Removal of cadmium from aqueous solution by immobilized *Microcystis aeruginosa*: Isotherms, kinetics and thermodynamics

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Abstract: The *Microcystis aeruginosa* (MA) was immobilized on sodium alginate and used as biosorbent for removal of Cd(II) ions from aqueous solution. The biosorption process is pH dependent, and the optimum biosorption was observed at pH 6.0 with the biosorption capacity of 98.38 mg/g. Among Langmuir, Freundlich and Temkin isotherm models, the Freundlich and the Temkin isotherm fit well with the experimental data. Cd(II) ions biosorption follows the pseudo-second-order kinetic model. The rate controlling mechanism study reveals that film diffusion is the rate-limiting step and intraparticle diffusion is also involved in biosorption. Thermodynamic parameters, such as Gibbs free energy (ΔG°), the enthalpy (ΔH°) and entropy (ΔS°) were calculated, and revealed that the biosorption process is spontaneous, exothermic and random. Furthermore, the immobilized MA can be regenerated using 0.1 mol/L HCl solutions.

Key words: cadmium; immobilized Microcystis aeruginosa; biosorption; isotherms; kinetics; thermodynamics

1 Introduction

The environmental pollution increases by toxic metals, because of their carcinogenic properties, non-biodegradability and bio-accumulation [1]. Every year, large amounts of wastewater containing cadmium is produced by the metal plating, metallurgical alloying, mining, ceramics and other industrial activities [2–3]. Cadmium is one of the most toxic metals of considerable environmental and occupational concern for it combines with sulfhydryl group in protein and restrains the activity of enzyme, and it can be ingested by humans, causing severe kidney and bone damage or even death [4].

There are various methods to remove heavy metals, such as filtration, chemical precipitation, biosorption, electrodeposition, membrane systems, and ion exchange process [5]. Compared with other methods, the biosorption process has received increasing attention for removal and recovery of heavy metals from effluents even from dilute solution because of low operating cost and high efficiency [6–7]. Many scientists focus on finding biosorbents by generating low-cost alternatives in recent years [8], and many new biosorbents have been

found to be able to remove heavy metals from water system [4], such as algae [9–10], bacteria [11], fungi [12] and yeast [13]. *Microcystis aeruginosa* (MA) is an abundantly occurring bloom cyanobacterium worldwide, with several functional chemical groups such as amino, amido, sulfate and carboxyl on algal cell surface. These groups can attract and sequester heavy metal ions, that is why the algae proved to be the most promising sorbent for heavy metal recovery [14].

The free application of biomass as a biosorbent has been limited by problems associated with physical characteristics of these materials, but immobilization of the biomass could overcome these disadvantages by providing ease of regeneration and reuse of the biomass, mechanical strength, easier solid-liquid separation and so on [5]. Nowadays, there are several methods of immobilization including biosorption, covalent binding, embedding and cross bonding in gel. Immobilization of algal biomass is usually obtained by the entrapment of the cells into a matrix of the natural polymers such as alginate, chitosan, chitin and cellulose derivatives [15–16]. Alginate, as a skeletal component of marine algae, is commercially available as sodium salt of alginic acid at low cost, and it has the property of being strong

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and at the same time being flexible.

This work was aimed at using immobilized *Microcystis aeruginosa* (MA) to remove cadmium from aqueous solution in a batch system. The factors that effect biosorption capacity, such as pH, initial cadmium concentration, temperature and time, were examined. So as to better understand the biosorption characteristic, and some isotherm, kinetic and thermodynamic models were employed to evaluate the biosorption process.

2 Materials and methods

2.1 Main instruments and materials

All chemicals used in this work were of analytical grade obtained from Tianjin Pharmaceutical Co. Ltd. or Sinapharm Chemical Reagent Co. Ltd. in China. Ultrapure water was prepared by a pure hyperfiltration water system (Labconco, Water Pro Plus, USA). Stock solution of Cd(II) ions (1000 mg/L) was prepared using $Cd(NO_3)_2 \cdot 4H_2O_1$ The solutions of different concentrations used in various experiments were obtained by dilution of the stock solution. The concentration of Cd(II) ions was determined by the flame atomic absorption spectrometry (FAAS) (PerkinElmer AA700, USA).

