



Cadmium biosorption by *Stenotrophomonas humi* and *Micrococcus luteus*: kinetics, equilibrium and thermodynamic studies

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ABSTRACT

In the present study, the biosorption capacity of *Stenotrophomonas humi* and *Micrococcus luteus* has been assessed for removal of cadmium from the synthetic solution under varying Cd^{2+} concentrations (50–250 ppm), pH (2–8), and contact time (10–270 min). The maximum biosorption capacity (q_m) of *S. humi* and *M. luteus* were 97.08 and 42.55 mg/g at 30°C, respectively. The experimental isotherm data were analyzed using the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) equations. The equilibrium data fit well in the Freundlich isotherm for *S. humi* and *M. luteus*. The R_L values ranged between 0 and 1, and rate constant value of Cd^{2+} uptake demonstrated its efficient removal from the solution. Kinetic study showed that pseudo-second-order model describes the biosorption process better than the Lagergren pseudo-first-order and intraparticle diffusion model. The thermodynamic parameters such as free energy, entropy, and enthalpy change for the adsorption of Cd^{2+} have also been computed and discussed. Based on D–R isotherm value, physiosorption appears to be one of the major mechanisms for adsorption of Cd^{2+} by the bacteria. The interactions between heavy metals and functional groups on the cell wall surface of bacterial biomass were confirmed by Fourier transform infrared spectroscopy (FTIR) analysis, which indicate the possible removal of Cd^{2+} ions from the environment by *S. humi* and *M. luteus*.

Keywords: Physiosorption; Biosorption; Cd^{2+} uptake; FTIR

1. Introduction

Heavy metal pollution of environment is one of the major problems of growing magnitude, which results in severe health hazards, including prenatal and developmental defects as well as many biological effects on aquatic organisms. Industries, such as electroplating, plastic and paint manufacturing, mining and metallurgical processes, paper and pulp, petro-

chemical and battery manufacturing industries, are a potential source of pollution caused by the release of toxic heavy metals [1], like chromium, lead, mercury, arsenic etc. Cadmium is one of the largely used heavy metal in developing countries and is of major concern because of its nondegradable nature which often poses potential hazard to humans and the environment. Renal dysfunction (Fanconi Syndrome), bone degeneration (itai-itai syndrome), liver damage, and blood damage are the major consequences of chronic

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exposure to elevated level of Cd^{2+} . Cadmium also inhibits DNA replication and enzymatic activities. The International Agency for Research on Cancer (IARC) has classified cadmium as Class-I carcinogenic element [2]. Biological effects of cadmium may result in the structural changes in planktonic community [3].

The conventional methods for heavy metal removal include precipitation, lime coagulation, ion exchange, reverse osmosis, filtration, and solvent extraction [4]. Most of the above technologies involve high capital and regeneration costs [5]. These challenges led to the focus on other cost-effective methods such as the use of biological material for the adsorption of heavy metals. Several biomass has been reported to have high uptake capacities for heavy metals [6,7], microorganisms, due to high surface and contact area happen to be one among them which can easily interact with metals, adapt physiologically and remain active in the stressed environment [8]. Bacteria have been used previously in various heavy metal removal studies [9–11]. Bacteria can be specific to one or few metals [12] and bind high concentrations of heavy metals [13–16] according to a variety of mechanisms. They can potentially accumulate metals either by a metabolism independent (passive) or a metabolism-dependent (active) process and can remove heavy metals through bioaccumulation or biosorption. Metal ions after diffusion to the cell surface bound to functional groups present on the bacterial cell wall such as the carboxylate, hydroxyl, sulfate, phosphate, and amino functional groups. This step contains a number of passive accumulation processes, including adsorption, ion exchange, coordination, chelation and microprecipitation, which are fast and reversible [17,18].

The screening of cadmium-resistant microorganisms has been achieved by others [19–21] to determine the ability of their cadmium biosorption. Biosorption of Cd^{2+} by bacterial species is well studied [22,23]. However, there is little research to estimate the biosorptive capacity of Cd^{2+} ions by *Stenotrophomonas humi* and *Micrococcus luteus*. The objective of this research was to evaluate the biosorptive capacity of Cd^{2+} by cadmium-resistant bacteria in response to metal concentration, pH, and contact time. Main governing mechanism for Cd biosorption and related thermodynamic parameters were also determined while fitting the biosorption data to establish adsorption isotherm models.

2. Materials and methods

2.1. Sample collection, isolation and identification of Cd^{2+} -resistant bacteria

The industrial effluent samples were collected from 10 different sites of an electroplating industry located at the Pantnagar industrial area that is, State

Industrial Development Corporation of Uttarakhand Limited (SIDCUL) in the US Nagar district of Uttarakhand, India and employed for the analysis of various physico-chemical characteristics using standard methods [24] (Table 1). Effluent was used as a source of Cd^{2+} -resistant bacteria that are isolated in mineral salt media containing (g/L): Peptone, 10 $MgSO_4 \cdot 7H_2O$, 0.247, and NaCl, 5, in distilled water.

