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Pb(II) biosorption by compound bioflocculant: performance and mechanism

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ABSTRACT

Biosorption behavior of compound bioflocculant (CBF), produced by a mixed culture of *Rhizobium radiobacter* F2 and *Bacillus sphaeicus* F6, was investigated for Pb(II) removal under various parameters (pH, initial Pb(II) concentration, temperature, and stirring rate). Biosorption kinetics, isotherm, thermodynamics, and Fourier transform infrared (FTIR) spectra were studied to explore the biosorption mechanism. Additionally, principal factor analysis was also performed with a statistical method to identify the main influencing factor. Optimum pH was determined as 7.0 and biosorption equilibrium was attained within 60 min. The order of effects caused by the four operational parameters was pH > initial Pb(II) concentration ≈ stirring rate > temperature. The experimental data obeyed the pseudo-first-order kinetic model well. Langmuir model fitted the equilibrium data best among Langmuir, Freundlich and Redlich–Peterson models. Negative ΔG° and positive ΔH° indicated that the biosorption process was spontaneous and endothermic in nature. FTIR analysis showed that –OH, –NH, and –C=O groups were involved in the biosorption. These results demonstrate that CBF could be a promising alternative for Pb(II) removal from aqueous solution.

Keywords: Biosorption; Compound bioflocculant; Pb(II); Kinetics; Principal factor analysis

1. Introduction

Many industries discharge aqueous effluents containing heavy metals, which are persistent environmental contaminants since they could not be degraded or destroyed [1,2]. Due to the toxic effects on humans, animals, and environmental balances, heavy metal pollution has raised a great concern [3]. Conventional separation techniques, including chemical precipitation/neutralization, chemical oxidation or reduction, membrane separation, filtration, ion exchange, electrochemical methods, etc., have been developed to respond this challenge [4]. However, these methods are limited in practice due to the drawbacks such as formation of undesirable metallic by-products [5], rigorous conditions, or expensive cost [6,7].

Biosorption technology, one of the emerging methods for metal removal, has been regarded as a cheaper and more effective alternative [8]. Biological materials used as biosorbents include bacteria, algae, fungi, yeast, and their derivatives [9]. Relevant researches indicate that extracellular polymeric substances (EPSs), which are produced by micro-organisms during their growth and rich in functional groups of carboxyl, hydroxyl, and amino groups, play an

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important role in biosorption process [10,11]. Thus, attention is guided towards removing heavy metals by EPSs directly. According to Yin et al. [12], the maximum sorption capacities of *A. fumigatus* EPS calculated from the Langmuir model were 40 mg/g and 85.5 mg/g for Cu(II) and Cd(II), respectively. Guibaud et al. [13] examined the ability of EPSs of different anaerobic granular sludge to bind Pb(II) and Cd(II), and results indicated that the EPSs displayed an excellent binding ability. Sun et al. [14] reported that LB-EPSs (loosely bound EPSs) of the aerobic granules showed strong binding properties towards Zn(II) and Co(II) and the main chemical groups involved in the interactions were alcohol, carboxyl, and amino groups. These results demonstrate that it is feasible to remove heavy metals from aqueous solution by EPSs. EPSs have many obvious advantages, such as easy production, good biodegradability, cost effectiveness, and extensive supply [11,13].

In our previous work, the compound bioflocculant (CBF), EPSs secreted during the mixed culture of *Rhizobium radiobacter* F2 and *Bacillus sphaeicus* F6, has been found to show excellent flocculating activity against solid particles in wastewater [15]. In addition, the CBF was characterized to be high molecular weight and abundant in functional groups [16]. So, it is reasonable to expect that CBF may have a good adsorption capability for metal ions in aqueous solutions. This study was therefore implemented to investigate the applicability of CBF as a biosorbent for the removal of heavy metals. Pb(II) is a prevalent contaminant in aquatic environment since it is widely employed in storage battery, manufacturing, printing pigments, fuels, etc. [7]. Exposure to Pb(II) may cause severe damage to kidney, nervous system, reproductive system, liver, and brain [17]. Pb(II) was thus selected as the target pollutant in this study. Biosorption performance under various conditions (including pH, initial Pb(II) concentration, temperature, and stirring rate) was investigated, and principal factor analysis was conducted to determine the main influencing factors. Kinetics, isotherms, thermodynamics, and Fourier transform infrared (FTIR) characterization were also studied to explore the mechanism of the biosorption process.