2.2 Routine algal culture and acclimatization

The Microcystis aeruginosa used in this work was obtained by the Institute of Hydrobiology, Chinese Academy of Sciences. It was cultivated in the BG11 culture medium (500 mL) in a light incubator (2000 lux) at 298.15 K for 15 d, where the composition of the medium was as follows: 1.5 g NaNO₃, 0.04 g $K_2HPO_4 \cdot 3H_2O$, 0.075 g MgSO₄ $\cdot 7H_2O$, 0.036 g CaCl₂·2H₂O, 0.006 g citric acid, 0.006 g Ferric ammonium citrate acid, 0.001 g disodium EDTA salt, 0.02 g Na₂CO₃, and 1 mL trace elements solution A₅ in 1 L of ultra-pure water. The composition of the trace elements solution A₅ was as follows: 2.86 g H₃BO₃, 1.81 g MnCl₂·H₂O, 0.222 g ZnSO₄·7H₂O, 0.079 g $CuSO_4 \cdot 5H_2O$, 0.39 g $Na_2MoO_4 \cdot 2H_2O$, 0.049 g $Co(NO_3)_2 \cdot 6H_2O$ in 1 L of ultra-pure water. The initial pH of the medium was adjusted to 7.0-7.3 by using 0.1 mol/L HCl and 0.1 mol/L NaOH solutions.

2.3 Immobilization of Microcystis aeruginosa

After cultivation, 500 mL algae biomass (about 3×10^5 cells/mL) was harvested by centrifugation (2500 r/min for 15 min), 50 mL of algae suspension was obtained by removing 450 mL of supernate. Sodium alginate (2 g) was dissolved in 50 mL of distilled water and mixed with the 50 mL of algae suspension. The mixture was injected drop-wise into a CaCl₂ solution (4%) with an injector to form beads. The resultant beads

were of (3.0 ± 0.2) mm diameter and cured in the CaCl₂ solution for 30 min to enhance their mechanical stability. The beads were rinsed and transferred into culture medium in conical flasks. After 5 d in a light incubator (2000 lux) at 298.15 K, the active immobilized MA beads (the dry/wet mass ratio was measured to be 3.48%) were collected and rinsed as biosorbent for use.

2.4 Batch biosorption experiments

All the biosorption experiments were carried out as follows: 2 g of beads (wet mass) were added to flasks containing 100 mL of Cd(II) ions solution and the initial pH was adjusted. Flasks were shaken at 150 r/min at the temperature needed. The initial and the final Cd(II) ions concentrations in supernatant fluid were determined by the flame atomic absorption spectrometry. Each of the experiment was replicated twice and the average values were obtained.

The metal uptake on the unit amount of the biosorbent (mg Cd(II) ions per g wet biosorbent) was calculated using the following expressions:

$$q = \frac{(C_0 - C)V_0}{m} \tag{1}$$

where C_0 and C are the initial and final metal concentrations in solution (mg/L), respectively, V_0 is the initial solution volume (L) and *m* is the mass of the biosorbent used (g).

The study of the pH (3.0–8.0) dependency of Cd(II) ion biosorption on immobilized MA was carried out as follows: An amount of 2 g of beads were added to flasks containing 100 mL of Cd(II) ion solution with initial concentration of 100 mg/L. Flasks were shaken at 150 r/min at 298.15 K for 3 h. The pH value was adjusted by 0.1 mol/L NaOH or 0.1 mol/L HCl.

For isotherm analysis, biosorption experiments were conducted by contacting 2 g beads with 100 mL of Cd(II) ions solution at different initial concentrations (20, 40, 60, 80, 100, 120, 160 and 200 mg/L) shaking at 150 r/min for 3 h. The experiments were performed at 288.15, 298.15 and 308.15 K.

The kinetic biosorption experiment was carried out as follows: 2 g beads were added to 100 mL of Cd(II) ions solution with three different concentrations (60, 100 and 200 mg/L), and the samples were shaken for designated time periods (10, 20, 30, 60, 120, 180, 360, 540 and 720 min) at 298.15 K.