Two strains encoding Cd4 and Cd5 were selected as the most resistant isolates for Cd^{2+} by inoculating each isolate with increased concentration of Cd^{2+} (50, 100, 150, 200 and 250 ppm) until the growth is inhibited. The growth was measured by spectrophotometer (UV-5704 ECIL) at optical density of 660 nm in order to determine the minimum inhibitory concentration. Most resistant isolates, inoculated in nutrient agar plates, identified on the basis of morphological and biochemical properties by using the Gram staining and API 20 NE system (Analytical Profile Index, France), were used in subsequent experiments.

2.2. Preparation of reagents and biosorbent

A stock Cd^{2+} solution of 1,000 mg/L was prepared by dissolving 2.3709 g $CdSO_4 \cdot 8/3H_2O$ in a 1,000 mL of deionized water. The chemicals used for this study were of analytical grade and supplied by Sigma Aldrich (Sigma-Aldrich, St. Louis, MO). The heavy metals stock solutions were sterilized by autoclaving at a pressure of 1.5 atm and a temperature of 121°C for 10 min.

The bacteria were cultured in Nutrient broth (pH 7.0) that contains (per liter of deionized water): Peptone 10 g/L, Yeast extract 5 g/L, NaCl 5 g/L for 48 h at 30°C and then used in subsequent experiments.

Table 1
Initial physicochemical characteristics of the electroplating industrial effluent

Parameter	Effluent (value)	CPCB (1995)
Colour	Light yellow	–
pH	6.7 ± 0.9	5.5–9.0
BOD (mg/l)	96 ± 0.01	30
COD (mg/l)	315.6 ± 0.02	250
TS (mg/l)	542 ± 0.11	–
TDS (mg/l)	456 ± 0.01	2,100
TSS (mg/l)	86 ± 0.10	100
Cd (mg/l)	21.3 ± 0.01	2.0
Cr (mg/l)	165 ± 0.012	2.0
Ni (mg/l)	274 ± 0.02	3.0
Pb (mg/l)	25.4 ± 0.011	0.1
Cu (mg/l)	280 ± 0.01	3.0

Average ± SD from triplicate samples.

2.3. Batch biosorption

Experiments were conducted to optimize pH, metal concentration, contact time and to study the adsorption isotherms, Kinetics and mechanism. To study the effect of different concentration of metal ion, pH, and contact time, batch biosorption studies were carried out using 0.04 g bacterial cells at 30°C for initial metal ion concentration varying from 50–200 ppm, pH ranging from 2–8 and contact time from 10–270 min.

Biosorption isotherm experiment, employing the two bacteria separately, was carried out by using 0.04 mg of biosorbent dose in 100 mL of reaction volume with 200 ppm of Cd²⁺ and shaken at 150 rpm/min for 180 min. The temperature was kept at 30°C. Equilibrium was allowed to maintain between Cd²⁺ biosorbed and Cd²⁺ in solution in the experimental conditions. Kinetic study was also performed in the same conditions and analyzed at the time intervals ranging from 10 to 270 min.

2.4. Desorption experiment

Amount of both bacterial cells and heavy metal loading were doubled in the desorption experiment. HNO₃ was employed as a desorbing agent. Metal loaded biomass of two bacteria were filtered and then dried overnight at 60°C for subsequent desorption test. Cd²⁺ loaded biomass were then suspended separately in a series of HNO₃ solution at different concentration (0.1–0.14 mol L⁻¹) and agitated on a rotary shaker at 175 rpm. Biosorbent was washed with distilled water to maintain pH, and the cycle was repeated for five times. Reaction mixture was then subjected to filtration followed by analysis of metal ions by AAS. Percentage of the amount of the released metal ions in relation to the amount of metal ions adsorbed by the bacterial cells was used as a measure of desorption efficiency. The cell solution (3 mL from each flask) was filtered through 0.2 μm filter membranes and the supernatant was analyzed for metal ions, using atomic absorption spectrophotometer (AAS, GBC Avanta Ver. 1.33). An air–acetylene flame was employed and the working current/wavelength for Cd²⁺ was 4 mA/326.1 nm. Deuterium background correction was used. The amount of metal absorbed was calculated as mg/L and the metal uptake (mg/g dry wt.) was calculated according to the equation.

$$\text{Metal uptake} = V \frac{(C_I - C_F)}{W} \quad (1)$$

where C_I, initial metal concentration (mg/L); C_F, final metal concentration (mg/L); V, volume of reaction (L); W, total biomass (g).

2.5. FTIR analysis

Fourier transform infrared spectroscopy (FTIR spectra) for the samples under investigation was performed in order to give a qualitative and preliminary characterization of the main functional chemical groups present on the bacterial biomass which are responsible for heavy metal biosorption. Raw samples of bacterial biomass and biomass loaded with Cd²⁺ were analyzed using FTIR (Bio-Rad, FTS, 3000 MX) adopting KBr disk technique [25].