2. Experimental

2.1. Preparation and properties of CBF

R. radiobacter F2 and *B. sphaeicus* F6 obtained from State Key Laboratory of Urban Water Resource and Environment (China) were used in this study to prepare CBF according to a previous study [16]. CBF was identified as a polysaccharide bioflocculant composed of rhamnose, mannose, glucose, and galactose, respectively, and its molecular weight was about 4.79×10^5 Da. CBF suspension with a concentration of 5.0 g/L was prepared by magnetic stirrer in deionized water.

2.2. Batch biosorption procedure

Stock solution of Pb(II) used in this study was prepared by dissolving $Pb(NO_3)_2$ (Tianjin Kemiou Chemical Reagent Co. Ltd., China) in deionized water with a concentration of 50.0 mg/L. Pb(II) solutions of different concentrations in biosorption experiments were prepared by proper dilution from the stock solution.

Batch biosorption experiments were carried out using a 1.0 l beaker on a ZR4-6 Agitator (Zhongrun Water Industry Technology Development Co. Ltd., China) at room temperature (298.0 ± 2.0 K). Initially, the water sample containing Pb(II) and 1.0 mg CBF was mixed at a stirring rate of 120 rpm for 60 min. After 1.0 h of quiescent settling, the supernatant sample was withdrawn from about 20 cm below the surface and filtered through a 0.45 μm glass fiber membrane for Pb(II) concentration analysis by ICP-OES Optima 5300 DV (Perkin–Elmer Co. Ltd., USA) with working wavelengths at 220.35 nm.

Effect of pH was investigated in the range of 4.0–8.0 with an initial Pb(II) concentration of 2.0 mg/L. pH higher than 8.0 was not studied because alkaline condition would result in insoluble hydroxide precipitates, making Pb(II) biosorption studies complicated [18]. pH of solution was adjusted using 1.0 M HCl and 1.0 M NaOH at the beginning and then not further controlled. For each experiment, a CBF-free control was conducted to determine the loss of Pb(II) in the filtration process. Leaching of other metals from CBF was also measured. Results indicated that the loss of Pb(II) in filtration was negligible and CBF did not release any metal ion into the aqueous solutions. The effects of initial Pb(II) concentration (0.1–5.0 mg/L), temperature(278.0–308.0 K), and stirring rate (40–200 rpm), were studied, and samples under designed conditions were taken for analysis at definite time intervals.

Chemicals used in this study were of analytical grade and used without further purification. The experiments were carried out in triplicate and results were given as average values.

2.3. FTIR analysis

The chemical characteristics of CBF before and after Pb(II) biosorption were analyzed by FTIR. FTIR spectra were collected on an Avatar 360 spectrometer (Thermo Fisher Nicolet Instrument Co. Ltd., USA) at 298.0 K in the wave number range of 4,000–700 cm^{-1} in transmission mode. Samples were ground with a fixed amount of spectral grade KBr (Tianjin Kemiou Chemical Reagent Co. Ltd., China) (1% w/w) in an agate mortar.

2.4. Data treatment

The amount of adsorbed Pb(II) on per gram of CBF was obtained by the following equations:

$$q_t = [(C_i - C_t) \cdot V]/M \tag{1}$$

$$q_\text{e} = [(C_i - C_\text{e}) \cdot V]/M \tag{2}$$

Langmuir (Eq. 3), Freundlich (Eq. 4), and Redlich–Peterson (Eq. 5) isotherms [19] were used to investigate the isotherm of the biosorption process:

$$q_\text{e} = Q_0 b C_\text{e}/(1 + bC_\text{e}) \tag{3}$$

$$q_\text{e} = K_F C_\text{e}^{1/n} \tag{4}$$

$$q_\text{e} = K_R C_\text{e}/\left(1 + a_R C_\text{e}^{b_R}\right) \tag{5}$$

Pseudo-first-order (Eq. 6), pseudo-second-order (Eq. 7) [20], and Elovich (Eq. 8) [21] kinetic equations were employed for testing the experimental data:

$$\log(q_\text{e} - q_t) = \log(q_\text{e}) - \frac{k_1}{2.303} t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_\text{e}} \tag{7}$$

$$q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t \tag{8}$$

The change in free energy (ΔG^o) was calculated from the following Eq. (22):

$$\Delta G^o = -\text{RT} \ln K_D \tag{9}$$

The enthalpy (ΔH^o) of biosorption was estimated by Eq. (10):

$$\ln K_D = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{\text{RT}} \tag{10}$$