To investigate the thermodynamic characteristics of the biosorption process, experiments were carried out as follows: 2 g beads were added to 100 mL of Cd(II) ions solution with three different concentrations (60, 100 and 200 mg/L) and different temperatures (288.15, 298.15 and 308.15 K). The samples were shaken for designated time periods (10, 20, 30, 60, 120, 180, 360, 540 and 720 min).

2.5 Desorption experiments

In order to determine the reusability of the biosorbents, the beads were reused in four biosorptiondesorption cycles. 2 g of immobilized MA was contacted with 100 mL of 200 mg/L Cd(II) ions solution with the agitated speed 150 r/min at 298.15 K for biosorption. After biosorption, the beads was washed by ultra-pure water and then added to 50 mL of 0.1 mol/L HCl for desorption in 250 mL flasks, shaken at 150 r/min and 298.15 K for 3 h.

3 Results and discussion

3.1 Characterization of immobilized *Microcystis* aeruginosa

Scanning electron micrographs (SEM) for the immobilized MA before and after the biosorption of Cd(II) are presented in Fig. 1(a) and Fig. 1(b), respectively. Figure 1(a) shows uneven and irregular surface, where there are many pores, which may exist some chemical groups. Porous structure is benefited from algae embedded and it is also considered helpful for mass transfer of Cd(II) ions to the immobilized beads. After biosorption, the surface of the biosorbent became abnormal and a great deal of crystal adhered to the surface.



Fig. 1 SEM characterization of immobilized MA: (a) Before biosorption (5000×); (b) After biosorption (5000×)

The FT-IR spectrum has been widely used for the structural investigation of a biosorbent because it can provide considerable insight into the various function

groups in the biosorbent, and it is also used to investigate the interactions of biosorbent with metals ions [17]. Certain amount of immobilized MA was dried at 333.15 K and then ground and sieved through 75 µm sieve for FT-IR analysis (Nexus 470 FT-IR). The FT-IR spectra of the immobilized MA before and after biosorption are presented in Fig. 2. A number of absorption peaks are shown in Fig. 2(a), indicating the presence of different types of functional groups for the immobilized MA before biosorption. A strong and wide band appeared around 3500 cm^{-1} is assigned to -OHstretching vibrations and -NH2 stretching, while a strong peak at 1596 cm⁻¹ is associated to structural vibrations of antisymmetrical stretching of -COOgroups and intensity peak around 1400 cm⁻¹ is attributed to symmetrical stretching of $-COO^{-}$ groups [18]. Compared with the FT-IR spectrum of the immobilized MA after biosorption, some differences can be observed. The results reveal that these functional groups such as -OH, -NH₂, and -COO⁻ are available for interacttion with Cd(II) ions.



Fig. 2 FTIR spectra of immobilized MA before (a) and after (b) biosorption

3.2 Influence of solution pH

Metal ions biosorption on biosorbent from aqueous solution is dependent on solution pH as it affects the availability of metal ions in solution and the metal binding sites on biosorbent surface [12]. Little or no biosorption of metal ions was observed for pH less than 3.0 [19]. Since insoluble cadmium hydroxide starts precipitating from the solution at higher pH values, the pH value was investigated from 3.0 to 8.0 [20].

The effect of initial solution pH on Cd(II) ions removal by immobilized MA is shown in Fig. 3. Within pH range of 3.0-8.0, the Cd(II) uptake capacity of the biosorbent increases rapidly and the maximum value is obtained at pH 6.0 and the biosorption capacity decreases drastically with the increase of pH. The results indicate that the optimum pH is 6.0, and the maximum biosorption capacity is 98.38 mg/g. Similar results were observed for other types of biosorbent, such as the maximum biosorption capacities of Cd(II) ions on *Oscillatoria sp.* and *Spirulina platensis* were also observed at pH 6.0 [9, 21]. The pH between 4 and 8 are widely accepted as an optimum for metal uptake for almost all types of biomass [22]. Thus, pH of 6.0 was selected as the optimum pH for the following biosorption experiment.



Fig. 3 Effect of initial solution pH on Cd(II) ions removal by immobilized MA

3.3 Isotherm studies

Biosorption isotherm studies are important to determine the efficacy of biosorption. Some models can be used to describe experimental data of biosorption isotherms precisely and specify the parameters that can be determined. In this work, the equilibrium data were modeled with the Langmuir, Freundlich and Temkin models.