3. Results and discussion

3.1. Identification and growth response in presence of Cd²⁺

On the basis of results of Gram reaction and biochemical tests (Table 2), the strain Cd4 was identified as *S. humi* while the strain Cd5 was identified as *M. luteus*. Cd4 was found to be Gram-negative, rod-shaped, showing positive citrate, oxidase, gelatin, and nitrate reductase activity with ability to utilize maltose, lactate, citrate, and acetate as C-source. On the other hand, Gram-positive cocci strain Cd5 showed positive test for oxidase, urea and gelatin with ability to utilize propionate as C-source. Growth curves of both the bacteria are represented in Fig. 1. Growth pattern indicated that both bacteria grow rapidly during exponential phase even in the presence of Cd²⁺, although growth rate was decreased on increasing the concentration of Cd²⁺ for both bacteria. *S. humi* (Fig. 1(a)) and *M. luteus* (Fig. 1(b)) showed no further increase in growth after 40 h of incubation period. Rapid increase in growth was due to the presence of highly active enzymes during exponential phase. At highest concentration of Cd²⁺, a marked decrease in optical density was observed with 275 ppm found to be MIC for both bacterial cells.

3.2. Effect of increasing metal concentration on tested bacteria

The effect of initial metal concentration on metal biosorption by *S. humi* and *M. luteus* was analyzed at pH 7.0 (Fig. 2(a)). The maximum biosorption for *S. humi* and *M. luteus* were 148 and 88 mg/L at the initial Cd²⁺ concentrations of 200 mg/L. The biosorption rate of the metal ions increased with an increase in initial metal concentration up to 200 ppm. The increase in biomass adsorption capacity with the increasing metal concentration has been previously reported for both single and mixed metal solutions and is attributed to the higher mass transfer and kinetic energy, thus the increased probability for

Table 2
Biochemical tests for *S. humi* and *M. luteus*

Effluent bacteria	Cd4	Cd5
<i>Morphological</i>		
Colony colour	Yellow	Yellow
Gram nature	–	+
Cell morphology	Rod	Cocci
motility	+	+
<i>Biochemical test</i>		
Citrate	+	–
Oxidase	+	+
Urea	–	+
Gelatin	+	+
Nitrate reduction	+	–
L-leucine	–	–
Hydrolysis of Tween 80	–	–
<i>Utilization of C-sources</i>		
Maltose	+	–
DL-Lactate	+	–
DL-3-Hydroxybutyrate	–	–
Citrate	+	–
Acetate	+	–
Lactose	–	–
Propionate	–	+
Malate	–	–

collision between metal ions and the biosorbents [26]. No further increase in percentage of biosorption after 200 ppm metal concentration may be attributed to unavailability of free binding sites on biosorbent for Cd^{2+} biosorption. Increase in metal uptake on increasing concentration was also confirmed by others [11].

3.3. Effect of contact time

Effect of contact time on biosorption of Cd^{2+} ions by *S. humi* and *M. luteus* was observed from 10 to 270 min (Fig. 2(b)). Maximum biosorption efficiency was observed at 180 min of contact time for both bacterial biomass. Thus, this represents the equilibrium time that was used in all subsequent experiments. Obtained experimental data were used to study the kinetics of biosorption. 180 min of equilibrium time was also observed for other bacterial species [27].

3.4. Effect of pH

Biosorption capacities for Cd^{2+} increased with an increase in pH until reaching the optimum at pH 7.0 for *S. humi* and *M. luteus* (Fig. 2(c)). However, at pH higher than 7.0, Cd^{2+} ions begin to precipitate for *S. humi* and *M. luteus*. At low pH, protons would compete

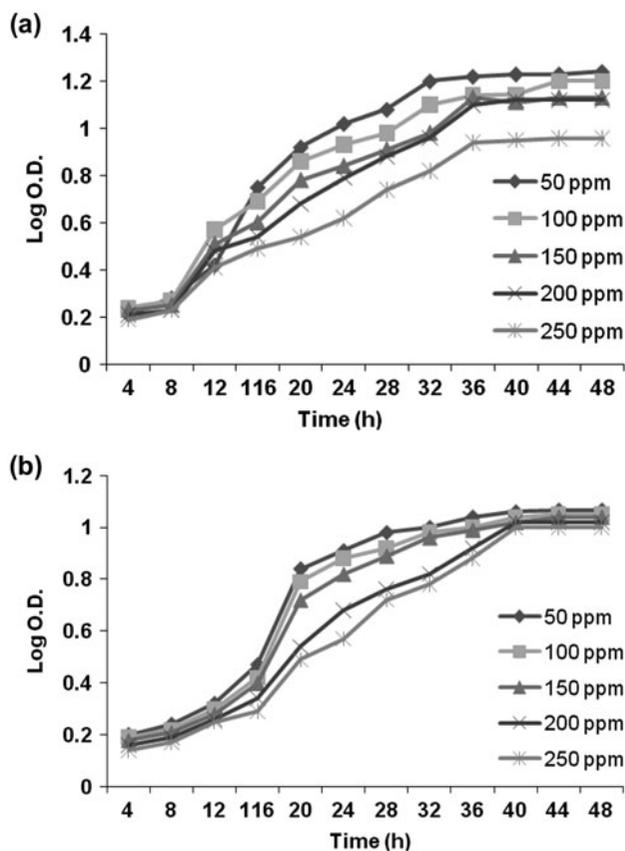


Fig. 1. Growth curve of (a) *S. humi* and (b) *M. luteus* in presence of Cd^{2+} .

with metals for the active sites responsible for the biosorption, would have declined the metal sorption. At low pH, all the binding sites may be protonated, thereby even desorbed all the metals bound with biomass [28]. As the pH increased, more ligands such as carboxyl, phosphate, imidazole, and amino groups would be exposed and carried negative charges with a subsequent attraction of metallic ions with positive charge and biosorption onto the cell surface [29].

