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Biosorption of cadmium by *Brevundimonas* sp. ZF12 strain, a novel biosorbent isolated from hot-spring waters in high background radiation areas

Nasrin Masoudzadeh[a,b,1], Fardideh Zakeri[a,c,1], Tayebe bagheri Lotfabad[a], Hakimeh Sharafi[a,b], Fatemeh Masoomi[a], Hoseein Shahbani Zahiri[a], Gholamreza Ahmadian[a], Kambiz Akbari Noghabi[a,*]

[a] *Department of Molecular Genetics, National Institute of Genetic Engineering and Biotechnology (NIGEB), P.O. Box 14155-6343, Tehran, Iran*
[b] *Department of Biology, Science and Research Branch, Islamic Azad University, Tehran, Iran*
[c] *National Radiation Protection Department – Nuclear Science and Technology Research Institute, Tehran, Iran*

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ABSTRACT

The aim of this study is to screen cadmium biosorbing bacterial strains isolated from soils and hot-springs containing high concentrations of radium (^{226}Ra) in Ramsar using a batch system. *Brevundimonas* sp. ZF12 strain isolated from the water with high ^{226}Ra content caused 50% removal of cadmium at a concentration level of 250 ppm. The biosorption equilibrium data are fitted well by the Langmuir adsorption isotherm and kinetic studies indicated that the biosorption follows pseudo second-order model. The effect of different physico-chemical parameters like biomass concentration, pH, cadmium concentration, temperature and contact time on cadmium sorption was also investigated using FTIR, SEM and XRD analytical techniques. A high desorption efficiency (above 90%) was obtained using a pH range of 2.0–4.0. Reusability of the biomass was examined under consecutive biosorption–desorption cycles repeated thrice. In conclusion, *Brevundimonas* sp. ZF12 is proposed as an excellent cadmium biosorbent that may have important applications in Cd removal from wastewaters.

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1. Introduction

Contaminations of the environment with hazardous and toxic compounds such as heavy metals are one of the major problems facing the industrialized nations today. Cadmium is attracting the attention of environmentalists as one of the most toxic heavy metals. It is identified as a soft, blue-white malleable, lustrous metal or a grayish white powder that is insoluble in water and reacts readily with dilute nitric acid. Cadmium may come from various industrial sources such as electroplating, fertilizers, mineral processing and battery manufacturing [1]. Wastewaters from these industries have permanent toxic effects on living organisms and constitute a threat for the environment [2,3]. Cadmium contamination in human beings was first reported in Japan in the 1950s where the municipal sewage sludge was used as a fertilizer for the rice crop. Cadmium exposure may result in adverse effects such as cancer, lung insufficiency, renal dysfunction (Fanconi syndrome), bone degradation disturbances in cardiovascular system, liver and kidney damage [4,5].

There are several methods for treating Cd contaminated effluents such as ion exchange, adsorption, chemical precipitation, oxidation, reduction, and reverse osmosis. However, many of these approaches can be less cost effective or difficult for practical use. Also, most of these are ineffective or excessively expensive when the metal concentrations are less than 100 mg L^{-1} [6]. In the past few decades, biosorption using microbial biomass as the adsorbent has emerged as a potential alternative technique to the existing methods for metal removal [7]. Biosorption process offers the advantages of low operating costs, possibility of metal recovery, potential biosorbent regeneration, minimization of the volume of chemical and/or biological sludge to be disposed of and high efficiency in detoxifying very dilute liquid streams [8]. Biosorbing properties of bacterial biomasses are widely reported in the literature [9–12].

Cell wall composition is one of the most important factors affecting bacterial biosorbing properties. The anionic functional groups present in the peptidoglycan and teichoic acids of gram-positive bacteria, phospholipids and lipopolysaccharides of gram-negative bacteria are the main elements responsible for the anionic character and the metal-binding ability of the cell wall. Also, extracellular polysaccharides are capable of binding heavy metals, but their availability depends on the bacterial species and growth conditions [13].

Cadmium biosorption by different living and nonliving biomasses have been studied by several authors [14–17]. However, there are no reports on the Cd sorption, removal and recovery by bacteria tested in the present study, i.e. *Brevundimonas* sp., under

* Corresponding author. Tel.: +98 21 44580352; fax: +98 21 44580395.
E-mail addresses: Akbari@nigeb.ac.ir, kambizakb@yahoo.com (K.A. Noghabi).
[1] Equal contribution.

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batch experimental conditions. The reason for screening the intrinsic ability of isolates from high background radiation areas (HBRAs) of Ramsar for cadmium biosorption is that these areas are known to have the highest ^{226}Ra levels and as extreme habitats are populated by highly specialized organisms-extremophiles, which must in contrast to other species bridge different stress condition such as radiation and temperature. Also their potential for ^{226}Ra sorption has been reported recently [18].

By considering the condition discussed above, appropriate bacterial strains were selected for Cd biosorption. ZF12 strain as the most potent sorbent has been selected for further studies on equilibrium isotherms, kinetics and the effects of various parameters such as contact time, pH, initial Cd concentration, initial biomass concentration and temperature on Cd biosorption efficiency.

2. Materials and methods

2.1. Bacterial strains and culture conditions

The biosorbents used in this study were *Enterobacter* sp. ZF08, *Shewanella* sp. ZF13, *Brevundimonas* sp. ZF12 and ZF02, *Bacillus* sp. ZF10, *Rhodococcus* sp. ZF05 and *Rothia* sp. ZF11 species, which were isolated from hot spring waters of HBRAs of Ramsar because of their ability to tolerate high ^{226}Ra levels [18]. They were cultured in Nutrient Broth at 30 °C and 180 rpm. 200 μL of overnight grown cultures were used to inoculate 80 mL Nutrient Broth in 250 mL Erlenmeyer flask and incubated at 30 °C with constant shaking at 180 rpm in an orbital shaker for 18 h.