The Langmuir model assumes that a monomolecular layer is formed when biosorption takes place without any interaction between the adsorbed molecules [23]. The Langmuir model can be represented as

$$q_{\rm e} = \frac{q_{\rm max} K_{\rm L} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}} \tag{2}$$

where C_e is the concentration of cadmium in simulated solution (mg/L) at equilibrium, q_e is the amount of biosorption of cadmium per gram of biosorbent at equilibrium (mg/g), K_L is the Langmiur constant related to the energy of biosorption (L/mg) and q_{max} is the biosorption capacity of the biosorbent (mg/g) [23].

The empirical Freundlich equation based on biosorption on a heterogeneous surface is given by the following equation [24]:

$$q_{\rm e} = K_{\rm F} C_{\rm e}^{\frac{1}{n}} \tag{3}$$

where $K_{\rm F}$ and *n* are the Freundlich constants. $K_{\rm F}$ and *n*

are indicators of biosorption capacity and biosorption intensity, respectively. The Freundlich isotherm has generally been considered as an empirical relationship and has been widely used to fit the experimental data. The Freundlich constants $K_{\rm F}$ and *n* were obtained from the nonlinearized plot of above equation [9].

The Temkin isotherm equation assumes that the heat of biosorption of all the molecules in the layer decreases with coverage due to biosorbent-sorbate interactions, and that the biosorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. Temkin model is given by

$$q_{\rm e} = \frac{RT}{\Delta Q} \ln K_0 C_{\rm e} \tag{4}$$

where *R* is the universal gas constant (kJ/(mol·K)), *T* is the temperature (K), ΔQ is the variation of biosorption energy (kJ/mol), and K_0 is the Temkin equilibrium constant (L/g) [25].

The equilibrium biosorption of Cd(II) ions on the biosorbent and the fitting plot of the three isotherm models are shown in Fig. 4. As can be seen in Table 1,



Fig. 4 Langmuir, Freundlich and Temkin isotherms for biosorption of Cd(II) on immobilized MA

 Table 1
 Langmuir, Freundlich and Temkin isotherms

 parameters for biosorption of Cd(II) on immobilized MA

Madal	Demonster	Temperature/K			
Model	Parameter	288.15	298.15	308.15	
	$q_{\rm max}/({\rm mg}{\cdot}{\rm g}^{-1})$	210.210	204.546	209.244	
Langmuir	$K_{\rm L}/({\rm L}\cdot{\rm mg}^{-1})$	0.033	0.029	0.024	
	R^2	0.991	0.983	0.988	
Freundlich	п	1.992	2.096	1.838	
	$K_{\rm F}/({\rm L}\cdot{\rm mg}^{-1})$	17.533	18.149	12.785	
	R^2	0.956	0.981	0.953	
Temkin	$\Delta Q/(kJ \cdot mol^{-1})$	0.052	0.086	0.055	
	$K_0/(\mathrm{L}\cdot\mathrm{g}^{-1})$	0.324	1.743	0.230	
	R^2	0.995	0.939	0.994	

the experimental data exhibit high correlation with Langmuir model within the studied temperature range. However, the maximum biosorption capacities are far higher than the experimental sorbed amounts at equilibrium corresponding to the plateau of the sorption isotherms. This means that the equilibrium isotherms cannot be described by the Langmuir model. The Freundlich isotherm correlates well with the experimental data. The results indicate that heterogeneity biosorption of Cd(II) ions relates to the binding sites, which may be contributed to the active groups on the immobilized MA surface, such as -OH, -NH₂, -COO- groups and so on. This parallels that made for Pb and Cu biosorption by aspergillus flavus biomass [26]. Table 1 depicts that the experimental data also have a good correlation with the Temkin isotherm. Typical bonding energy range for ion-exchange mechanism is reported to be in the range of 8-16 kJ/mol while physisorption processes are reported to have biosorption energies less than -40 kJ/mol [27]. Values of ΔQ (0.052, 0.086, 0.055 kJ/mol at a temperatures of 288.15, 298.15 and 308.15 K, respectively) obtained in the present work indicate rather weak ionic interaction between the sorbate and the present biosorbent. The Cd(II) ions removal seems to involve chemisorption and physisorption.