3.5. Equilibrium studies

Equilibrium biosorption data of Cd^{2+} are represented in Fig. 3. The pollutant removal efficiency of a biosorbent can be determined by the use of these data. Therefore, to optimize the design of sorption system to remove heavy metals from effluents, it is important to establish the most appropriate correlation for the equilibrium curves [30]. Biosorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich models are commonly used to fit experimental data when solute uptake occurs by monolayer biosorption [31,32].

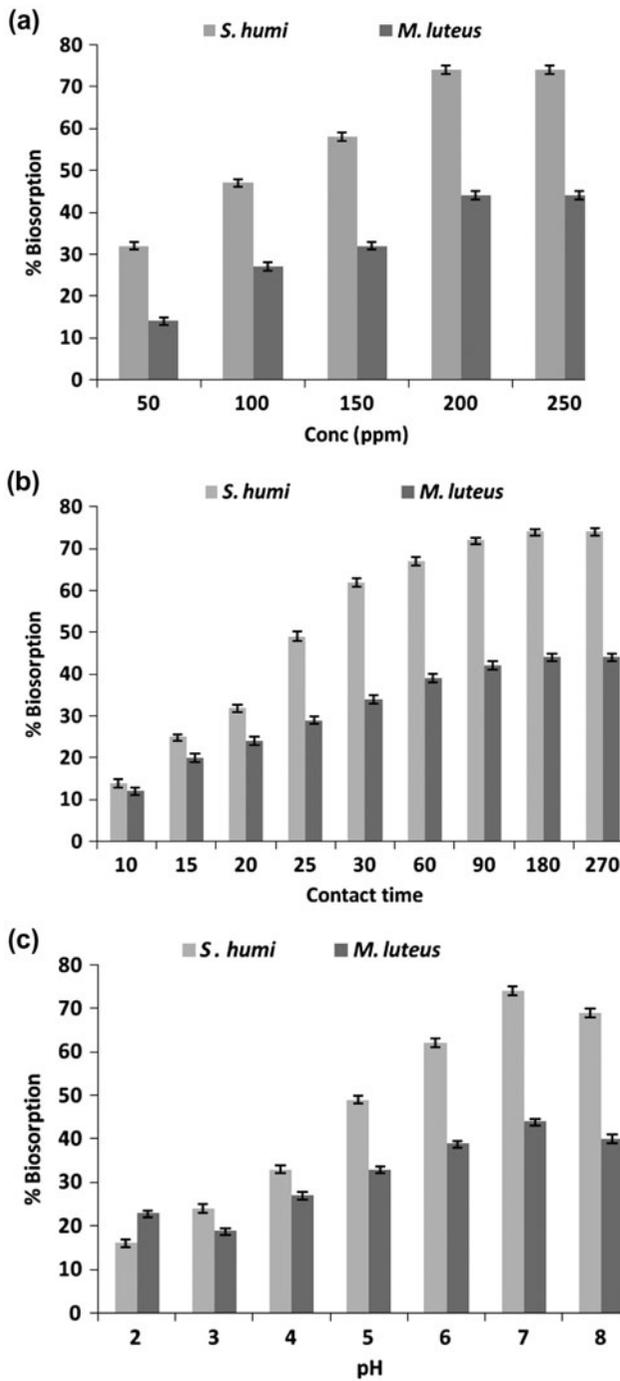


Fig. 2. Cadmium uptake by *S. humi* and *M. luteus*: (a) effect of different cadmium concentration(mg/l), (b) effect of different contact time (min) and (c) effect of different pH.

Langmuir isotherm assume monolayer biosorption, and is described by Eq. (2):

$$\frac{1}{q_e} = \left(\frac{1}{bQ_m} \right) \frac{1}{C_e} + \frac{1}{Q_m} \quad (2)$$

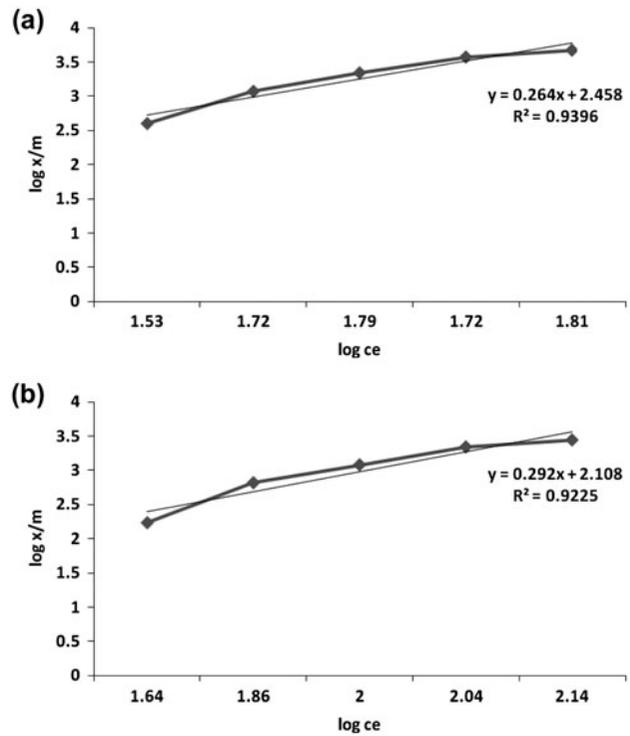


Fig. 3. Freundlich isotherm for cadmium biosorption by (a) *S. humi* and (b) *M. luteus* respectively.

