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Biosorption of Zn (II) by *Pseudomonas aeruginosa* isolated from a site contaminated with petroleum

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ABSTRACT

In this present study, biosorption of Zn (II) from aqueous solutions by living bacteria *Pseudomonas aeruginosa* was investigated in batch experiments. The effects of pH, bacterial dosage, initial Zn (II) concentration, contact time, and temperature were studied. Removal process was influenced significantly by the variation of pH, biosorbent concentration, initial Zn (II) ion concentration, temperature, and contact time. Optimum biosorption conditions were found to be initial pH of 6, bacterial dosage of 0.5 g/l, initial Zn (II) ion concentration of 100 mg/l at room temperature, and contact time of 90 min. The maximum uptake capacity of *P. aeruginosa* for Zn (II) ions was found to be 46.1 mg/g at optimum conditions. The correlation coefficient for the second-order kinetic model was 0.997. The Langmuir and Freundlich isotherm models were also applied to the equilibrium of system and data were better fitted with the Freundlich isotherm. Finally, *P. aeruginosa* adsorption capacity was compared with other biosorbents. The abundant and economic biomass *P. aeruginosa* could be used for removal of Zn (II) from wastewater. Results showed that *P. aeruginosa* was an efficient biosorbent in the removal of Zn (II) ions from an aqueous solution.

Keywords: Biosorption; *Pseudomonas aeruginosa*; Heavy metals; Equilibrium isotherm; Kinetic

1. Introduction

Heavy metal pollution has felt an upthrust with the vast expansion of industrialization and urbanization [1–3]. Industrial sectors and operations like metal plating and finishing, metallurgical units and chemical processing units, electroplating, leather tanning, textile dyeing, mining, and paint and pigment industries contribute significantly to heavy metal pollution in ambient freshwater and marine environment [1–6]. Heavy metals are persistent environmental contaminants since they cannot be degraded or destroyed [7]. These heavy metals have tendency to accumulate inside living beings and food chain and impart long-lasting adverse health effects [8–10]. In the series of toxic heavy metals, zinc stands at 74th position with an aggregate of 932.9 points (CERCLA). Zinc toxicity primarily affects the gastrointestinal system followed by circulatory, renal, and neurological disturbances [11]. According to water standards used in most countries, levels of heavy metal ions in wastewater must be controlled and reduced to a set value [6]. United

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States Environmental Pollution Agency and Central pollution control board has defined the permissible limit of zinc exposure in drinking water as 5 mg/l [12]. Hence, the removal of zinc from effluent becomes necessary before effluent discharge in main water sources.

The conventional methods for Zn (II) removal from industrial effluents usually include chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, membrane technologies, and recovery by evaporation. However, these methods are ineffective or expensive, and are not eco-friendly [13,14]. Therefore, research for efficient, eco-friendly, and inexpensive Zn (II) adsorption has been initiated. Biological methods such as biosorption/bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physicochemical methods [15]. Various biomaterials such as bacteria, fungi, algae, yeasts, and agricultural by-products have been examined for their biosorptive properties [16–18].

Metal removal by micro-organisms is a complex process that depends on the chemistry of the metal ions, cell wall composition of micro-organisms, cell physiology, and physicochemical factors such as pH, temperature, contact time, ionic strength, and metal concentration [19]. Various naturally occurring bacteria exhibit high capacity for binding of metals. Intact microbial cells (live or dead) and their products can be effective bioaccumulators of both soluble and particulate forms of metals [16]. The uptake of metals by microbial cells or biological materials do not need the cell viability and biochemical energy and could include the following mechanisms (i) extracellular accumulation/ precipitation, (ii) cell surface sorption, complexation, or ionic exchange, (iii) intracellular accumulation after passive diffusion and present generally fast reactions [1,20]. A variety of functional groups located on the bacterial cell wall are known to be included in metal biosorption. These include carboxyl, amine, hydroxyl, phosphate, and sulfhydryl groups. The mechanism of metal biosorption by bacterial biomass occurs through complexation, coordination, physical adsorption, chelation, ion exchange, inorganic precipitation, and/or a combination of these processes [21].

The main objective of this work was to study the maximum biosorption capacity *Pseudomonas aeruginosa* isolated from a site contaminated with petroleum for removal of Zn (II) ions. Factors affecting biosorption and mechanisms of biosorption were also studied. Biosorption isotherms and kinetics parameters were determined from biosorption measurements.