3. Results and discussion

3.1. Biosorption performance

3.1.1. Effects of influencing factors

Fig. 1(a) shows that Pb(II) biosorption on CBF was strongly dependent on pH of solution. In general, Pb (II) biosorption was low at pH 4.0–6.0 and increased with increasing pH. The biosorption continued to increase till pH 7.0. Further, pH increase deteriorated Pb(II) removal. The maximum Pb(II) biosorption capacity on CBF was obtained at pH 7.0, which was applied in the following experiments. pH of solution can affect the ionization state of the functional groups like carboxylate, phosphate, imidazole, and amino groups on the surface of adsorbent, thus influencing the adsorption of metal ions [23]. At lower pH, the positive surface charge of the adsorbent inhibits the approach of metal ions. In addition, protons in the solution compete with metal ions for binding sites, thereby decreasing the interaction of metal ions with the adsorbent [24]. When pH is increased, protons begin to be desorbed, and the metal ions hook up the free binding sites. Hence, the metal adsorption is enhanced. Similar phenomena were obtained by other researchers. Rakhshaee et al. [25] observed that metals uptake on pre-treated *Lemna minor* biomass was negligible at pH 1.0 and increased continuously with pH from 2.0 to 7.0, 5.0, and 6.0 for Hg(II), Cr(II), and Cu (II), respectively. Huang et al. [26] noticed that removal of Pb(II) by *Agaricus Bisporus* was enhanced with increasing solution pH and the maximum was reached at around pH 4.0. It was reported by Sari and Tuzen [27] that the biosorption efficiency of macrofungus (*Amanita rubescens*) biomass increased from 40 to 80% for Pb(II) and from 35 to 70% for Cd(II) with pH increasing from 2.0 to 4.0, and the maximum biosorption was found to be 98% and 97% for Pb(II) and Cd (II) at pH 5.0, respectively. The optimum pH for Pb(II) biosorption by CBF is neutral, which benefits the practical application of CBF.

Pb(II) biosorption as a function of initial Pb(II) concentration (C_i) was investigated in the time range of 5.0–60.0 min with C_i varying from 0.1 to 5.0 mg/L at pH 7.0 (Fig. 1(b)). Results indicated that as C_i increased, Pb (II) uptake was enhanced. When C_i increased from 0.1 to 5.0 mg/L, Pb(II) biosorption increased from 1.99 ± 0.14 mg/g to 90.47 ± 1.30 mg/g. The removal efficiency was maintained above 97.0% when the C_i was in the range of 0.1–2.0 mg/L, but decreased to 89.90% with C_i increasing to 5.0 mg/L. Therefore, the optimum Pb(II) concentration 2.0 mg/L was selected for further experiments. The enhancement of biosorption capacity