The Freundlich isotherm is described by Eq. (3):

$$\frac{X}{M} = K_F C_e \frac{1}{n} \quad (3)$$

where q_e and Q_m are the equilibrium and maximum uptake capacities (mg/g biosorbent), respectively, C_e is the equilibrium concentration (mg/L solution), b is the equilibrium constant, X is the amount of impurities absorbed at equilibrium (mg/L), M is the mass of adsorbent (g), K_F and n are Freundlich constants characteristic of the system. The value of Langmuir constant b , can be obtained by a plot of $1/q_e$ vs. $1/C_e$ while Freundlich constant K_F and n can be determined by plotting $\log X/M$ vs. $\log C_e$. The model parameters were tabulated in Table 3. The experimental data were best described by the Freundlich isotherm (Fig. 3). The regression coefficient (R^2) was 0.94 for *S. humi* while 0.92 for *M. luteus* in the Freundlich isotherm (Table 3).

In order to predict the efficiency of adsorption process, the dimensionless equilibrium parameter R_L was determined using equation [33,34].

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where C_0 is the initial concentration and b is the Langmuir constant. The value of R_L for initial cadmium

Table 3
Langmuir, Freundlich and D–R isotherm parameter values for Cadmium ion biosorption at pH 7

Biosorbent	Langmuir constants			Freundlich constants			D–R constants		
	b (1/g)	Q_m (mg/g)	R^2	K_f	n	R^2	E	β	R^2
<i>S. humi</i>	0.21	97.08	0.73	287	3.8	0.94	0.91	0.61	0.93
<i>M. luteus</i>	0.26	42.55	0.68	127	3.4	0.92	0.86	0.67	0.92

concentration for both *M. luteus* and *S. humi* were found to be 0.019 for *M. luteus* and 0.023 for *S. humi*. These value ($R_L < 1$) indicated that adsorption was favorable.

In order to understand the adsorption type and mechanism, the equilibrium data were applied to Dubinin–Radushkevich (D–R) isotherm model [35]. The linearized form of D–R equation is expressed as the following:

$$\ln q_e = \ln q_{mDR} - \beta \varepsilon^2 \quad (5)$$

where q_{mDR} is maximum uptake amount of cadmium ions by biosorbent (mg/g), β is the constant linked to sorption energy (mol^2/kJ^2) and ε is the Polanyi potential [36] which is expressed as $RT \ln(1 + 1/C_e)$, where R and T are the gas constant (kJ/molK) and temperature (K), respectively. The plot of $\ln q_e$ vs. ε^2 results is a straight curve (Fig. 4). The slope of the D–R plot provides the β constant value, while q_e is calculated from the intercept of the plot (Table 3). The mean free energy of biosorption, E can be approximated using the obtained β value from D–R isotherm via the following equation [33,37]:

$$E = \frac{1}{(2\beta)^{0.5}} \quad (6)$$

E can be further described as the energy needed to transfer one mole of cadmium ion (sorbate) to the surface from infinity (that is, bulk fluidic environment).

The value of E is used to determine the governing adsorption mechanism whereby an E value lesser than 8 kJ/mol indicates the predominance of physisorption mechanism, while an E value higher than 8 kJ/mol indicates that chemisorption is the main governing mechanism [38]. The fact that E value is lower than 8 kJ/mol for both bacterial cells (Table 3) further validated that physisorptions was the main governing biosorption mechanism in present study.

3.6. Kinetics of metal uptake

The kinetic mechanism of Cd adsorption was studied to evaluate the uptake rate of *M. luteus* and

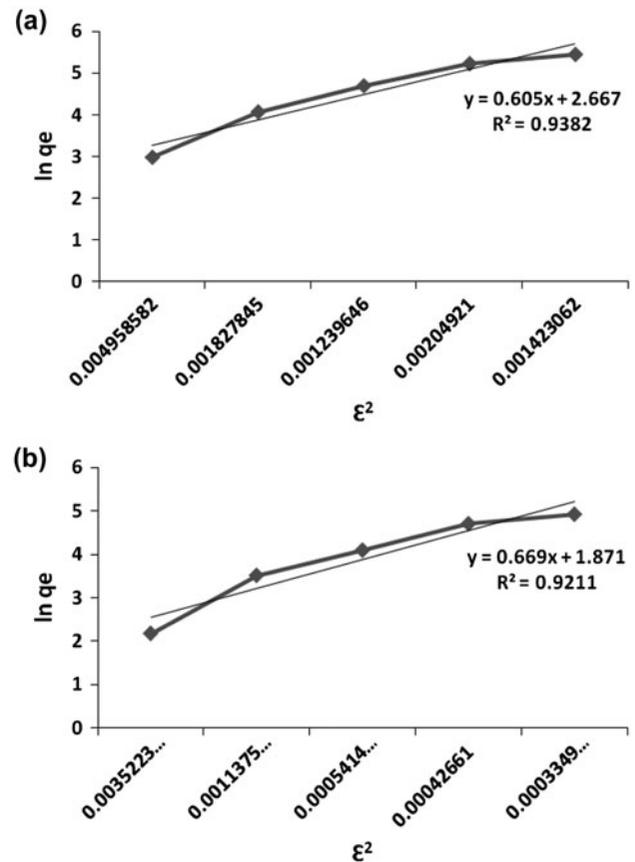


Fig. 4. D–R isotherm model for (a) *S. humi* and (b) *M. luteus* respectively.