2. Materials and methods

2.1. Micro-organism and its preparation for biosorption

The micro-organism used for this experiment was *P. aeruginosa* isolated from a soil contaminated with petroleum at the Naft Shahr of Kermanshah, Iran (34˚00´04´´N, 45˚29´44´´E). The isolate was purified and identified according to Bergey's manual (2005) [22]. The bacterial strains were cultured in nutrient broth (pH 7.0) and incubated for 48 h at 30˚C, then harvested by centrifugation for 15 min at 5,000 rpm. The cell pellet was rinsed thrice with sterile deionized water, then freeze dried using oven at 60˚C. The bacterial biomass was used in further experiments for Zn (II) removal from aqueous solutions.

2.2. Preparation of metal solutions

Stock solution (1,000 mg/l) was prepared by dissolving the Zn $(NO3)_2{\cdot}4H_2O$ salt (Merck) in deionized water, the working solutions were prepared by diluting the stock solutions to the desired concentrations in deionized water. Concentrations of solutions were determined using the atomic absorption spectrophotometer (Chem Tech Analytical model CTA2000). All chemicals used in this study were of analytical-reagent grade.

2.3. Kinetic and isotherm test

All biosorption experiments were performed by the batch technique, 0.01 M $NaNO_3$ as the background electrolyte to buffer ionic strength adds to the solutions. The experiments were conducted in 250 mL flasks containing Zn (II) solution and biomass with pH from 2 to 6. The pH value was adjusted to required value using 0.1 M HNO_3 and 0.1 M NaOH. Effect of initial Zn (II) concentration from 25 to 150 mg/l and the effect of bacterial dosage from 0.5 to 2.5 g/l were studied. The mixtures were transferred to the shaker with 100 rpm for 90 min. The biosorbent was filtered through a Whatman paper filter, then centrifuging for 10 min at 4,000 rpm. The final concentration of Zn (II) was determined by atomic absorption spectrophotometer. Amounts of Zn (II) adsorbed by the biomass were calculated using the following equation:

$$q = \frac{V(C_i - C_e)}{M} \quad (1)$$

where q is the amount of Zn (II) adsorbed by biomass (mg/g), C_i is the initial concentration of Zn (II)

(mg/l), C_e is the concentration of Zn (II) (mg/l) at equilibrium, V is the volume of the metal solution (l), and M is the mass of adsorbent (g) [23,24].

Sorption studies were conducted in 1 L conical flasks at pH value 6. The *P. aeruginosa* biomass, which was well-dried (100 mg/l), were carefully mixed with 1 l of Zn (II) solution (100 mg/l) separately, and the suspensions were shaken at 25°C temperature. A sample quantity of 5 ml were collected from duplicate flasks at required time intervals, viz. 10, 20, 30, 60, 90,120, and 240 min and then were filtered through Whattman No. 1 filter paper. The filtrates were analyzed for residual Zn (II) concentration in the solution.

3. Results and discussion

3.1. Bacterial biosorbent

Bacterial strains were used in biosorption studies was *P. aeruginosa* that isolated from the soil contaminated with petroleum. This bacterium was identified according to Bergey's manual (2005) [22] and the biochemical tests for identification of the isolate are shown in Table 1. *P. aeruginosa* a gram-negative bacterium in the uptake of toxic metals is of good efficiency. Compared to other bacteria, this is readily available. The cell wall of bacteria has the ability to bind toxic metals.

Table 1
Morphological and biochemical characterization of strain *P. aeruginosa*

Test employed	Characteristics observed
Cell morphology	Cocobasil
Gram reaction	–
Spore formation	–
Catalase	+
Oxidase	+
Motion	–
Indole	–
H_2S	–
Methyl Red	–
Voges Proskauer	–
Glucose	+
Lactose	+
Urease	+
Citrate	+
Nitrate reduction	+
Pigment	+

"–" and "+" indicate positive and negative reaction, respectively.

3.2. Effect of pH

It has been shown that the affinity of cationic species for the functional groups presents on the cellular surface is strongly dependent on the pH of the solution. The effect of pH on the biosorptive capacity of Zn (II) by *P. aeruginosa* is shown in Fig. 1. It can be seen from Fig. 1 that the biosorptive capacity of Zn (II) by bacteria is very low at low pH values and increases with pH until reaching an optimum at pH 6.0. However, at pH higher than 6.0, the Zn (II) begins to precipitate due to formation of Zn $(OH)_2$. At low pH values, cell wall ligands are closely associated with hydronium ions and restrict the biosorption of Zn^{2+} as a result of competition between H_3O^+ and Zn (II) with the bacterial biosorbent cell wall ligands. As the pH increases, more ligands, such as carboxyl, phosphate, and imidazole, would be exposed and carry negative charges which attract Zn (II) and biosorbed it onto the bacterial cell surface [21]. Biosorption being a physical/chemical reaction between positively charged metal ions and anionic groups of all surfaces, the metal uptake is strongly influenced by the pH which affects the speciation of metal and reactive groups.