2.2. Screening the performance of the isolated bacteria for Cd sorption

After the growth, the cells were harvested by centrifugation (7000 rpm for 15 min) then the pellet was washed twice by distilled water and freeze-dried. 20 mg of dried biomass of each bacterial isolate was suspended in 10 mL of a metal solution with an initial concentration of 150 ppm and the solution was continuously stirred on a shaker (180 rpm) at 30 °C for 2.5 h. A stock Cd(II) solution of 1000 mg L^{-1} was prepared by dissolving 2.3709 g of $CdSO_4{\cdot}8/3\ H_2O$ (Merck, Germany) in 1000 mL of deionized water and then sterilized by autoclaving at a pressure of 1.5 atm at 121 °C for 10 min [19]. After 2.5 h the supernatant was collected by centrifugation at 8000 rpm for 15 min, filtered through 0.2 μm filter membranes and analyzed for metal ions, using atomic absorption spectrophotometer (AAS, Varian AA-220, Australia). The amount of Cd sorbed to the bacterial biomass was determined from the difference between the Cd added to the solution and the Cd remaining in the solution after 2.5 h. All the biosorption experiments were repeated twice to confirm the results. Also blank (without biomass) experiments were conducted to ensure that no adsorption had taken place on the walls of the apparatus used.

2.3. Effect of chemo-physical factors on Cd uptake

The effect of biomass concentration, pH, temperature, different concentrations of Cd and contact time was studied under similar experimental conditions. To investigate the effect of biomass concentration on biosorption, 20–80 mg biomass solutions were exposed to the 150 ppm cadmium solution at pH 7. The flasks were shaken (170 rpm) at 30 °C for 2.5 h. The cell solution was centrifuged and the supernatant was analyzed for Cd uptake, using atomic adsorption spectrometry.

Also the effect of pH (2–10), initial Cd concentration (50–300 ppm) and different temperatures (20–45 °C) at optimum biomass concentration on Cd sorption was tested. Effect of contact time was studied at interval times of 0, 5, 15, 30, 60, 90, 120 min and 24 h.

The Cd uptake were calculated by using the following Eq. (1)

$$Q_e = \frac{V}{m}(C_i - C_e) \tag{1}$$

where Q_e is the specific metal biosorption (mg metal/g biomass), C_i and C_e are the initial and final Cd concentration (mg metal/L) in the solution, respectively. V is the volume of aqueous solution (L) and m is dry weight of biomass (g).

2.4. Isotherm studies

During the biosorption, a rapid equilibrium is established between metal ions on biosorbent (q_e) and metal ions remaining in solution (C_e).

This equilibrium can be described by the Langmuir or Freundlich adsorption isotherms.

The Langmuir equation assumes that (i) the solid surface presents a finite number of identical sites which are energetically uniform; (ii) there is no interaction between adsorbed species, meaning that the amount adsorbed has no influence on the rate of adsorption; (iii) a monolayer is formed when the solid surface reaches saturation [5]. The isotherm equation assumes the following form:

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

where q_{max} is the maximum metal ion per unit weight of cell to form a complete mono layer on the surface bound at high C_{eq} (mg g^{-1}) and b (L mg^{-1}) represents the affinity of the sorbate for binding site on the biosorbent. The empirical Freundlich equation based on sorption on a heterogeneous surface is given as:

$$q_e = kc_e^{1/n} \tag{3}$$

These models can provide information of metal uptake capacity and difference in metal uptake among various species [20–22].

2.5. Kinetic studies

In order to investigate the mechanism of biosorption of Cd by the ZF12 strain and the potential rate-controlling steps such as chemical reaction and mass transfer, kinetic models have been used to test experimental data [23].

Many kinetic models have been proposed to describe the reaction order of adsorption system based on solution concentration. Kinetic models based on the adsorbent capacity have also been presented, such as the Lagergren's equation and Ho's second-order expression. The pseudo first-order and second-order models fitted the data very well in a large quantity of literature sources for biosorption [24].

The Lagergren first-order rate expression based on solid capacity is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

where q_e and q_t are the amount of metal biosorbed per unit weight (mg g^{-1} dry weight) of biosorbent at equilibrium and at any time t (min), respectively, and k_1 is the rate constant of pseudo first-order sorption (min^{-1}). The integrated form of the above equation after applying the initial and boundary conditions, for $t = 0$, $q_t = 0$, becomes

$$\log(q_e - q_t) = \log\ q_e - \frac{k_1}{2.303} \times t \tag{5}$$

Pseudo second-order model is derived on the basis of the sorption capacity of the solid phase, expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

where k_2 is the equilibrium rate constant (mg g^{-1} min^{-1}), q_e is the metal ion sorbed at equilibrium (mg g^{-1}), q_t is the amount of metal ion adsorbed at time t (min). Eq. (6) can be rearranged as:

$$\frac{t}{q_t} = \frac{1}{k_2\ q_e^2} + \left(\frac{1}{q_e}\right) t \quad (7)$$

The pseudo first-order and second-order constants were determined by plotting $\log(q_e - q_t)$ against t and t/q against t, respectively [25].

2.6. Desorption experiments

After biosorption experiments, the Cd-loaded biosorbents were harvested from the cell-Cd solutions. The biosorbents were then rinsed and resuspended with Cd-free deionized water. Proper amounts of 0.1 M HCl [26] were added into solutions containing Cd loaded biomass to adjust the pH value to 2.0, 3.0, 4.0 and 5.0, respectively.