S. humi, the effectiveness of Cd removal from synthetic solution and its possible release. In order to describe the kinetic models of the biosorption, data of Cd adsorptions by *M. luteus* and *S. humi* have been modelled by Lagergren pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetics model (Table 4).

The Lagergren pseudo-first-order equation is the most widely used in liquid phase metal sorption processes [39] and is given as:

$$\log(q_e - q_t) = \frac{\log q_e - K_1}{2.3} \times T \quad (7)$$

where K_1 (min) is the Lagergren rate constant of adsorption, and q_e and q_t are the amounts of metal adsorbed ($\mu\text{g/g}$) at equilibrium and at any time t , respectively. The K_1 value, calculated from the graph plotted between $\log(q_e - q_t)$ and time T (min) and the correlation coefficients (R^2), indicated the adequate model to describe the kinetics.

Pseudo-second-order kinetic model is also applied in the form of linear equation as [40] (Fig. 5):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where K_2 (g/mg min) is the rate constant of the pseudo-second-order equation, q_t (mg/g) is the amount of biosorption time t (min) and q_e is the amount of biosorption equilibrium (mg/g). Plot of t/q_t vs t provides the value of the biosorption rate constants (K_2).

Experimental data are also analyzed in terms of intraparticle diffusion model by using following equation [41] (Table 4):

$$q_t = K_{id} t^{0.5} + C \quad (9)$$

where K_{id} is the intraparticle diffusion rate constant ($\text{mg}/(\text{g min}^{-0.5})$) and C is the intercept.

The relationship between concentration and rate followed a kinetic of pseudo-second-order for *S. humi* and *M. luteus*. Greater value of R^2 represented better fitness of experimental data (Table 4). The study of kinetics of adsorption (from 10 to 270 min), in addition, confirmed the ability of *M. luteus* and *S. humi* to remove Cd^{2+} from the medium according to different rate order model. Moreover, these results demonstrated that *M. luteus* and *S. humi* interacts with Cd^{2+} ions and efficiently adsorb them.

3.7. Thermodynamic parameters

Thermodynamic parameters were also calculated in order to explain the nature of adsorption using following equation [33,37]:

$$K_c = \frac{C_A}{C_R} \quad (10)$$

Table 4

Kinetic parameters values for pseudo-first-order, pseudo-second-order and intraparticle diffusion for Cd^{2+}

Biosorbent	Lagergren first-order		Pseudo-second-order		Weber and Morris	
	K_1 (min^{-1})	R^2	K_2 ((g/mg)min)	R^2	K_{id} ((mg/g)min ^{-0.5})	R^2
<i>S. humi</i>	0.052	0.64	0.017	0.764	57.18	0.76
<i>M. luteus</i>	0.024	0.68	0.03	0.754	33.36	0.75

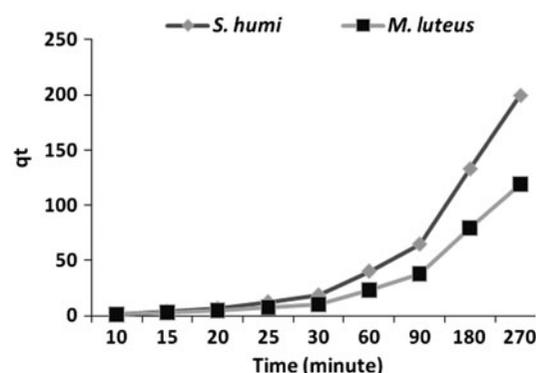


Fig. 5. Kinetics of metals removal by Pseudo-second-order for Cd^{2+} (\diamond) *S. humi*. (\blacksquare) *M. luteus*.

$$\Delta G^\circ = -RT \ln K_c \quad (11)$$

where K_c is the equilibrium constant, C_A is the solid phase concentration in equilibrium (ppm), C_B , the equilibrium concentration in solution (ppm), T is the temperature (K) and R is universal gas constant (8.314 J/mol K) [42]. ΔG° represents changes in free energy. The thermodynamic parameters are tabulated in Table 5. The values of ΔH and ΔS were calculated from the intercept and slope of a plot of $\log K_c$ versus $1/T$ plots. The negative value of enthalpy change ΔH° ($-3.16 \text{ kJ mol}^{-1}$ for *S. humi* and $-0.28 \text{ kJ mol}^{-1}$ for *M. luteus*) indicated that process was exothermic thereby demonstrating that process was energetically stable. The positive standard entropy change ($0.05 \text{ kJ mol}^{-1} \text{ K}^{-1}$ for *S. humi* and $0.03 \text{ kJ mol}^{-1} \text{ K}^{-1}$ for *M. luteus*) indicated the increasing randomness at the solid–solution interface during the adsorption process [43]. The negative Gibbs's Free Energy (ΔG°) value at 30°C confirmed that process was favorable and spontaneous.

