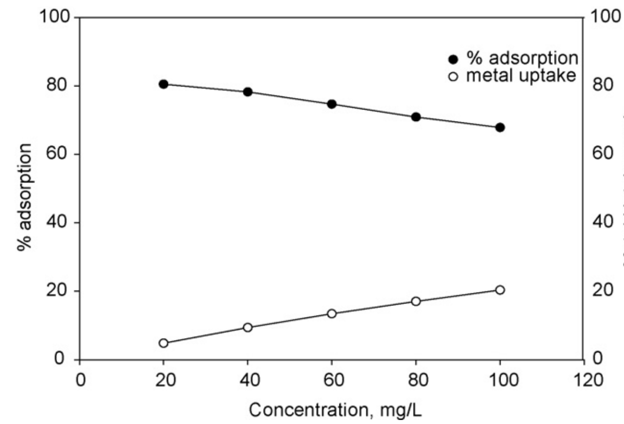


Fig. 3. Effect of metal concentration on the adsorption of zinc by *S. cumini* L. at 0.1 g/30 mL of adsorbent concentration.

the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of zinc displays an opposite trend. At lower concentrations, all zinc ions present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher zinc ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

### 3.4. Effect of adsorbent size

The effect of different adsorbent particle sizes on percentage removal of zinc is investigated and showed in Fig. 4. It reveals that the adsorption of zinc on *S. cumini* L. decrease from 80.51 to 68.32% with the increased particle size from 75 to 212 μm at an initial concentration of 20 mg/L. The smallest size obtained was 75 μm due to the limitation of available grinder configuration. It is well known that decreasing the average particle size of the

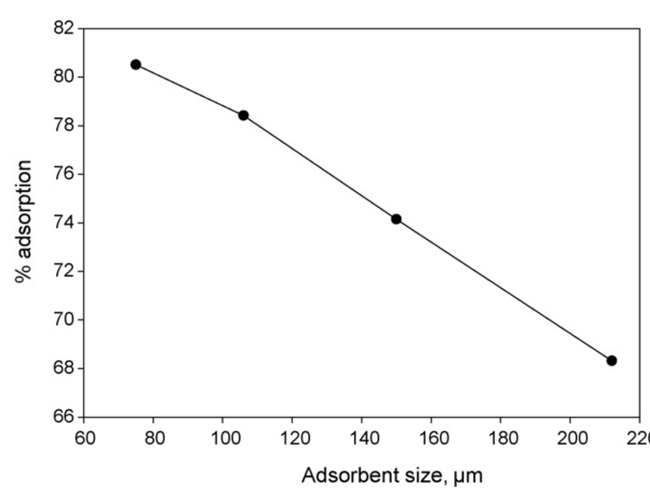


Fig. 4. Effect of *S. cumini* L. particle size on adsorption of zinc for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentration.

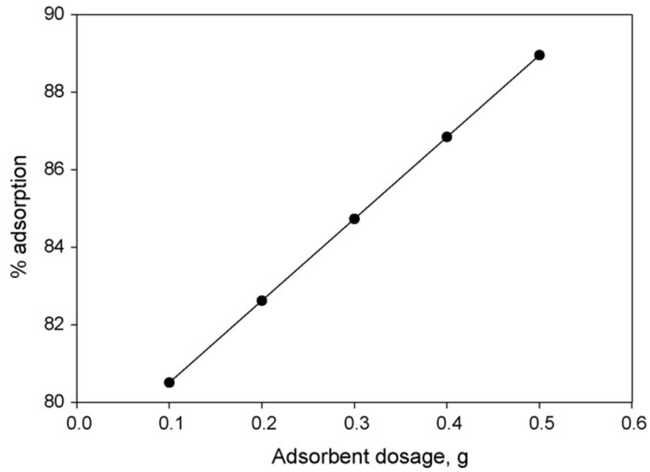


Fig. 5. Effect of *S. cumini* L. dosage on adsorption of zinc for 20 mg/L of metal concentration.

adsorbent increases the surface area, which in turn increases the adsorption capacity.

### 3.5. Effect of adsorbent dosage

Fig. 5 shows the effect of adsorbent dosage on the % removed at equilibrium conditions. It was observed that the amount of zinc adsorbed varied with varying adsorbent dosage. The amount of zinc adsorbed increases with an increase in adsorbent dosage from 0.1 to 0.5 g. The percentage zinc removal was increased from 80.51 to 88.95% for an increase in adsorbent dosage from 0.1 to 0.5 g at initial concentration of 20 mg/L. The increase in the adsorption of the amount of solute is obvious due to increasing biomass surface area. Similar trend was also observed for zinc removal using *Azadirachta indica* as adsorbent [23].

## 4. Biosorption equilibrium

The equilibrium biosorption of zinc on the *S. cumini* L. as a function of the initial concentration of zinc is shown in Fig. 6.