3.4 Kinetic studies

Figure 5(a) shows the time profiles of Cd(II) ions biosorption on immobilized MA with different initial concentrations (60, 100 and 200 mg/L). It indicates that the biosorption rate of metal uptake is very fast and the maximum uptake is observed within 3 h. Data on the biosorption rates of Cd(II) ions by various biosorbents have shown a wide range of biosorption times. For example, the Cd(II) biosorption equilibrium time on immobilized *Fucus vesiculosus* is 8 h [28].

In order to investigate the biosorption kinetics of the Cd(II) ions on immobilized MA, the pseudo-firstorder, and pseudo-second-order were used to test the experimental data. The pseudo-first-order kinetic model is given as [29]

$$\log(q_{\rm e} - q_t) = \log q_{\rm e} - \frac{k_1}{2.303}t$$
(5)

where k_1 is the rate constant of pseudo-first-order biosorption (min/L); q_e and q_t denote the amounts of biosorption at equilibrium and at time t (mg/g), respectively.

The pseudo-second-order kinetic equation proposed by BLANCHARD et al [30] was derived on the basis of the biosorption capacity of the solid phase. The differential form of the model is expressed as



Fig. 5 Biosorption kinetics of Cd(II) inos on immobilized MA: (a) Biosorption of Cd(II) ions on immobilized MA at different contact time; (b) Pseudo-first-order sorption kinetics; (c) Pseudo-second-order sorption kinetics, and (d) Intraparticle diffusion kinetics

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2 (q_\mathrm{e} - q_t)^2 \tag{6}$$

where q_t is the amount of biosorption at time t, q_e is the biosorption capacity calculated by the pseudo-secondorder kinetic model (mg/g), k_2 (g/(mg·min)) is the pseudo-second-order rate constant for the biosorption process. Integrating and applying boundary conditions t=0 to t=t and $q_t=0$ to $q_t=q_t$, Eq. (6) becomes

$$q_{t} = \frac{k_{2}q_{e}^{2}t}{1+k_{2}q_{e}^{2}}$$
(7)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(8)

Figure 5(b) shows the plot of $log(q_e-q_t)$ vs t for biosorption of Cd(II) ions for the pseudo-first-order equation. The values of pseudo-first-order rate constants, k_1 , and equilibrium biosorption capacities, q_e , for each initial Cd(II) concentration were calculated from slopes and intercepts of straight lines in Fig. 5(b). The values of pseudo-first-order equation parameters together with correlation coefficients are given in Table 2. The correlation coefficients for the pseudo-first-order equation obtained at all the studied concentrations are low. This suggests that this biosorption system is not a pseudo-first-order reaction.

Figure 5(c) shows the plot of t/q_t vs t for biosorption of Cd(II) for the pseudo-second-order equation. The straight lines in plot of linear pseudo-second-order equation show good agreement of experimental data with the pseudo-second-order kinetic model for different initial Cd(II) concentrations. The values of pseudosecond-order equation parameters together with correlation coefficients are listed in Table 2. The correlation coefficients for the pseudo-second-order equation are 0.999 for all concentrations. The calculated $q_{\rm e}$ values also agree very well with the experimental data. This strongly suggests that the biosorption of Cd(II) on immobilized MA is most appropriately represented by a pseudo-second-order rate process. It is more likely to predict that the biosorption behaviour may involve valency forces through sharing of electrons between transition cadmium ions and biosorbent [31]. Some studies on the kinetics of biosorption of Cd(II) on various biosorbents have also reported higher correlations for pseudo-second order model [20, 32].

3.5 Biosorption mechanism studies

In immobilized MA-Cd(II) systems, the biosorption process can be described in three consecutive steps: Film diffusion, intraparticle diffusion, and chemical reaction [33]. In this work, film diffusion and intraparticle diffusion were studied using the intraparticle (internal) diffusion model and Boyd model. The intraparticle diffusion model can be described as [23]

$$q_t = k_3 t^{0.5} + C (9)$$

where k_3 is the intraparticle diffusion rate constant (mg/g·min^{0.5}) and *c* of biosorption constant is the intercept. The Boyd model is expressed as

$$Bt = -0.4997 - \ln(1 - \frac{q_t}{q_e}) \tag{10}$$

where *B* is the time constant (\min^{-1}) [34].