After 2 h of gentle agitation, samples were taken from the suspensions. The samples were centrifuged immediately and the Cd concentration in the supernatant was determined with AAS. In order to determine the reusability of the ZF12 strain, consecutive biosorption–desorption cycles were repeated thrice. The efficiency of adsorption and desorption was determined according to the following equation:

$$\text{Desorption efficiency}\,(\%) = \frac{\text{md}}{\text{mb}} \times 100 \quad (8)$$

where md is the amount of Cd ions released in the supernatant solution (mg) and mb represents the metal ions initially adsorbed on the ZF12 strain (mg).

2.7. FTIR, XRD and SEM analysis

Structural and compositional features of ZF12 strain under standard and Cd stressed conditions were analyzed using FTIR spectroscopy by Perkin-Elmer Spectrometer (FTIR GX 2000). For the FTIR study, samples of unloaded and Cd-loaded biomass of ZF12 strain were dried first and then ground before performing FTIR analysis. The dried powder was mixed with a KBr matrix (Sigma). The spectra were in the range of 400–4000 cm^{-1} with 8 cm^{-1} resolution. The resulting spectra were the average of 16 scans. ZF12 biomass before and after the Cd biosorption testes were freeze-dried overnight, and were subsequently examined by X-ray powder diffraction (Bruker XRD D8 Advance) coupled with a copper X-ray tube. The scans were collected in a range of 2θ from 5° to 80° at a rate of 0.02°/min. An X-ray diffraction analysis was performed for two samples.

In order to observe how the sorption of Cd on the ZF12 strain would alter the cell-surface morphology scanning electron microscopy (SEM) analysis was employed. Metal loaded and metal free biosorbent cells (control) were fixed with 0.1 M phosphate buffer (pH 7.2) containing 1% glutaraldehyde for 2 h, washed with distilled water and were then dehydrated through a graded ethanol series for 7 min. The final dehydration process was repeated twice. The dried samples were mounted on stubs and sputter-coated with gold. Micrographs were taken on a SEM instrument (Philips XL30, USA).

3. Results and discussion

3.1. Characterization of the bacterial isolates

Based on 16S rRNA gene analysis and biochemical identification of the organisms by the analytical profile index (API kits, Biomérieux, France), and according to Bergey's Manual of Systematic Bacteriology the isolates were affiliated to the *Enterobacter*, *Shewanella*, *Brevundimonas*, *Bacillus*, *Rhodococcus* and *Rothia* species. The selected bacterium, *Brevundimonas* sp. ZF12 strain has been identified as a variant of *Brevundimonas vesicularies* (98.3% identity) [18].

3.2. Screening the performance of the isolated bacteria for cadmium sorption

It was desirable to compare the sorption performance of biosorbents ZF08, ZF13, ZF12 and ZF02, ZF10, ZF05 and ZF11 species for Cd biosorption. It is obvious that there exist seven separate sorption isotherms each characterizing one of the bacterial materials. However, available is only one point for each curve. For each of the C_f values obtained there is one corresponding q which can serve as a basis for sorption comparison. The correct comparison can only be done along the same line of the same C_f for all the materials. Obviously, this is not possible when the whole sorption isotherm plots are not available. Therefore, the "% Removal" values can serve the purpose of crude orientation, adequate for quick and approximate screening of (bio) sorbent. The result based on "% Removal" values (Fig. 1) showed that *Brevundimonas* sp. ZF12 strain isolated from the hot-spring waters with the highest radium contamination has the highest uptake value of 45% removal. Consequently, ZF12 strain was selected as the best sorbing bacteria strain for detailed work. The neighbor-joining tree based on the 16S rRNA sequence of ZF12 strain is shown in Fig. 2.

3.3. Effect of chemo-physical factors on cadmium biosorption by ZF12 strain

3.3.1. Effect of biomass concentration on cadmium biosorption

The dosage of biosorbent strongly influences the extent of Cd biosorption by ZF12 strain. Across the increment of the concentration of biosorbent from 20 to 80 mg the removal percentage was increased from 43% to 66%. This observation was due to the increased adsorption surface and the availability of free adsorption sites.

Conversely, the quantity of biosorbed solute per unit weight of ZF12 strain decreased with increments of biosorbent concentration,

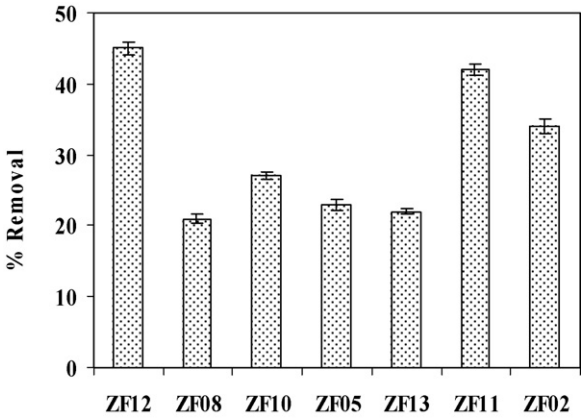

Fig. 1. Preliminary screening for selection of the best sorpting bacteria strain (Error bars show standard deviation).