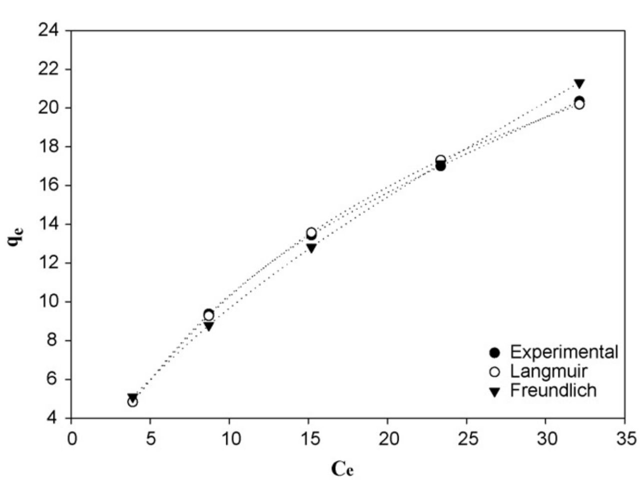


Fig. 6. Equilibrium curves for zinc onto *S. cumini* L.

Table 1
Langmuir, Freundlich isotherm constants and correlation coefficients

| | | |
|---|---|---|
| Langmuir | $Q$ (mg/g) | 35.84 |
| | $b$ (L/mg) | 0.0401 |
| | $R^2$ | 0.9971 |
| Freundlich | $K_f$ (mg/g) | 2.027 |
| | $n$ (g/L) | 0.678 |
| | $R^2$ | 0.9908 |

There was a gradual increase of adsorption for zinc ions until equilibrium was attained. The Langmuir and Freundlich models are often used to describe equilibrium sorption isotherms. The calculated results of the Langmuir and Freundlich isotherm constants are given in Table 1.

It is found that the adsorption of zinc on the *S. cumini* L. was correlated well with the Langmuir equation and Freundlich equation under the concentration range studied.

## 5. Kinetics of adsorption

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Fig. 7 shows the plot between amount adsorbed, $q_e$ (mg/g) versus time, $t$ (min) for an initial concentration of 20 mg/L. The adsorption rate within the first 5 min was observed to be very high and thereafter the reaction proceeds at a slower rate till equilibrium and finally a steady state was obtained after equilibrium. The saturation time was found to be 10 min based on the initial metal concentration. The kinetics of the adsorption data was analysed using two kinetic models, pseudo-first- and pseudo-second-order kinetic model. These models correlate solute uptake, which are important in predicting the reactor volume. These models are explained as follows:

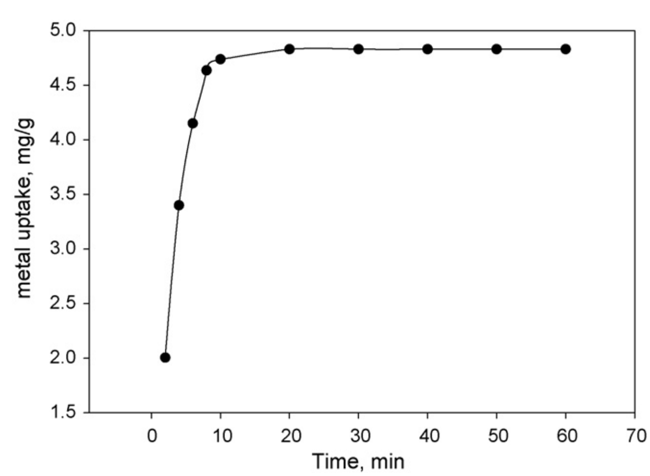


Fig. 7. Effect of contact time on zinc uptake by *S. cumini* L. for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentration.

Table 2
Kinetic constants for zinc onto *Syzygium cumini* L.

| Initial concentration (mg/L) | Pseudo-first-order | | | Pseudo-second-order | | |
|---|---|---|---|---|---|---|
| | Rate constant, $k_1$ (min$^{-1}$) | Amount of zinc adsorbed on adsorbent, $q_e$ (mg/g) | Correlation coefficient, $R_1^2$ | Rate constant, $k_2$ (min$^{-1}$) | Amount of zinc adsorbed on adsorbent, $q_e$ (mg/g) | Correlation coefficient, $R_2^2$ |
| 20 | 0.4392 | 7.6647 | 0.9775 | 0.1604 | 4.9726 | 0.9986 |

### 5.1. The pseudo-first-order equation

The pseudo-first-order equation of Lagergren [24] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

where $q_e$ and $q_t$ are the sorption capacities at equilibrium and at time $t$, respectively (mg/g) and $k_1$ is the rate constant of pseudo-first-order sorption (min$^{-1}$). After integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$; the integrated form of Eq. (6) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{7}$$

The pseudo-first-order rate constant $k_1$ can be obtained from the slope of plot between $\log(q_e - q)$ versus time, $t$ (not shown). The calculated $k_1$ values and their corresponding linear regression correlation coefficient values are shown in Table 2. The linear regression correlation coefficient value $R_1^2$ found 0.9775, which shows that this model cannot be applied to predict the adsorptionkinetic model.