The relation plots of q_t versus $t^{0.5}$ are shown in Fig. 5(d). The data exhibit a multilinear plot, indicating that more than one stage influences the biosorption process for each concentration of Cd(II) ions: 1) the initial curved region correspondes to boundary laver diffusion, about 1 h; 2) the second stage is attributed to intraparticle diffusion from 1 to 3 h, where intraparticle diffusion is rate-controlled; 3) the final plateau region indicates equilibrium biosorption [17]. The figure should be a straight line passing through the origin when biosorption mechanism follows the intraparticle diffusion process only. However, the plots do not go through suggesting that the adsorption involves origin, intraparticle diffusion, but it is not the only rate controlling step for the whole process [23].

The *Bt* values at different contact time can be calculated using Eq. (10). The linearity test of *Bt* versus *t* plots was employed to distinguish whether the rate controlling step of mass transfer is film diffusion or particle diffusion. If the plot (having slope *B*) is a straight line passing through the origin, then the biosorption rate is governed by particle diffusion [35]. The plots of *Bt* versus *t* of our work are shown in Fig. 6. It can be observed that the plots at various initial concentrations are scattered, and they are neither linear nor pass through the origin, indicating the film- diffusion-controlled mechanism.

 Table 2 Kinetic parameters for biosorption of Cd(II) on immobilized MA

$C_0/(\mathrm{mg}\cdot\mathrm{L}^{-1})$	Ps	Pseudo-first-order			Pseudo-second-order		
	k_1 /min	$q_{\rm e}/({\rm mg}{\cdot}{\rm g}^{-1})$	R^2	$k_2/(g \cdot mg^{-1} \cdot min^{-1})$	$q_{\rm e,2}/({\rm mg}\cdot{\rm g}^{-1})$	R^2	
60	5.366×10 ⁻³	13.003	0.399	2.137×10 ⁻³	62.111	0.999	
100	7.231×10^{-3}	36.947	0.864	6.768×10^{-4}	102.041	0.999	
200	8.107×10^{-3}	48.879	0.842	5.159×10 ⁻⁴	153.846	0.999	



Fig. 6 Boyd plots for biosorption of Cd(II) on immobilized MA

3.6 Thermodynamic studies

Thermodynamic parameters such as Gibb's free energy (ΔG°), enthalpy change (ΔH°) and change in entropy (ΔS°) for the biosorption of Cd(II) ions on immobilized MA have been determined by using the following equations:

$$\Delta G^{\rm o} = -RT \ln K^{\rm o} \tag{11}$$

$$\ln K^{\circ} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$
(12)

where *R* (8.314 J/(mol·K)) is the universal gas constant, *T*(K) is the absolute temperature and K° can be calculated by plotting $\ln K_d(K_d=q_e/C_e)$ versus C_e and extrapolating C_e to zero. The values of ΔH° and ΔS° can be obtained from the slope and intercept of a plot of $\ln K^{\circ}$ against 1/Tfrom the Fig. 7. The calculated results are reported in Table 3. The value of ΔG° for all tested temperatures was calculated to be negative, which suggests that the



Fig. 7 Plot of $\ln K^{\circ}$ versus 1/T for estimation of thermodynamic parameters for the biosorption of Cd(II) on immobilized MA (Volume, 100 mL; biosorbent dose, 2.0 g; initial concentration, 20, 40, 60, 80, 100, 120, 160, 200 mg/L; pH value, 6.0; contact time, 3 h; temperature, 288.15, 298.15, 308.15 K; agitation speed, 150 r/min)