3.8. FTIR analysis

The FTIR analysis was done, in the range of $500\text{--}4,000 \text{ cm}^{-1}$, to confirm the presence of functional groups responsible for the biosorption process (Figs. 7 and 8)). The frequency of the absorptions provides information about structure, conformation and intermolecular interactions [44]. Adsorption peaks in

Table 5
Thermodynamic parameters for biosorption of cadmium

Biosorbent	Temp. (K)	K_c	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
<i>S. humi</i>	298.15	1.7	-1339.7	-3.16	0.05
	303.15	2.86	-2638.4		
	308.15	1.94	-1670.7		
<i>M. luteus</i>	298.15	0.5	-1,727	-0.28	0.03
	303.15	0.78	-625.9		
	308.15	0.59	-1,342		

the FTIR of *S. humi* reflect the complex nature of the biosorbent. Binding of Cd^{2+} ions with amino and hydroxyl group was primarily responsible for the change in peak position. Peaks in the region of $3,400\text{--}3,350\text{ cm}^{-1}$ are due to the stretching of the N–H bond of the amino group and indicates the presence of bonded hydroxyl group [45]. The absorption peak at $2,900\text{ cm}^{-1}$ is due to asymmetrical CH_2 vibrations for *S. humi*, while a peak at $2,956\text{ cm}^{-1}$ resulted due to the stretching of asymmetrical CH_3 vibration in the FTIR spectra of *M. luteus*. Other characteristic peaks for *M. luteus* at $1,240$, $2,876$, $1,313$ and 550 cm^{-1} are due to the vibration of phosphate or carboxyl moieties, symmetrical CH_3 vibrations, stretching of C–O of carboxylic acids and glycogen, respectively. A change in the spectral pattern was observed at $\sim 1,240\text{ cm}^{-1}$ can be attributed to vibrations of either phosphate [46] or carboxyl moieties [47]. Interaction of Cd with the cells may occur in association with both groups [e.g. 48]. The absorption peaks in the range of $1,250\text{--}1,256\text{ cm}^{-1}$ in the FTIR spectra of both bacterial species indicates the PO_2 asymmetric stretching band. The absorption peaks at $1,742$ and $1,739\text{ cm}^{-1}$ are assigned to $>C=O$ ester stretching vibration mainly due to triglycerides. Presence of amine, hydroxyl, carboxyl and phosphate groups in the bacterial cells was confirmed by the spectral data. FTIR results suggest that Cd binding

onto the bacterial biomass involves either phosphoryl or carboxyl sites, or both.

3.9. Desorption

Desorption experiments is carried out for biomass and heavy metal regeneration. Effect of HNO_3 concentration on desorption efficiency was illustrated in Fig. 6. Lowest efficiency of 55 and 45% was obtained

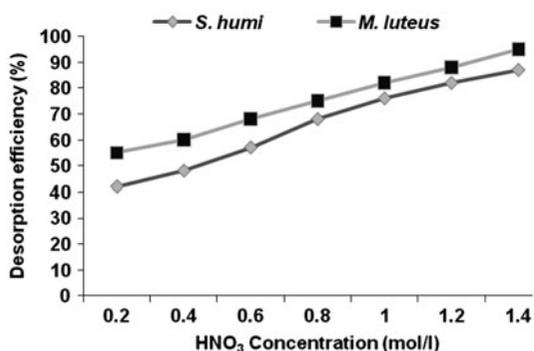


Fig. 6. Desorption of cadmium ions from (\diamond) *S. humi* and (\blacksquare) *M. luteus* with different concentrations of HNO_3 solution.

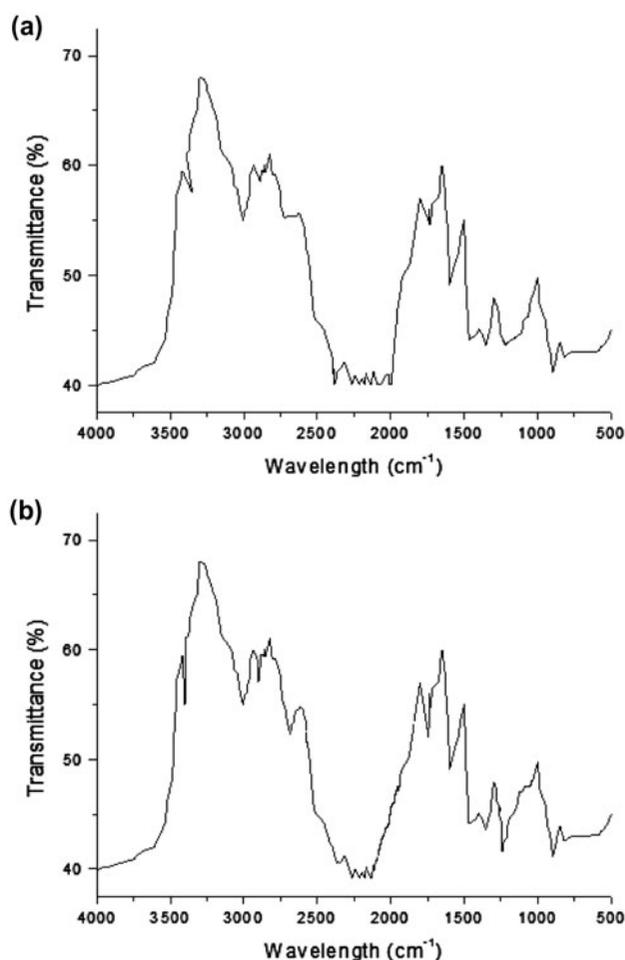


Fig. 7. FTIR spectra of *S. humi* (a) control (b) Cd^{2+} loaded biomass.