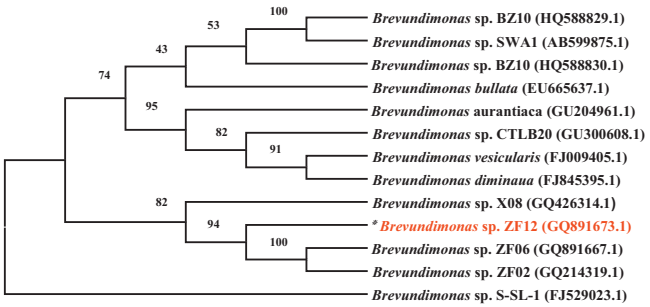

Fig. 2. Phylogenetic tree (the neighbor-joining tree) based on the 16S rRNA sequence of selected bacteria of *Brevundimonas* sp. ZF12 strain isolated from hot spring water in high background radiation area.

which may be due to the fact that the available solute was insufficient to completely cover the available exchangeable sites on the ZF12 strain, resulting in low solute uptake at high biomass concentration (Fig. 3).

Also, as suggested by Gadd et al. [27], a low specific uptake as the result of interference between binding sites, due to biosorbent concentration, cannot be overruled. This result is in good agreement with those obtained in other studies [28,29].

3.3.2. Effect of pH on cadmium biosorption

One of the most important factors affecting the biosorption process is the pH values of the solution. The result of the solution pH on Cd uptake by ZF12 strain showed the highest metal uptake capacity occurred at pH values of 6 and 8, therefore a pH value of 6 as selected for the other biosorption experiments (Fig. 4). The pH values of the final suspensions at equilibrium sorption condition and by the end of the experiment showed significant changes at higher pH (between 7 and 10). However this was not shown at low pH values. Also, at higher pH the solubility of metal complexes decreases to a great extent allowing metal hydroxide precipitation, which may complicate the sorption process [7]. In general, pH 3–6 has been found favorable for the biosorption of metal ions by microbial biomass [10].

3.3.3. Effect of cadmium concentration on the biosorption

An increase in the initial Cd concentration increased the mass transfer driving force of the metal ions between the aqueous solution and ZF12 strain phases which lead an increase in metal ions uptake [30]. The uptake of Cd gave a plateau at 250–350 ppm

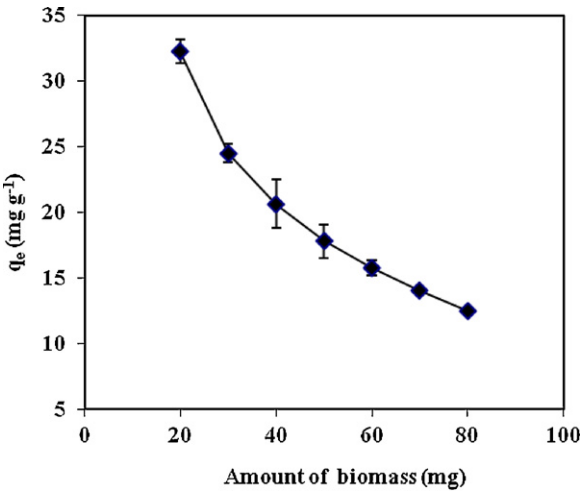

Fig. 3. Effect of biomass concentration on Cd biosorption by *Brevundimonas* sp. ZF12 strain (Error bars show standard deviation).

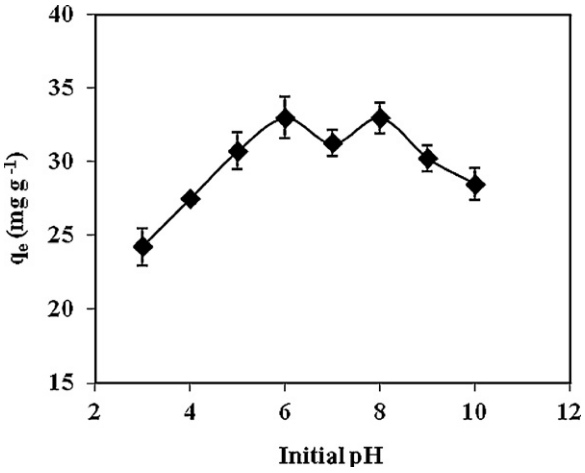

Fig. 4. Effect of pH values on Cd biosorption by *Brevundimonas* sp. ZF12 strain (Error bars show standard deviation).

showing the saturation of binding sites at higher concentration levels. However, within the range of initial Cd concentration (C_0) of 50–350 ppm, the percentages of biosorbed metals were decreased with increasing initial metal concentrations (Fig. 5). In fact, for an initial Cd ion concentration of 50 ppm, the ions removal achieved was 60% compared to 20% for 350 ppm within 2.5 h. This indicates that at higher metal concentrations, the available sites for biosorption were limited, consequently, the biosorption yields decreased [31].

3.3.4. Effect of temperature on cadmium biosorption

The effect of temperature on biosorption of Cd on lyophilized cells of ZF12 was investigated by testing different temperatures from 20 (293 K) to 45 °C (318 K). Results (Fig. 6) showed that the temperature had no significant effect on Cd biosorption. These findings indicated that the temperature was not a primary factor to influence upon Cd adsorption, and that Cd adsorption was independent of energy. The temperature of the adsorption medium could be important for energy dependent mechanisms in metal biosorption. Energy-independent mechanisms are less likely to be affected by temperature, since the processes responsible for biosorption in this case seems to be largely physico-chemical (electrostatic forces) in nature [18].