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Table 3 Thermodynamic parameters for biosorption of Cd(II) on immobilized beads at 288.15, 298.15 and 308.15 K

lnK°	$\Delta G^{\rm o}/$ (kJ·mol ⁻¹)	$\Delta H^{\rm o}/$ (kJ·mol ⁻¹)	$\Delta S^{\rm o/}$ (J·K ⁻¹ ·mol ⁻¹)	R^2					
8.613	-20.634								
8.495	-21.058	-12.320	29.001	0.930					
8.278	-21.208								
	lnK ^o 8.613 8.495 8.278	$\frac{\ln K^{\circ}}{(\text{kJ} \cdot \text{mol}^{-1})} \frac{\Delta G^{\circ/}}{(\text{kJ} \cdot \text{mol}^{-1})}$ 8.613 -20.634 8.495 -21.058 8.278 -21.208	$ \frac{\ln K^{\circ}}{(kJ \cdot mol^{-1})} \frac{\Delta G^{\circ}}{(kJ \cdot mol^{-1})} \frac{\Delta H^{\circ}}{(kJ \cdot mol^{-1})} \\ 8.613 -20.634 \\ 8.495 -21.058 -12.320 \\ 8.278 -21.208 $	$\frac{\Delta G^{\circ/}}{(kJ \cdot mol^{-1})} \frac{\Delta H^{\circ/}}{(kJ \cdot mol^{-1})} \frac{\Delta S^{\circ/}}{(J \cdot K^{-1} \cdot mol^{-1})}$ 8.613 -20.634 8.495 -21.058 -12.320 29.001 8.278 -21.208					

biosorption of Cd(II) onimmobilized MA is spontaneity and indicates that immobilized MA has a high affinity for the biosorption of Cd(II) from solution under experimental conditions [36]. The standard enthalpy and entropy changes of biosorption are -12.320 kJ/mol and 29.001 J/(mol·K), respectively, and the correlation coefficient is 0.930. The value of ΔH° is negative, indicating that the biosorption is an exothermic reaction. The positive value of ΔS° reflects an increase in the randomness at the solid/solution interface during the biosorption process [37].

3.7 Desorption and regeneration

The biosorption-desorption studies are important to elucidate the behavior of biosorption, recycling of the biosorbent and the recovery of Cd(II) ions biosorbed on the biosorbent surface. To evaluate the reusability of the biosorbent, the successive biosorption-desorption processes were carried out for four times. From Fig. 8, it is observed that the biosorption capacity of immobilized MA for Cd(II) ions after four cycles only decreases from 150.86 to 118.18 mg/g. These results show that the immobilized MA can be successfully regenerated and repeatedly used in Cd(II) ions biosorption without appreciable losses in its biosorption capacity. These



Fig. 8 Biosorption-desorption cycles for immobilized MA. (Biosorption conditions: volume, 100 mL; biosorbent dose, 2.0 g; initial concentration, 200 mg/L; pH value, 6.0; contact time, 3 h; temperature, 298.15 K; agitation speed, 150 r/min. Desorption conditions: stripping solution 0.1 mol/L HCl; volume, 50 mL; contact time, 3 h; temperature, 298.15 K; agitation speed, 150 r/min)

findings indicate that the immobilized MA can be economically and effectively used for treatment of wastewater containing Cd(II) ions.

4 Conclusions

1) The immobilized MA can be efficiently used for Cd(II) removal from aqueous solution. Biosorption of Cd(II) ions is pH dependent and the maximum biosorption capacity is found at pH 6.0. The functional groups on the bead surface, such as -OH, $-NH_2$, and $-COO^-$, are essential for capturing Cd(II) from aqueous solution.

2) The equilibrium data can be well fitted with the Freundlich isotherm model and Temkin model.

3) The biosorption data are found to follow pseudosecond-order kinetics, evidencing that both chemical and physical biosorption are involved in the biosorption process. The mechanism is further identified by intraparticle diffusion model and Boyd model, indicating that film diffusion is the rate-limiting step and intraparticle diffusion is also involved in the biosorption process.

4) The thermodynamic parameters indicate that the biosorption reaction of Cd(II) on the immobilized MA is a feasible, spontaneous and exothermic process.

5) The biosorption-desorption cycle results demonstrate that there generation and subsequent use the immobilized MA will enhance the economics of practical applications for the removal of Cd(II) from wastewater.

6) Based on these results, it can be concluded that the immobilized MA is a very suitable material for removing and recovering Cd(II) ions from aqueous solution. Further research is required to investigate the application of immobilized MA in practical wastewater treatment.

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