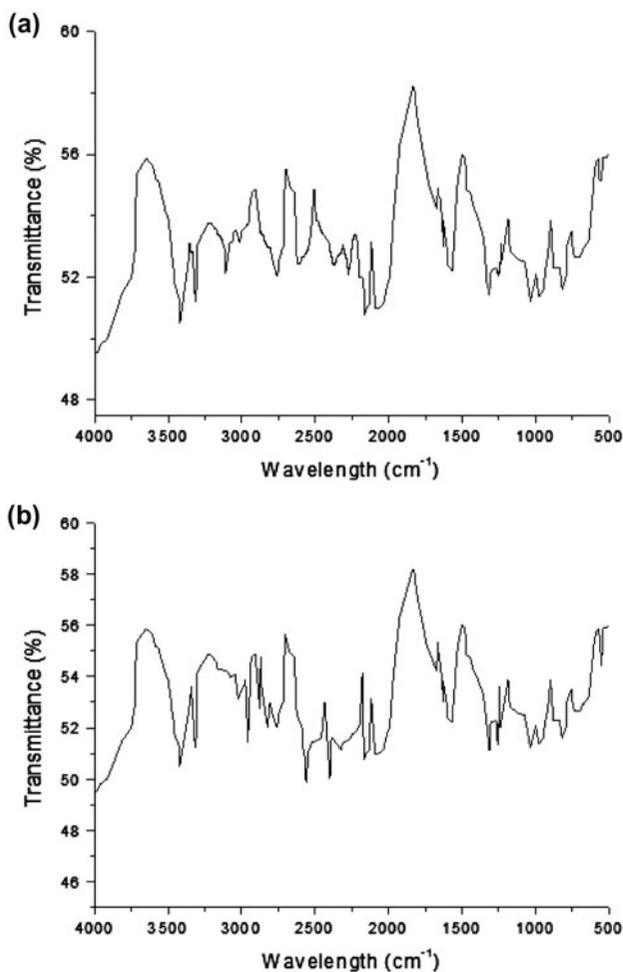


Fig. 8. FTIR spectra of *M. luteus* (a) control (b) Cd^{2+} loaded biomass.

for *S. humi* and *M. luteus*, respectively at 0.02 mol/L HNO_3 concentration. Desorption efficiency was increased with increase in HNO_3 concentration with maximum efficiency of 95 and 87% for *S. humi* and *M. luteus*, respectively. Efficiency of desorption is based on the competition between protons of desorbing agent, (acid) and the heavy metal ions bound to active sites, which will be released if eluant concentration is high enough and there is no steric impediment [49].

4. Conclusion

S. humi and *M. luteus* were isolated from industrial waste water. Results confirmed that both bacteria are suitable for cadmium removal from a concentration of 200 mg/L. *S. humi* was found to be more efficient for biosorption of Cd^{2+} ions than *M. luteus* as indicated by the value of Q_m . These bacteria had a high

adsorption capacity for the treatment of Cd containing wastewaters. The mechanism of biosorption includes mainly ionic interactions and formation of complexes between metal cations and acidic sites in the cell wall of bacteria and it was confirmed by FTIR results. Biomass of both the bacteria can be regenerated efficiently with an efficiency of 95 and 87% for *S. humi* and *M. luteus*. As such, the study clearly demonstrated that the native microorganisms of metal polluted area could be used as an effective tool for the recovery and removal of toxic metals from the contaminated site.

Abbreviations

b	—	Langmuir constants related to sorption energy (g^{-1})
C_e	—	equilibrium concentration (mg/L)
C_F	—	final metal concentration (mg/L)
C_I	—	initial metal concentration (mg/L)
D–R	—	Dubinin–Radushkevich
ε	—	polanyi potential (kJ/mol)
E	—	sorption energy (kJ/mol)
FTIR	—	Fourier Transform Infrared Spectroscopy
K	—	empirical constants of Freundlich isotherm (mg/g)
K_2	—	rate constant of the second-order equation (g/mg min)
K_f	—	sorptive capacity
K_{id}	—	intraparticle diffusion rate constant (mg/(g min ^{-0.5}))
K_1	—	Lagergren rate constant of adsorption (min)
n	—	sorptive intensity
q_e	—	specific metal biosorption
q_{max}	—	maximum adsorption capacity of the metal ion (mg/g)
q_t	—	amount of biosorption (mg/g) at time t (min)
R	—	universal gas constant (J/mol K)
R_2	—	regression coefficient
T	—	solution temperature (K)
V	—	volume of metal solution (L)
β	—	constant related to biosorption energy (mol/J) ²
ΔG°	—	Gibbs free energy change (kJ/mol)
ΔH°	—	change in enthalpy (kJ/mol)
ΔS°	—	change in entropy (kJ/mol K)

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