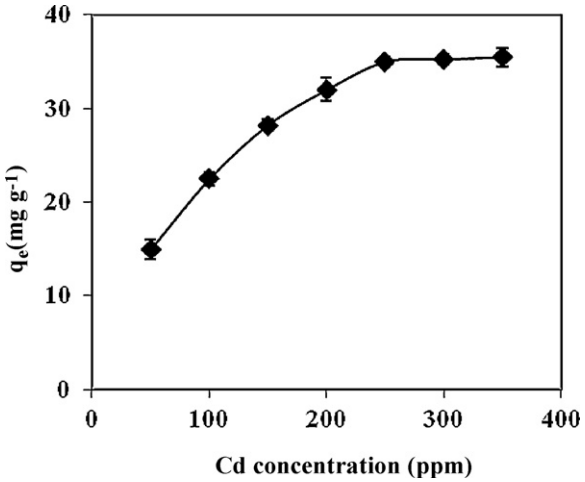

Fig. 5. Effect of Cd concentration on biosorption by *Brevundimonas* sp. ZF12 strain (Error bars show standard deviation).

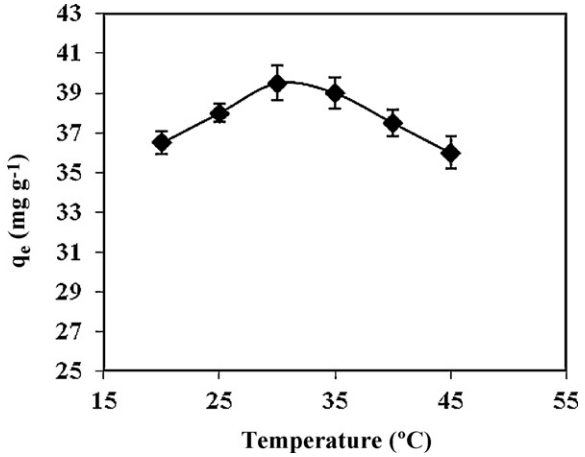

Fig. 6. Effect of temperature on Cd sorption by biomass *Brevundimonas* sp. ZF12 strain (Error bars show standard deviation).

3.3.5. Effect of contact time on cadmium biosorption

The time course of Cd adsorption depended on the nature of ZF12 strain that was used in this study. It is known that Cd ion adsorption by lyophilized cell of ZF12 strain, which is a metabolism-independent passive binding to cell walls, reaches equilibrium within 5–15 min (Fig. 7). The metal adsorption by the bacteria was also a rapid process, which took place within a few minutes. The Cd uptake by lyophilized cells in 15 min was 58.5 mg g^{-1}, which did not increase significantly up to 120 min. It was also obvious that various steps are involved in the transfer of metal from metal solution to binding sites. The most important and rapid step is the first phase in which the bulk transport of metal ions onto biomass takes place in a few minutes due to mixing and adjective flow [7].

3.4. Biosorption isotherm

Adsorption isotherm plays a crucial role in the predictive modeling procedures for the analysis and design of an adsorption system. Therefore, in this study, the adsorption data of Cd were tested with Langmuir and Freundlich isotherm models within a metal ion concentration range from 50 to 350 ppm at 30 °C (Fig. 8a and b). The equilibrium data are fitted well by the Langmuir adsorption isotherm showing a high value of determination coefficient (R^2 = 0.9966). Freundlich model was less accurate with a lower R^2 value of 0.9605. This suggests that Cd biosorption by ZF12 is more likely to be monolayer sorption than heterogeneous surface

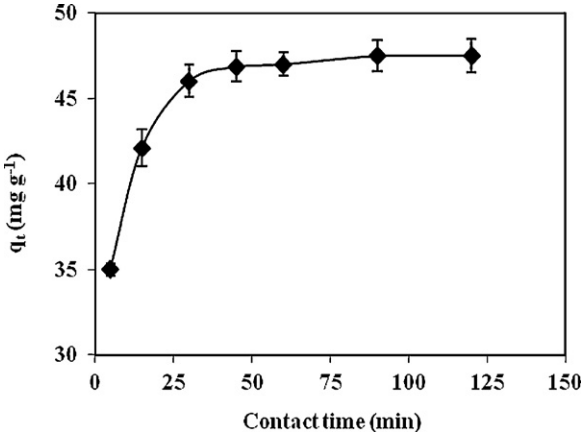

Fig. 7. Effect of contact time on Cd sorption by biomass *Brevundimonas* sp. ZF12 strain (Error bars show standard deviation).

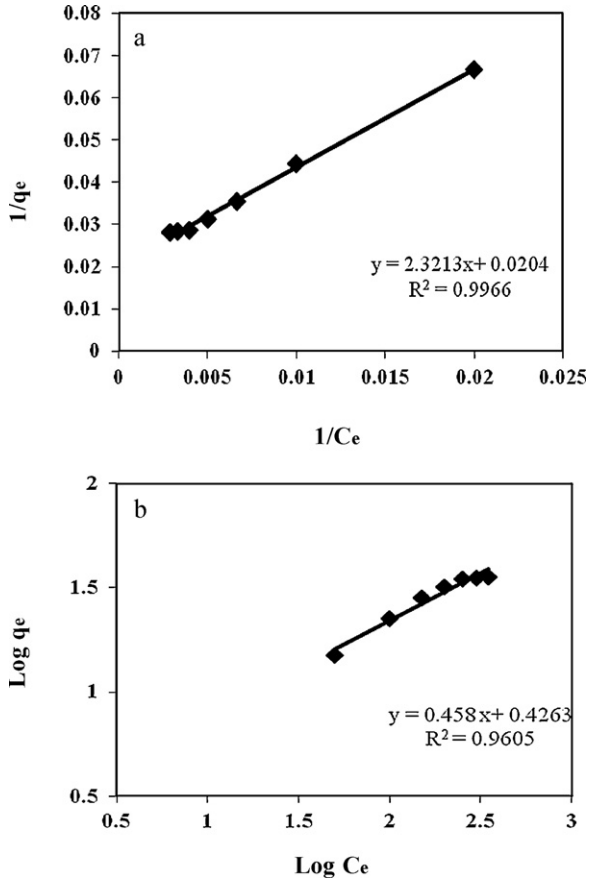

Fig. 8. The linear form of Langmuir (a) and Freundlich (b) adsorption isotherms of Cd by lyophilized cell of *Brevundimonas* sp. ZF12 strain.