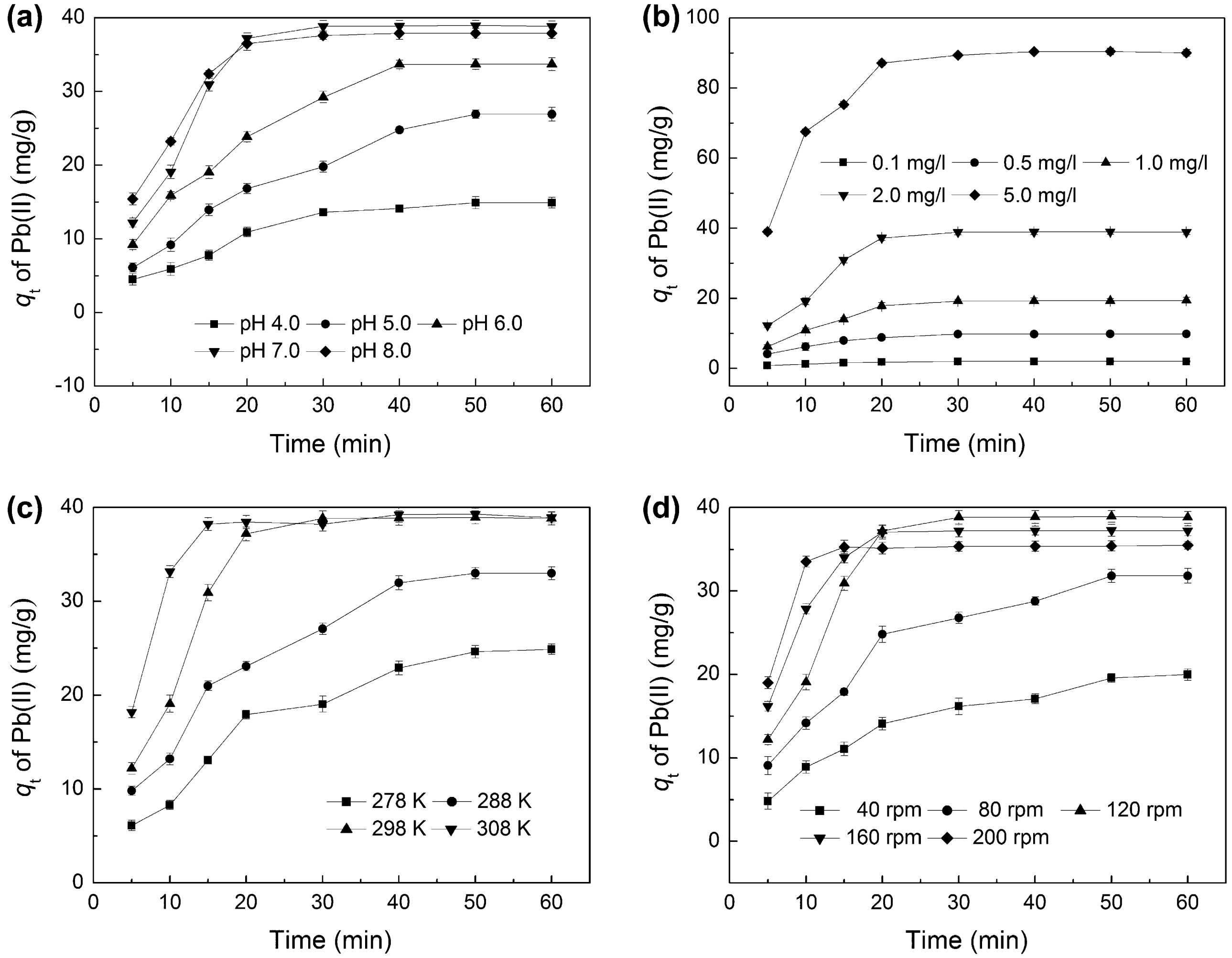

Fig. 1. Effects of influencing factors on Pb(II) biosorption by CBF. (a) Effect of pH (C_i 2.0 mg/L; temperature 298.0 K; and stirring rate 120 rpm). (b) Effect of initial Pb(II) concentration (pH 7.0; temperature 298.0 K; and stirring rate 120 rpm). (c) Effect of temperature (pH 7.0; C_i 2.0 mg/L; and stirring rate 120 rpm). (d) Effect of stirring rate (pH 7.0; C_i 2.0 mg/L; and temperature 298.0 K).

with increasing C_i could be partially explained by higher availability of metal ions for biosorption. Furthermore, higher C_i in solution provided higher driving force to overcome all mass transfer resistance, resulting in higher probability of collision between metal ions and adsorbents. Hence, higher C_i led to more effective metal uptake. Additionally, the biosorption process consisted of an initial rapid stage and a second slow stage. At the initial stage, which lasted for approximately 20 min, q_t increased rapidly. The second stage occupied a small part of the total biosorption capacity. This could be explained by the occupancy of the binding sites in the initial stage, which led to less efficient biosorption in the following time. The biosorption equilibrium was obtained within 60 min. Therefore, the contact time of 60 min was selected for further experiments. The high biosorption capacity and short equilibrium time suggested that chemisorption mainly contributed to the biosorption process [28].