3.3. Effect of bacterial dosage

The effect of initial bacterial dosage 0.2–2.5 g/l was investigated at same pH, initial Zn (II) concentration, and room temperature, as shown in Fig. 2. The optimum bacterial dosage was observed 0.5 g/l. The dosage of a biosorbent strongly influences the extent of biosorption. In many instances, lower biosorbent dosages yield higher uptakes. An increase in the biomass concentration generally increases the amount of solute biosorbed, due to the increased surface area of the

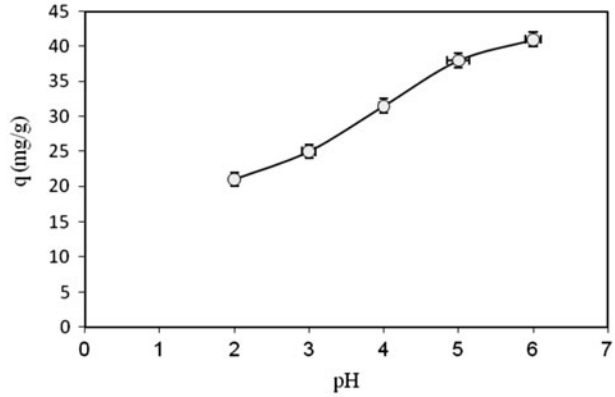

Fig. 1. Effect of pH on Zn (II) biosorption on *P. aeruginosa* (T = 25°C, bacterial dosage = 1 g/l, C_i = 100 mg/l, contact time = 120 min).

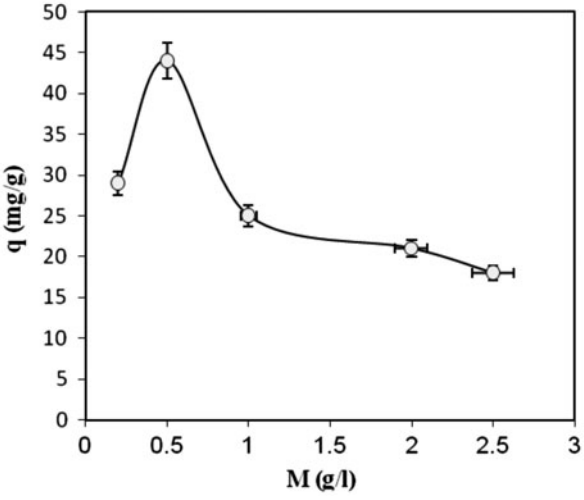

Fig. 2. Effect of bacterial dosage on Zn (II) biosorption on *P. aeruginosa* (pH = 6, *T*: 25˚C, C_i = 100 mg/l, contact time = 120 min).

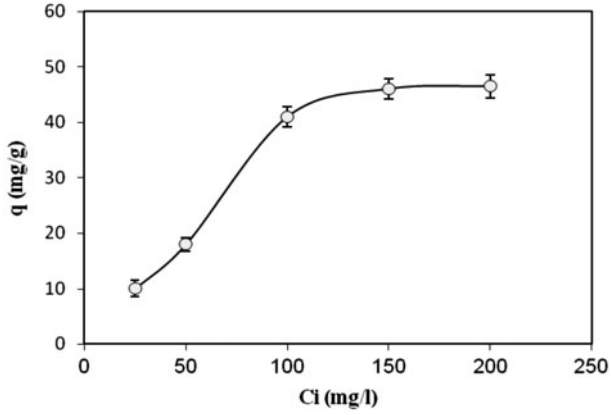

Fig. 3. Effect of initial concentration of metal on Zn (II) biosorption on *P. aeruginosa* (pH 6, *T*: 25˚C, bacterial dosage = 0.5 g/l, contact time = 120 min).

biosorbent, which in turn increases the number of binding sites conversely, the quantity of biosorbed solute per unit weight of biosorbent decrease with increasing biosorbent dosage, which may be due to the complex interaction of several factors. An important factor at high sorbent dosages is that the available solute is insufficient to completely cover the available exchangeable sites on the biosorbent, usually resulting in low solute uptake. Also, as suggested by the interference between binding sites due to increased biosorbent dosages cannot be overruled, as this will result in a low specific uptake [25].