adsorption. The Langmuir model assumes uniform energies of adsorption onto the surface of ZF12 strain and no transmigration of the adsorbate. Also the essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor for equilibrium parameter, R_L as given by the following:

$$R_L = \frac{1}{1 + bc_e} \quad (9)$$

where b is the Langmuir constant and C_0 is the highest Cd concentration. As reported by Wona et al. [32], the parameter R_L indicates the shape of the isotherm and nature of the biosorption process (irreversible $R_L = 0$, favorable $0 < R_L < 1$, linear $R_L = 1$ or unfavorable $R_L > 1$). The R_L was found to be 0.2472 for a concentration of 350 ppm of Cd ions confirming the favorable uptake of Cd process by ZF12 strain.

The various constants relating to the two models were calculated and are presented in Table 1. Similarly, biosorption results for Cd ions using *H. splendens, Pseudomonas veronii* 2E, and *Sargassum* sp. are found to follow the Langmuir model [3,5,33].

3.5. Biosorption kinetic

The time-course adsorption data showed that adsorption of Cd occurred rapidly within the first 100 min. This is quite normal because biosorption is considered as a spontaneous process which occurs very rapidly. Pseudo-second order kinetic model is more likely to predict kinetic behavior of biosorption with chemical sorption being the rate-controlling step. The linear form of pseudo first-order model and the linear plots of t/q_t versus t for the pseudo-second order model for the biosorption of Cd ions by ZF12 strain

Table 1
Isotherm and kinetic parameters obtained for the biosorption of Cd by *Brevundimonas* sp. ZF12 strain using the linear method (data calculated by equation of regression line obtained by software of Excel.2007).

Models	Parameters	ZF12
Isotherm		
Langmuir model	q_{max} (mg g^{-1})	49.01
	b (L mg^{-1})	0.0087
	R^2	0.9966
Freundlich model	K	2.66
	n	2.18
	R^2	0.9605
Kinetic		
Pseudo-first order model	q_e (mg g^{-1})	9.51 (cal.)
		48 (exp.)
	k_1 (min^{-1})	0.037
	R^2	0.9458
Pseudo-second order model	q_e (mg g^{-1})	47.61 (cal.)
		48 (exp.)
	k_2 (mg g^{-1} min^{-1})	−0.017
	R^2	0.992

were shown in Fig. 9a and b, respectively. The rate constants (k^2), R^2 and q_e values are given in Table 1. It is clear from these results that the R^2 value is 1 for the Cd biosorption by ZF12 cell. It can be inferred that the pseudo second-order kinetic model provides a good correlation for the biosorption of Cd ions by ZF12 strain in contrast to the pseudo first-order model.

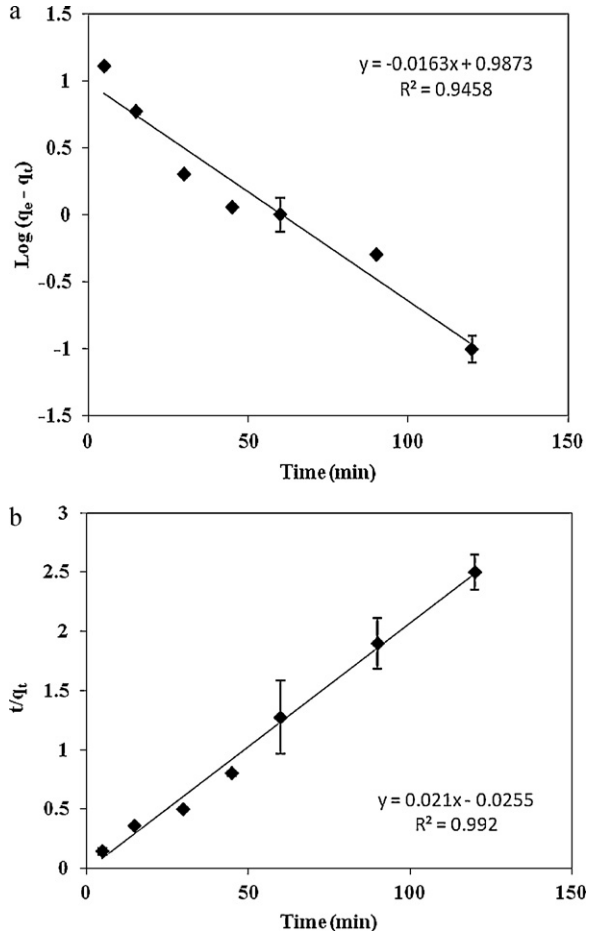

Fig. 9. The linear form of pseudo-first (a) and pseudo-second-order model (b) for Cd adsorption by lyophilized cell of *Brevundimonas* sp. ZF12 strain.

Table 2
Comparison of maximum adsorption capacities (q_{max}) of Cd with various biosorbents.

Adsorbent	q_{max} (mg g^{-1})	pH	Temperature (°C)	Reference
Alcaligenes sp.	10	4–8	25	[35]
Arthrobacter globifirmis	0.2	7	20	[36]
Arthrobacter viscosus	1.4	7	20	[36]
Gram-negative bacteria	13.5	6.7	30	[37]
Gram-positive bacteria	18.5	6.6	30	[37]
Bacillus jeotgali U3	53.5	7	30	[34]
Enterobacter sp.	46.2	5	30	[26]
Brevundimonas sp. ZF12	49.01	6	30	Present study

3.6. Comparison with other adsorbents

Table 2 compares maximum adsorption capacities obtained in this study with some other values reported in the literature. The adsorption capacity for Cd using the ZF12 strain is of the same order of magnitude or greater than what has been found using similar biosorbents [25,34–37].