Temperature affects biosorption usually by influencing the stability of the metal-biosorbent complex and the ionization of the functional groups [29]. The effect of temperature on the biosorption was investigated with temperature ranging from 278.0 K to 308.0 K (Fig. 1(c)). Results showed that biosorption capacity of CBF for Pb(II) increased from 24.89 ± 0.56 mg/g to 38.92 ± 0.58 mg/g with elevating temperature from 278.0 to 308.0 K, revealing that the biosorption may be an endothermic process. Meanwhile, q_t was also enhanced with increasing temperature, denoting that the biosorption was more favorable at higher temperature. These results indicated CBF possessed excellent thermostability within the investigated temperature range and could be used in a wide temperature range.

As also can been seen from Fig. 1(c), when the temperature increased from 298.0 to 308.0 K, difference in Pb(II) biosorption after 30 min reaction time was minor, revealing that the optimum temperature was at standard temperature ranges.

Fig. 1(d) presents the influence of stirring rate on biosorption. The overall biosorption increased significantly when the stirring rate was increased from 40 to 120 rpm. However, a slight drop was observed when stirring rate further rose to 160 rpm and above. The optimum stirring rate was taken as 120 rpm accordingly. The change in Pb(II) biosorption with stirring rate may be attributed to the difference in floc structure. As mentioned by Bo et al. [30], floc strength depended on the bonding strength in the flocs. Therefore, flocs would break if the shear force applied on the surface was larger than the bonds between particles of the flocs. It was also noticed that the q_t within 15 min was improved with increasing stirring rate, and the biosorption reached the equilibrium faster at higher stirring rate. This might be ascribed to more contact chances between Pb(II) and CBF when higher stirring rate was applied.

3.1.2. Principal factor analysis

In order to investigate the sensitivities of Pb(II) biosorption on CBF towards the influencing factors discussed above and identify the primary factors, static method was adopted for biosorption data. Factors with different units were converted into dimensionless variables for comparison in a method as follows [31]:

$$v_{D_i} = \left| \frac{v_{R_i} - v_{R_{i,0}}}{\max(v_{R_i}) - v_{R_{i,0}}} \right| \tag{11}$$

$$k_i' = \left| \frac{k_i - k_{i,0}}{v_{Di}} \right| \tag{12}$$

where v_{Di} denotes the dimensionless variable, v_{R_i} the value of investigated factor, $v_{R_{i,0}}$ the median within the v_{R_i} range, $\max(v_{Ri})$ the maximum of v_{Ri}, k_i the pseudo-first-order rate constant (k_1) shown in Table 3, $k_{i,0}$ the median of k_i similar to $v_{R_{i,0}}$, and k'_i the variation of k_i per unit of v_{D_i}. A value of zero was assigned to k'_i corresponding to $v_{R_{i,0}}$ based on assumption that subtle change of v_{R_i} (differential of v_{R_i}, dv_{R_i}) resulted in no change in k_i. Range, the difference between the maximum and minimum of k'_i, was used for evaluation of the sensitivities of biosorption process towards the investigated operational parameters.

Results shown in Table 1 indicated that the influence of the investigated factors followed the sequence of pH (0.140) > initial Pb(II) concentration (C_i 0.063) ≈ stirring rate (0.060) > temperature (0.050). Conclusion can be obtained that pH was a key factor in the biosorption process while the effect of temperature was relatively small within the range of the study.

3.1.3. Biosorption capacity

The maximum monolayer biosorption capacity could be estimated as 189.31 mg/g from Langmuir isotherm. Maximum adsorption capacities of different adsorbents for Pb(II) collected from previous literatures along with the result of the present study were summarized (Table 2). Despite direct comparison of CBF with other adsorbents just had a relative meaning due to the different operating conditions, this comparison was useful to evaluate the applicability of CBF for Pb(II) removal. Obviously, CBF presented higher biosorption capacity than most of the biosorbents, reflecting a promising future for CBF utilization in Pb (II) removal from aqueous solutions.

3.2. Biosorption mechanism

3.2.1. Kinetics, isotherms, and thermodynamics

Kinetics and thermodynamics studies help to understand the rate-controlling steps and biosorption