### 5.2. The pseudo-second-order equation

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as [25]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{8}$$

where $q_e$ and $q_t$ are the sorption capacity at equilibrium and at time $t$, respectively (mg/g) and $k$ is the rate constant of pseudo-second-order sorption (g/(mg min)). For the boundary conditions $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$; the integrated form of Eq. (8) becomes:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{9}$$

where $t$ is the contact time (min), $q_e$ (mg/g) and $q_1$ (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, $t$. Eq. (9) does not have the problem of assigning as effective $q_e$. If pseudo-second-order kinetics is applicable, the plot of $t/q_t$ against $t$ of Eq. (9) should give a linear relationship, from which $q_e$ and $k$ can be determined from the slope and intercept

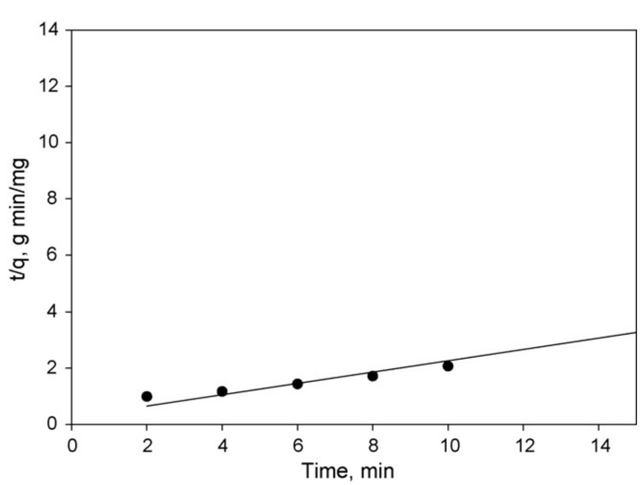


Fig. 8. Pseudo-second-order adsorption of zinc by *S. cumini* L. for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentration.

Table 3
Maximum adsorption capacities for zinc adsorption to different adsorbents

| Adsorbent material | Adsorption capacity (mg/g) | pH | Reference |
|---|---|---|---|
| Na-Mont morillonite | 3.61 | 5 | [26] |
| Crushed concrete fines | 33 | 5.5 | [27] |
| Coir | 8.6 | 5.5 | [28] |
| Barley straw | 5.3 | 5.5 | [28] |
| Peat | 11.71 | 5.5 | [28] |
| Coniferous bark | 7.4 | 5.5 | [28] |
| Sil/PE1/GA$_{0.5}$ | 32.79 | 5–6 | [29] |
| *Fontinalis antipyretica* | 14.7 | 5.0 | [30] |
| Activated carbon | 31.11 | 4.5 | [6] |
| *Streptoverticillium cinnamoneum* | 21.3 | 5.5 | [8] |
| *Aspergillus niger* 405 | 4.70 | 5.0 | [31] |
| *Penicillium digitatum* | 9.7 | 5.5 | [32] |
| *Streptomyces noursei* | 1.6 | 5.8 | [33] |
| *Mucor rouxii* (live) | 4.89 | 5.0 | [34] |
| *Mucor rouxii* (NaOH pretreated) | 5.63 | 5.0 | [34] |
| *Mucor rouxii* ($Na_2$CO3 pretreated) | 3.26 | 5.0 | [34] |
| *Mucor rouxii* ($NaHCO_3$ pretreated) | 6.28 | 5.0 | [34] |
| *Pseudomonas syringae* | 8.0 | n.a | [35] |
| *Rhizopus arrhizus* | 13.5 | 6–7 | [36] |
| *Citrobacter strain* MCMB-181 | 23.62 | 6.5 | [37] |
| *Sargassum* sp. | 24.35 | 4.5 | [38] |
| Animal bones | 11.55 | 5.0 | [39] |
| *Botrytis cinerea* biomass | 12.98 | 5–6 | [40] |
| *S. cumini* L. | 35.84 | 6 | Present study |

of the plot (Fig. 8) and there is no need to know any parameter beforehand.

The pseudo-second-order rate constant $k_2$, the calculated $q_e$ value and the corresponding linear regression correlation coefficient value $R_2^2$ are given in Table 2. At an initial zinc concentration of 20 mg/L, the linear regression correlation coefficient $R_2^2$ value was higher. The higher $R_2^2$ value confirms that the adsorption data were well represented by pseudo-second-order kinetic model.

A comparison of the maximum capacity $Q_{max}$ of *S. cumini* L. with those of some other adsorbents reported in literature is given in Table 3. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

## 6. Conclusions

The present study shows that the *S. cumini* L. was an effective biosorbent for the adsorption of zinc ions from aqueous solution. The effect of process parameters like pH, metal ion concentration, adsorbent dosage and adsorbent size on process equilibrium was studied. The uptake of zinc ions by *S. cumini* L. was increased by increasing the metal ion concentration and the adsorbent dosage and decreased by increasing the adsorbent size. The uptake was also increased by increasing pH up to 6. The adsorption isotherms could be well fitted by the Langmuir equation followed by Freundlich equation. The biosorption process could be best described by the second-order equation.

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