3.7. Desorption studies

3.7.1. Determination of optimum desorption pH

In order to determine the optimum desorption pH showing higher efficiencies to remove the sorbed Cd ions from the biomass surface, a set of desorption experiments was carried out following the biosorption process. The results in Table 3 show that higher desorption efficiencies of above 90% were obtained using solutions with pH values of 2.0, 3.0 and 4.0 respectively. Using a solution with a pH value of 5 yielded an efficiency of 78.7%.

Similar results can be observed in the literature. It has been shown that HCl solution used for the desorption of copper and Cd provided an efficiency ranging between 70% and 85% for both metal ions, depending on the type of the biomass used in the study [38]. In addition, findings of the desorption study, which was examined by Lu et al. [26] are similar to those, using HCl at different pH values of the present study. In the mentioned study, using of HCl for different pH, desoprtion of Cd was nearly complete for pH > 3, while desorption efficiency of Cu and Pb reached 90% when pH was decreased below 2.0. Another study reported that solutions of Na_2EDTA, $K_4O_7P_2$, HNO_3, HCl and $(NH_4)_2C_2O_4{\cdot}H_2O$, could recover more than 90% of the Ni^{2+} and Cu^{2+} ions sorbed on the biomass, respectively [39].

3.7.2. Reusability of the ZF12 cells in consecutive biosorption–desorption cycles

In the reuse study, reusability performance of the ZF12 cells was investigated by using it a consecutive biosorption–desorption cycle repeated thrice. Desorption experiments were carried out using a solution pH of 2.0–5.0. The results revealed that each solution pH (except for a pH of 5.0) could desorbs Cd ions with a high percentage (>95%) in first cycle. This result emphasizes that each of the solution pH values used for the reusability study has powerful desorptive features to recover Cd ions sorbed onto the biomass.

On the other hand, the biomass showed a good performance even if it had been used in 3 cycles. The best performance shown by the biomass during the reuse study was obtained at a pH of 2.0. If the amount of metal ion sorbed on biomass in the first cycle (63.00 mg g^{-1}) is compared with the amount of desorbed metal ion in the last cycle in terms of all the solutions used for the desorption process, it can be clearly seen that pH 2.0 solutions showed an excellent performance. In the case of using the solution with a pH of 5.0, there was approximately one-third of difference between the amounts of metal ions sorbed on biomass in the first cycle

Table 3
Sorption performance of the *Brevundimonas* sp. ZF12 strain and desorption efficiency of the HCl solution used for the reuse study.

Cycle number	Process applied	q_e value (mg g^{-1})				Desorption efficiency (%)			
		pH 2.0	pH 3.0	pH 4.0	pH 5.0	(a)	(b)	(c)	(d)
		(a)	(b)	(c)	(d)				
1	*Bio.	63	58	57.5	56.5	97.6	96.9	96.5	78.7
	**Des.	61.5	56.2	55.5	44.5				
2	Bio.	57	51.5	51	50.5				
	Des.	52.5	46.5	45	24	92.1	90.2	88.2	47.5
3	Bio.	54	49.5	50.5	49				
	Des.	47.5	43	42.5	18	87.8	86.8	84.6	36.7

* Biosorption.
** Desorption.

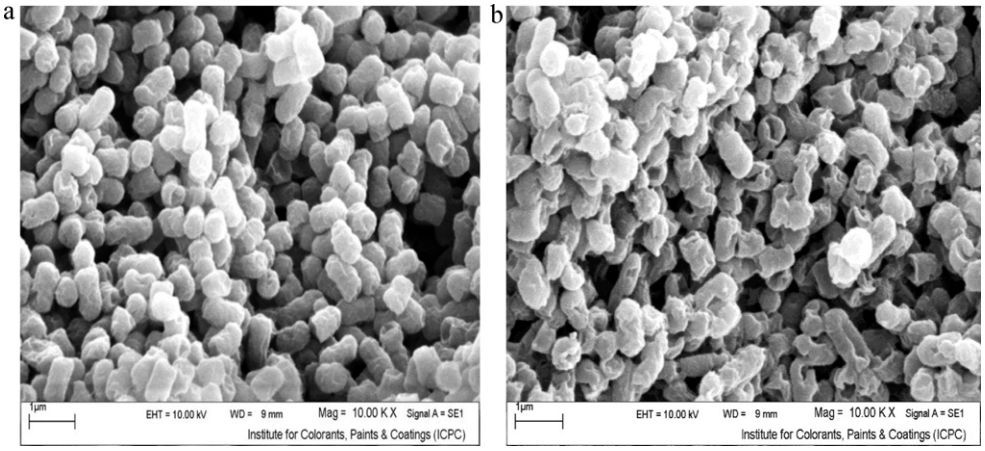

Fig. 10. Scanning electron micrographs of *Brevundimonas* sp. ZF12 strain cells before (a) and after (b) Cd stress.

(56.5 mg g^{-1}) with the amount of desorbed metal ion in the last cycle (18 mg g^{-1}).

Therefore solution of pH 5.0 used in this study can be assumed unsuitable for reusing of the ZF12 cells in Cd recovery.