Table 1
Principal factor analysis of operational parameters

Operational parameters	v_{R_i}	v_{D_i}	k_1 (min)	k_i' (min)	Range
pH 4.0	4	1	0.13	0.040	0.140
pH 5.0	5	0.5	0.10	0.140	
pH 6.0	6	0	0.15	0	
pH 7.0	7	0.5	0.20	0.060	
pH 8.0	8	1	0.24	0.070	
C_i 0.1 mg/L	0.1	1	0.23	0.010	0.063
C_i 0.5 mg/L	0.5	0.84	0.25	0.012	
C_i 1.0 mg/L	1.0	0.63	0.20	0.063	
C_i 2.0 mg/L	2.0	0	0.20	0	
C_i 5.0 mg/L	5.0	1	0.28	0.040	
278.0 K	278	1	0.17	0.050	0.050
288.0 K	288	0.33	0.21	0.030	
298.0 K	298	0	0.20	0	
308.0 K	308	1	0.27	0.050	
40 rpm	40	1	0.16	0.060	0.060
80 rpm	80	0.5	0.20	0.040	
120 rpm	120	0	0.20	0	
160 rpm	160	0.5	0.23	0.020	
200 rpm	200	1	0.28	0.060	

Table 2
Comparison between CBF and biosorbents produced from other micro-organisms

Microorganism	Q_0 (mg/g)	Operating conditions		Refs.
		pH	C_i (mg/L)	
Bacillus sp.	92.27	3.0	250	[32]
Mucor rouxii	35.69	5.0	10	[9]
Gloeocapsa gelatinosa	82.22	4.0	10	[33]
Acacia leucocephala	185.20	4.0	100	[20]
R. radiobacter and *B. sphaeicus*	189.31	7.0	2	Present study

mechanism, and adsorption isotherms can indicate the relationship between the mass of the adsorbate on per unit mass of adsorbent and the solute concentration at equilibrium [19]. Thus, kinetics, isotherms, and thermodynamics of the Pb(II) biosorption on CBF were investigated and discussed in this section.

The kinetic parameters of Pb(II) biosorption on CBF under different pH, initial Pb(II) concentration, temperature, and stirring rate are displayed in Table 3. By applying pseudo-first-order equation, the correlation coefficient (R^2) values were in the range of 0.93–0.99 and values of q_e were in good agreement with $q_{e,e}$. Fitting the experimental data by pseudo-second-order kinetic model and Elovich equation gave R^2 values in the range of 0.71–0.97 and 0.53–0.97, respectively. Therefore, the pseudo-first-order kinetic model showed the best fit to the experimental data, which assumes that a metal ion only sorbs on one sorption site [20].

The general adsorption isotherms that can be used for describing the aquatic adsorption behavior include Langmuir, Freundlich, and Redlich–Peterson models. The biosorption data of Pb(II) on CBF in this work were analyzed using these three models. The Langmuir model is suitable for describing numerous, homogeneous, and constant solution sorption systems [21], while the Freundlich isotherm applies to adsorption of a highly heterogeneous surface [34]. The Redlich–Peterson isotherm incorporates with the features of the Langmuir and Freundlich isotherms.

Table 3
Kinetics parameters of Pb(II) biosorption by CBF under various conditions

Operational parameters	$q_{e,e}$ (mg/g)	Pseudo-first-order			Pseudo-second-order			Elovich		
		k_1 (/min)	q_e (mg/g)	R^2	k_2 (mg/g/min)	q_e (mg/g)	R^2	α (g/mg/min)	β (g/mg)	R^2
pH 4.0	14.89	0.13	15.93	0.97	1.23×10^{-3}	21.33	0.95	2.10	0.20	0.92
pH 5.0	26.90	0.10	31.01	0.99	0.98×10^{-3}	44.44	0.93	3.13	0.12	0.91
pH 6.0	28.71	0.15	36.18	0.98	1.47×10^{-3}	46.08	0.92	4.81	0.10	0.86
pH 7.0	38.83	0.20	40.64	0.95	1.81×10^{-3}	49.74	0.87	11.06	0.09	0.83
pH 8.0	37.79	0.24	38.87	0.95	2.89×10^{-3}	45.44	0.88	15.87	0.11	0.84
C_i 0.1 mg/L	1.98	0.23	2.02	0.99	15.74×10^{-3}	2.19	0.91	5.19	1.14	0.79
C_i 0.5 mg/L	9.80	0.25	10.0	0.97	11.75×10^{-3}	11.30	0.85	10.38	0.56	0.66
C_i 1.0 mg/L	19.42	0.20	19.94	0.97	4.08×10^{-3}	24.04	0.97	4.59	0.18	0.87
C_i 2.0 mg/L	38.83	0.20	40.64	0.95	1.81×10^{-3}	49.74	0.87	11.06	0.09	0.83
C_i 5.0 mg/L	89.97	0.28	91.39	0.98	1.44×10^{-3}	106.23	0.93	22.69	0.05	0.85
278.0 K	24.89	0.17	26.37	0.99	1.02×10^{-3}	38.09	0.96	3.42	0.13	0.97
288.0 K	32.98	0.21	34.66	0.98	1.14×10^{-3}	45.54	0.96	10.32	0.10	0.95
298.0 K	38.83	0.20	40.64	0.95	1.81×10^{-3}	49.74	0.87	11.06	0.09	0.83
308.0 K	38.92	0.27	39.23	0.94	2.55×10^{-3}	43.97	0.81	7.40	0.14	0.65
40 rpm	19.98	0.16	20.47	0.99	1.79×10^{-3}	26.97	0.97	2.67	0.16	0.96
80 rpm	31.80	0.20	32.29	0.97	1.42×10^{-3}	41.71	0.93	4.90	0.10	0.96
120 rpm	38.83	0.20	40.64	0.95	1.81×10^{-3}	49.74	0.87	11.06	0.09	0.83
160 rpm	37.22	0.23	37.85	0.97	3.92×10^{-3}	43.11	0.93	21.99	0.13	0.78
200 rpm	35.47	0.28	35.76	0.94	5.63×10^{-3}	38.48	0.71	28.22	0.20	0.53