3.4. Effect of initial metal concentration

The initial metal ion concentration is another important factor that plays a role in metal sorption. The effect of initial Zn (II) concentration was investigated by varying initial Zn (II) concentration, ranging from 25 to 300 mg/l at same pH and room temperature. The results showed in Fig. 3 that the biosorption capacity (q) increased with the increasing initial Zn (II) concentration at the same pH and temperature, the optimum metal concentration was observed 150 mg/l. The initial solute concentration seems to have impact on biosorption, with a higher concentration resulting in a high solute uptake. This is because at lower initial solute concentrations, the ratio of the initial moles of solute to the available surface area is low; subsequently, the fractional sorption becomes independent of the initial concentration. However, at higher concentrations, the sites available for sorption become fewer compared to the moles of solute present and; hence, the removal of solute is strongly dependent on the initial solute concentration. It is always necessary to identify the maximum saturation potential of a biosorbent, for which experiments should be conducted at the highest possible initial solute concentration [25].

3.5. Effect of temperature and contact time

Temperature seems to affect biosorption only to a lesser extent within the range from 20 to 50˚C. Higher temperatures usually enhance sorption due to the increased surface activity and kinetic energy of the solute however physical damage to the biosorbent can be expected at higher temperatures. It is always desirable to conduct/evaluate biosorption at room temperature, as this condition is easy to replicate [25]. Table 2 shows that the biosorption capacity (q) increased with the increasing temperature. Fig. 4 shows that the removal rate of Zn (II) after a 90 min was constant.

Table 2
Effect of temperature (pH: 6, *t*: 90 min, bacterial dosage = 0.5 g/l, C_i = 100 mg/l)

T (˚C)	q (mg/g)
20	35.2
30	41.4
40	46.1
50	33.8

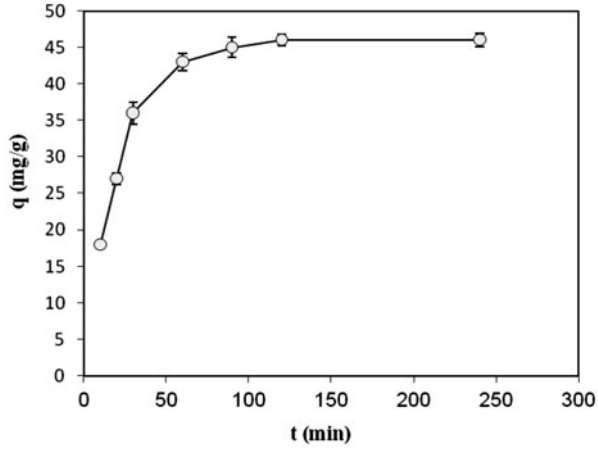

Fig. 4. Effect of contact time on Zn (II) biosorption on *P. aeruginosa* (pH 6, *T*: 25°C, bacterial dosage = 0.5 g/l, C_i = 100 mg/l).

3.6. Kinetic experiments

Two models were used to determine the data to examine the mechanism of adsorption process. The pseudo-first order assumes that metal ion binds only to one sorption site on the sorbent surface [26]. In Lagergren model [15]. The rate of occupation of biosorption sites is proportional to the number of unoccupied sites:

$$\log\left[\frac{q_e}{q_e - q_t}\right] = \frac{k_1}{2.303}\ t \tag{2}$$

where q_e and q_t are the amounts of adsorbed Zn (II) ions on the biosorbent at equilibrium and at time t (mg/g), respectively, and k_1 is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}) [15]. The slopes and intercepts of plot of log ($q_e - q_t$) vs. t were used to obtain the first-order rate constant k_1 and equilibrium adsorption density q_e. The adsorption kinetics may also be described by pseudo-second-order model. Metal ions are bound to two binding sites on the sorbent surface [26]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{3}$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption [15]. The slope and intercept of plot t/q_t vs. t were used to calculate the second-order rate constants k_2 and q_e. The straight lines obtained from plot of t/q_t vs. t showed good fitness of experimental data with the second-order kinetic model (Fig. 5). As shown in Table 3, the correlation coefficient for the pseudo-first-order and pseudo-second-order models were found to be 0.961 and 0.997, respectively. The amounts of adsorbed Zn (II) on the biosorbent at equilibrium (q_{ecal}) by first- and second-order models were 11.01 and 50 mg/g, respectively. Experimental value of q_{exp} was 36 mg/g. Hence, it was concluded that this sorption system was better described by second-order rate equation than by first.