3.8. SEM, XRD and FTIR analysis

The SEM micrographs of Cd-free and Cd-loaded ZF12 cells are shown in Fig. 10a and b, respectively. It is observed that the cell-surface morphology considerably changed after metal biosorption. Fig. 10b shows that the surface of metal-loaded cells looked vague, distorted and seemed to be damaged by the Cd ions.

The crystal phases of ZF12 cells before and after Cd biosorption were determined by X-ray powder diffraction (Fig. 11). The XRD of the Cd-free ZF12 cells contained a humped peak between 18° and 32°. After contamination with Cd the appearance of new peaks indicates that there was different crystals adsorption in Cd contaminated ZF12 cells and more complicated mechanisms would be involved in Cd biosorption. The appearance of low intensity peak indicates that adsorption would partially contribute to the removal of Cd by ZF12 cells.

The FTIR spectra of native ZF12 and Cd loaded biomass in the range of 400–4000 cm^{-1} were taken to obtain information on the nature of the possible ZF12-Cd ions interactions like complexation and presented in Fig. 12. The FTIR spectra of the control cells showed a number of peaks reflecting a complex nature of the ZF12 cell surfaces. There was a change in the intensity of the bands at different regions after 2 h of interaction with Cd.

A peak at 3300 cm^{-1} corresponds to the stretching bond of the N–H from amino group and indicates a bonded hydroxyl group. After the contact with Cd, the cell surface of ZF12 exhibited spectra with clear shifts of the N–H and OH stretching band to lower frequencies, two bands in the region of 2930 and 2850 cm^{-1} are assigned to the symmetrical and asymmetrical –CH– vibrations in lipids. The strong adsorption peaks at 1655 and 1540 cm^{-1} are attributed respectively to the amide I (–CO–) and amide II (–NH–) in proteins, the significant shifts in these peaks indicates the binding of Cd with amides I and II in cell surfaces of ZF12. A peak around 1455 is due to C–H bonding of CH_2 and CH_3 groups, an adsorption bond at the location 1080 cm^{-1} corresponds to the –COC– group vibrations in the cyclic structures of carbohydrates. The location of these bonds caused significance change for two conditions examined. At the lower wave numbers (580 cm^{-1}), there appeared an appreciable change in the spectra before and after Cd

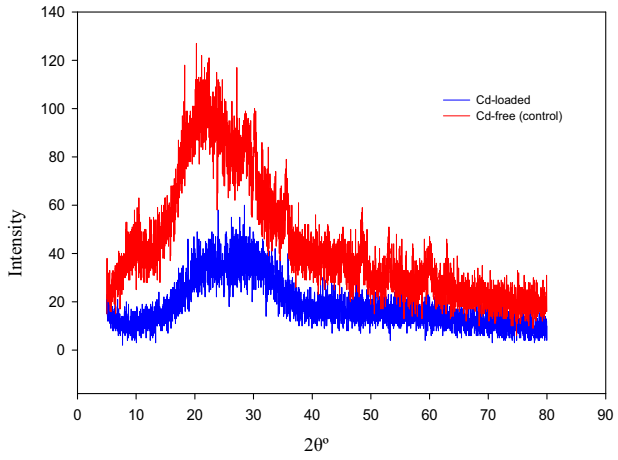

Fig. 11. X-ray diffraction profiles of dried powdered *Brevundimonas* sp. ZF12 strain cells before and after Cd-loading.

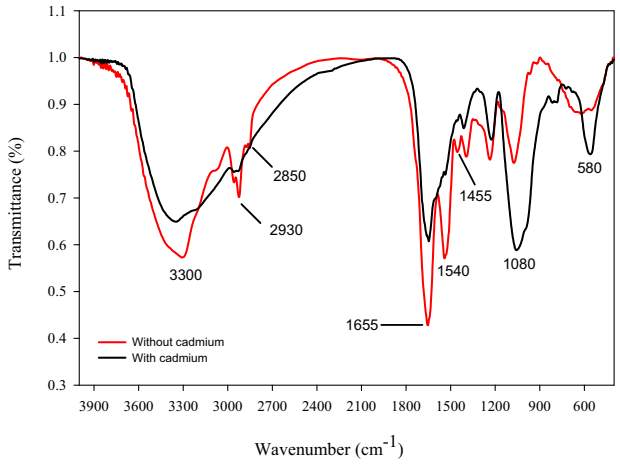

Fig. 12. Fourier transform infrared spectra of *Brevundimonas* sp. ZF12 strain cells before and after Cd-loading.

absorption, demonstrating that S, P containing groups contribute in cell-absorbing Cd. The above stated changes in peak locations and their intensities suggest that hydroxyl, carboxyl and carbonyl groups of saccharides and peptidic groups of proteins in ZF12 biomass are the most active groups for Cd absorption.

Taken as a whole, analysis of FTIR profiles corroborated that Cd sorption was highly attributable to the complexation of Cd with functional groups of proteins, polysaccharides and lipids of cell biomasses.

4. Conclusion

In this study, removal and recovery of Cd ions from aqueous solutions was examined under differential experimental conditions by a novel biosorbent *Brevundimonas* sp. ZF12, isolated from a high background radiation area. The differential parameters of the process, pH, and equilibrium time, were optimized at 6.0 and 60 min, respectively.

Increasing initial Cd concentration resulted in an increase in biosorption capacity of the biomass. The experimental data obtained from isotherm and kinetic studies were well fitted to Langmuir isotherm and pseudo second-order kinetic models. Among the different solutions pH, pH 2.0 showed the highest desorptive performance. Among several bacterial strains isolated, *Brevundimonas* sp. ZF12 strain is found to be an efficient cadmium biosorbent with the highest performance for Cd biosorption and could have important applications in Cd removal from wastewaters.

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