Values of Langmuir, Freundlich, and Redlich–Peterson parameters are presented in Table 4. By comparing values of R^2, Langmuir model was found to fit the equilibrium data best.

In order to describe thermodynamic behavior of Pb (II) biosorption on CBF, parameters including the change in free energy (ΔG°) and enthalpy (ΔH°) were studied. The ΔG° values were calculated as −8.19, −10.88, −16.09, and −17.99 kJ/mol at 278.0, 288.0, 298.0, and 308.0 K, respectively. The negative ΔG^o value was an indicator of thermodynamical feasibility and spontaneous nature of the biosorption [19]. The decrease in ΔG^o values with increasing temperature suggested an improvement in feasibility of biosorption at higher temperatures. The ΔH^o value was 88.39 kJ/mol, demonstrating that the biosorption process was endothermic.

To conclude, the biosorption process possesses the following characteristics: (1) monolayer adsorption; (2) finite adsorption sites; (3) one metal ion occupying one adsorption site; and (4) endothermic character.

3.2.2. FTIR characterization

The infrared spectra of pure CBF and Pb(II)-loaded CBF were taken to analyze the functional groups responsible for the biosorption process (Fig. 2). The CBF spectrum displayed a number of adsorption peaks, reflecting the complex nature of CBF. A broad stretching peak at 3,500–3,200 cm^{-1} was characteristic of –OH and –NH [5]. The absorption peaks at 2,900–3000 cm^{-1} were because of the asymmetric stretching of γC–H bond of the $-CH_2$ groups and that of the $-CH_3$ groups [35]. Both the peaks at 1,654 and 1,401 cm^{-1} represented the presence of carbonyl groups. The former was characteristic of –C=O in amide groups, while the latter could be assigned to the asymmetric C=O stretching in the carboxylate. The peak at 1,540 cm^{-1} was attributed to the N–H bending vibration. The intense peak at 1,072 cm^{-1} was caused by the C–O stretching vibration. The infrared spectrum of CBF evidenced the presence of carboxyl, hydroxyl, and amino groups.

Table 4
Isotherm parameters of Pb(II) on CBF

Langmuir parameters		Freundlich parameters		Redlich–Peterson constants	
Q_0 (mg/g)	189.31	n	1.40	K_R (L/g)	32.02
b (l/mg)	0.20	K_F	30.98	a_R	5.28
				b_R	2.06
R^2	0.99	R^2	0.93	R^2	0.83