Other technique used for identifying the mechanism involved in the adsorption process is by fitting the experimental data in an intraparticle diffusion plot. Intraparticle diffusion model used here refers to the theory proposed by Weber and Morris which can be used to assess this opinion:

$$q = f\left(\frac{Dt}{r_p^2}\right)^{\frac{1}{2}} = k_i t^{\frac{1}{2}} \tag{4}$$

where r_p is particle radius, D is the effective diffusivity of solutes within the particle, q_t (mg/g) is the adsorbed metal ion amount at any time, and K_i intraparticle rate constant (mg/g $min^{1/2}$).The slope of plot q vs. $t^{1/2}$ obtained k_i was 2.806 (mg/g $min^{1/2}$) in optimum conditions. It was observed that the biosorbed Zn (II) amounts by *P. aeruginosa* have the multi-linearity that two or more steps occur (Fig. 6). The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intraparticle diffusion is rate controlled. The third portion is final equilibrium stage where the intraparticle

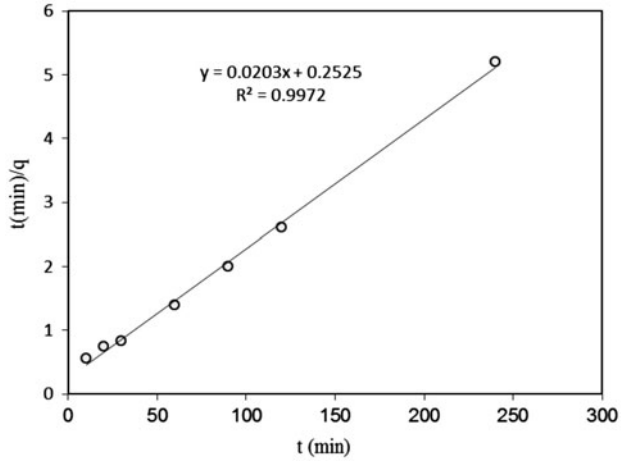

Fig. 5. Plot of the pseudo-second-order equation for the biosorption kinetics of Zn (II) on *P. aeruginosa* (pH 6, *T* = 25°C, bacterial dosage = 0.5 g/l, C_i = 100 mg/l).

Table 3
Kinetic models for biosorption of Zn (II)

Parameter	Pseudo-first-order	Pseudo-second order
q_e (mg/g)	11.01	50
K	0.022	1.6×10^{-3}
R^2	0.961	0.997

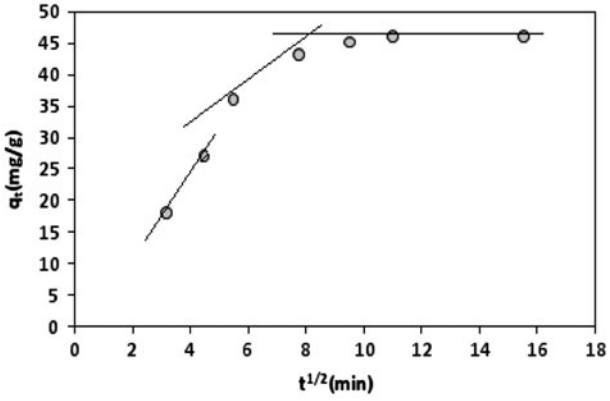

Fig. 6. Plot of the intraparticle diffusion (Weber–Morris model) for the biosorption kinetics of Zn (II) on *P. aeruginosa* (pH 6, $T = 25$ °C, bacterial dosage = 0.5 g/l, $C_i = 100$ mg/l).

diffusion starts to slow down due to extremely low solute concentrations in the solution [27].

3.7. Determination of equilibrium models

Langmuir and Freundlich isotherms were used to describe the equilibrium state for metal ion adsorption. The Freundlich isotherm is a nonlinear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules [28]. The logarithmic form of this model is:

$$\log q_e = \log K_F + 1/n \log C_e \tag{5}$$

where K_F (mg/g) and n are the Freundlich constants.

The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate [29]. The general Langmuir equation is commonly presented as the equation may be linearized as follow:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{6}$$

where q_e is the amount of metal ion removed (mg/g), C_e is the equilibrium concentration (mg/l), b is the Langmuir constant related to affinity, and $q_{\max}$ is the maximum metal uptake under the given conditions.