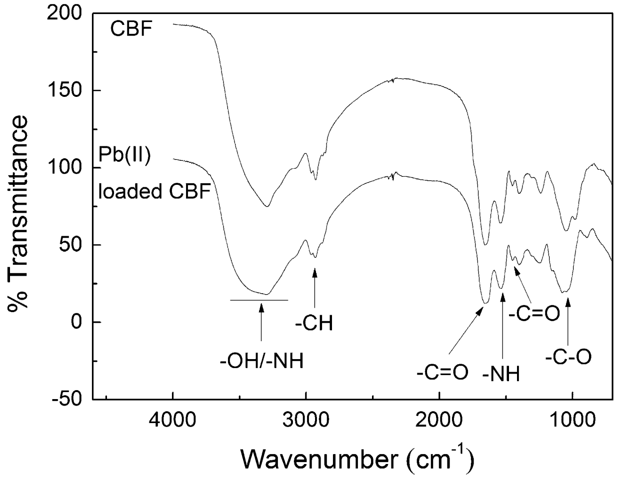

Fig. 2. FTIR spectra of CBF- and Pb(II)-loaded CBF.

According to the spectrum of Pb(II)-loaded CBF in Fig. 2, after Pb(II) biosorption the peaks of –OH and –NH groups became broader and shifted to 3,304 cm^{-1}, indicating the binding of Pb(II) with amino and hydroxyl groups. In addition, the C=O stretching band at 1,654 cm^{-1} shifted to 1,647 cm^{-1}. The peak for N–H bending vibration was relocated at 1,554 cm^{-1}. The C–O stretching peaks became broader compared to the CBF spectrum and were shifted to 1,010 cm^{-1} after Pb (II) biosorption. Pradhan et al. [36] and Volesky [37] affirmed that the main functional groups responsible for a biosorption process included the hydroxyl, carbonyl, carboxyl, sulfonate, amide, imidazole, phosphonate, and phosphodiester groups. Some of these groups were present on the CBF and may interact with the Pb(II), leading to the biosorption.

4. Conclusions

Results indicated that optimum operational conditions were as follows: pH – 7.0, initial Pb(II) concentration – 2.0 mg/L, temperature – 298.0–308.0 K, and stirring rate – 120 rpm. The order of effects caused by the four operational parameters was pH > initial Pb(II) concentration ≈ stirring rate > temperature. Adsorption equilibrium was attained within 60 min, and the kinetics under various parameters obeyed the pseudo-first-order equation well. The equilibrium biosorption data were in good agreement with Langmuir isotherm model. The theoretic maximum biosorption capacity of Pb(II) on CBF calculated by Langmuir equation showed outstanding advantage over similar biosorbents in previous work. The thermodynamic analysis illustrated that the biosorption process was spontaneous and endothermic in nature. Present study proved that CBF could be used as a potential alternative for the removal of Pb(II). It should be noted that our work has just given a preliminary attempt to use CBF as a biosorbent of heavy metals, and methods to solve the separation and recycle of CBF are needed to develop before its practical application.

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Nomenclature

CBF	—	compound bioflocculant
EPSs	—	extracellular polymeric substances
FTIR	—	Fourier transform infrared
q_t	—	amount of Pb(II) adsorbed on per gram of CBF at any given time t (mg/g)
q_e	—	amount of Pb(II) adsorbed on per gram of CBF at equilibrium (mg/g)
$q_{e,e}$	—	q_e obtained by experiments
C_i	—	initial Pb(II) concentration (mg/L)
C_t	—	Pb(II) concentrations at time t (mg/L)
C_e	—	Pb(II) concentrations at equilibrium (mg/L)
V	—	volume of the solution (l)
M	—	CBF dosage (g)
Q_0	—	monolayer adsorption saturation capacity (mg/g)
b	—	Langmuir constant related to adsorption energy (1/mg)
K_F	—	Freundlich parameters denoting adsorption capacity
n	—	Freundlich parameters denoting intensity
K_R	—	Redlich–Peterson parameter
a_R	—	Redlich–Peterson parameter
b_R	—	Redlich–Peterson parameter
k_1	—	pseudo-first-order reaction rate constant (1/min)
k_2	—	pseudo-second-order reaction rate constant (mg/g/min)
α	—	Elovich constant, initial adsorption rate (g/mg/min)
β	—	Elovich constant, desorption rate constant (g/mg)
R^2	—	correlation coefficient
ΔG^o	—	Gibbs free energy change (kJ/mol)
ΔH^o	—	enthalpy change (kJ/mol)
ΔS^o	—	entropy change (kJ/mol)
R	—	universal gas constant, 8.314 J/mol/K
T	—	absolutely temperature (K)
K_D	—	q_e/C_e, the distribution coefficient

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