The Freundlich and Langmuir constants, along with the regression coefficients have been calculated from the corresponding plots. The Freundlich constants (K_F and n) are shown in Table 4. The n value greater than 1.0 represents favorable biosorption conditions [30]. The maximum metal uptake ($q_{\max}$) under the optimal conditions and adsorption binding constant (b) in Langmuir model are shown in Table 4. The correlation coefficients for the Freundlich and Langmuir adsorption isotherm was found to be 0.933 and 0.786, respectively. R^2 values was same for two models, but $q_{\max}$ Langmuir is not in good agreement with the experimental data. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent while Langmuir model hints surface homogeneity of the adsorbent. The experimental data for the biosorption of Zn (II) on *P. aeruginosa* are given in Fig. 7.

3.8. Comparison with other biosorbents

Table 5 compares the maximum adsorption capacities obtained from this study with some other values reported in the literature. The adsorption capacity for Zn (II) using *P. aeruginosa* was found to be comparable with many of the reported literature values. Among the Gram-positive bacterium *Bacillus* and the Gram-negative bacteria *Pseudomonas*, aeruginosa has the highest efficiency in the absorption of Zn (II). However, a direct comparison of experimental data is not possible due to different experimental conditions such as pH, temperature, equilibrium time, heavy metal concentration, and biomass dosage.

Table 4
Equilibrium models for biosorption of Zn (II)

Freundlich			Langmuir		
K_f	n	R^2	$q_{\max}$ (mg/g)	b (mg/g)	R^2
1.11	1.34	0.933	46.1	6.9×10^{-3}	0.786

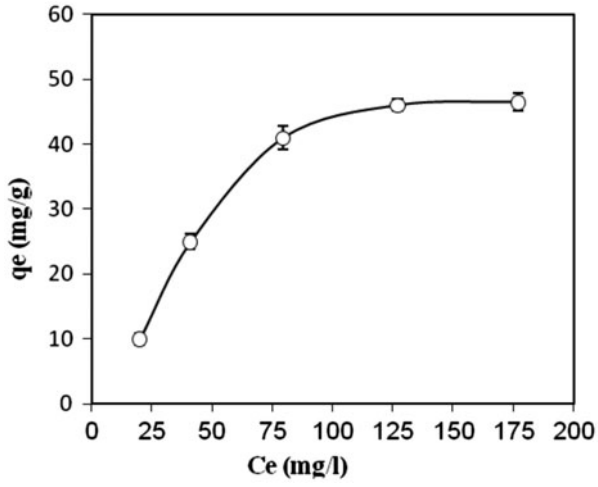

Fig. 7. Isotherm of Zn (II) biosorption on *P. aeruginosa* (pH 6, T = 25°C, bacterial dosage = 0.5 g/l, contact time = 90 min).

Table 5
Comparison data of biosorption capacities (q_{max}—maximum metal uptake capacity) for Zn (II) by *P. aeruginosa* and other biosorbents

Bacteria	q_{max} (mg/g)	Reference
Acinetobacter sp.	36	[7]
Delftia tsuruhatensis	14	[31]
Pseudomonas aeruginosa	66.6	[32]
Bacillus cereus	83.3	[32]
Pseudomonas aeruginosa ASU 6a	88.3	[20]
Bacillus cereus AUMC B52	66.6	[20]
Streptomyces ciscaucasicus strain	54	[33]
Pseudomonas aeruginosa AT18	77.5	[15]
Shewanella putrefaciens	34	[34]
Escherichia coli	65.9	[35]
Pseudomonas putida	17.7	[36]
Pseudomonas putida	6.9	[37]
Pseudomonas aeruginosa	46.1	This study

4. Conclusions

The optimum biosorption conditions were determined as initial pH 6, at temperature 40°C, biosorbent concentration 0.5 g/l, and initial Zn (II) concentration 100 mg/l. The biosorption capacity of Zn (II) increased with the increasing temperature and decreased with the increasing bacterial dosage at the same initial concentration of Zn (II), and increased as the initial concentration increased at the same pH. It was found that the Zn (II) biosorption attained to equilibrium after 90 min and this contact time was taken as the equilibrium. The Langmuir and Freundlich isotherm models were applied to the equilibrium data. The maximum uptake capacity of *P. aeruginosa* for Zn (II) ions was found to be 46.1 mg/g at optimum conditions. The correlation coefficient for the second-order kinetic model was 0.997. The Langmuir and Freundlich isotherm models were also applied to the equilibrium of system and data were better fitted with the Freundlich isotherm.

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