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Removal of Cr^{3+} from aqueous solution by biosorption with aerobic granules

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ABSTRACT

Aerobic granules were utilized as an effective biosorbent to remove Cr^{3+} from aqueous solution. The results showed that the initial pH, contact time, and Cr^{3+} concentration affected the biosorption process significantly. Both Freundlich and Langmuir isotherms were able to describe the equilibrium data reasonably with high correlation coefficients ($R^2 > 0.95$) and pseudo-second-order model best fitted the biosorption process at experimental conditions. Moreover, Environmental Scanning Electronic microscope (ESEM), X-ray energy dispersion (EDX), and Fourier transform infrared (FTIR) analyses revealed that metal complexation, chemical precipitation, and ion exchange were involved in the removal of Cr^{3+} with aerobic granules. Further analysis by a metal ion fraction test demonstrated that metal complexation could be the dominant mechanism of biosorption, whereas chemical precipitation and ion exchange appeared only to have minor role in the overall Cr^{3+} biosorption process.

1. Introduction

Heavy metal wastewater has become a global environmental concern due to serious health threaten to humans [1,2]. Trivalent chromium (Cr^{3+}) is one of the important heavy metal resources, but at the same time is one of the heavy metal pollutants commonly found in the effluents from chemical industry for mining, iron sheet cleaning, chrome plating, and leather tanning [3]. The presence of Cr^{3+} in final industrial effluents is extremely undesirable, as it is toxic to both lower and higher organisms.

Recent studies have focused on the biosorption process as an alternative method to remove toxic metals from wastewater due to its advantages such as low cost, short operation time, and reusability of biomaterials [4–6]. For the removal of Cr^{3+}, different types of biosorbents have been used in batch systems to determine the biosorption capacities, kinetics and equilibrium isotherms [7–9]. However, the majority of biosorbents explored in previous studies were small particles with low density, poor mechanical strength, and little rigidity, which would result in difficult post-separation of the treated effluent from the biosorbents especially in the practical application. To overcome these weaknesses, cell immobilization technology is developed and various immobilized biomaterials have been applied in the metal biosorption successfully [10–12].

Aerobic granules, a novel type of microbial aggregates, have been extensively used to remove nitrogen, phosphorus, and refractory compounds from wastewater on a laboratory scale [13–15]. Compared to the conventional bioflocs, aerobic granules have strong microbial structure, excellent settleability, high biomass retention, and resistance to toxic compounds [16,17]. These characteristics indicated that aerobic granules could be an excellent biomaterial for the removal of heavy metals. To our knowledge, there is no extensive study on the biosorption of Cr^{3+} using aerobic granules in literature.

The objective of this study is to investigate the feasibility of aerobic granules for the removal of Cr^{3+} from aqueous solution. Different experimental conditions such as initial pH, contact time, and Cr^{3+} concentration were studied to optimize the biosorption operation. Both biosorption isotherms and kinetics models were explored to describe the experimental data. Furthermore, Environmental Scanning Electronic microscope (ESEM), X-ray energy dispersion (EDX), Fourier transform infrared (FTIR), and metal ion fraction analyses were conducted to investigate the metal interaction with the biomass involved in the Cr^{3+} biosorption process.

2. Materials and methods

2.1. Materials

2.1.1. Aerobic granules

The aerobic granules used in this study were cultivated in a sequencing batch reactor (SBR) with a working volume of 5 L ($H = 120$ cm, $D = 8$ cm). The reactor was fed with the synthetic wastewater and operated under the sequential batch mode of 10 min feeding, 240 min aeration, 5 min settling, and 1 min effluent

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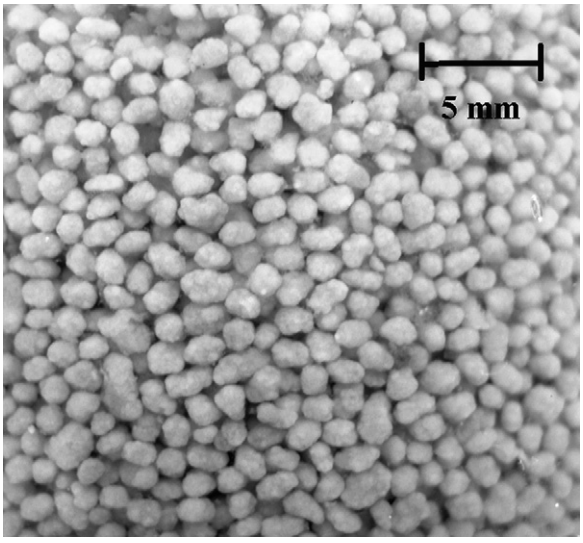

Fig. 1. The appearance of aerobic granules.

withdrawal. The composition of the synthetic wastewater was as follows: glucose (600 mg/L); NH_4Cl (150 mg/L), KH_2PO_4 (88 mg/L), $NaHCO_3$ (200 mg/L), $CaCl_2{\cdot}2H_2O$ (30 mg/L), $MgSO_4$ (93 mg/L), NaCl (63 mg/L) and $FeSO_4{\cdot}7H_2O$ (20 mg/L). Mature granules were nearly spherical in shape and had a compacted, integrated structure (Fig. 1). The mean size and specific density of the granules were about 1.0 mm and 1.008.

2.1.2. Chemicals

Stock solution of Cr^{3+} (1000 mg/L) was prepared by dissolving $CrCl_3{\cdot}6H_2O$ (Analytical grade) in deionized water (supplied by China Agriculture University) and further diluted to the concentrations required for the experiments.

2.2. Biosorption experiments

Biosorption experiments were performed with 500 mL shaking flasks containing 200 mL Cr^{3+} solutions in a rotary shaker (HYG-A) at 150 rpm and 30 °C. The initial aerobic granules concentration (X_o) was kept constant at 1.0 g/L (dry weight). A control experiment was carried out using the same solution and equipment in the absence of aerobic granules.

To study the effect of pH, the Cr^{3+} solution (50 mg/L) was adjusted to the desired pH (2.0–6.0) with HCl or NaOH. In the biosorption isotherm study, a series of Cr^{3+} solution with various concentrations (20–200 mg/L) were mixed with 0.2 g granules at optimum pH for 3 h. In the biosorption kinetics study, contact time was changed from 0 to 360 min and samples were collected at different intervals. In this study, the granules were separated from the solution easily after settling for 30 s. Before analyzing the concentration of Cr^{3+}, the supernatant solution of each sample was filtered by 0.45 μm membranes and diluted to the appropriate concentration of Cr (<10 mg/L). All the experiments were conducted in triplicate and the mean values were recorded.

In the study, biosorption capacity Q (mg/g) of Cr^{3+} was defined as follows:

$$Q = (C_o - C) \times \frac{V}{m} \quad (1)$$

where C_o and C are the initial and final Cr^{3+} concentrations (mg/L); V is the solution volume in the flask (L); m is the dry weight of the granules (g).

Table 1
Chemical extraction scheme for metal fraction.

Fraction	Extracting agent	Extraction conditions	
		Shaking time	Temperature
Exchangeable	1 mol/L $MgCl_2$ (pH 7.0)	1 h	25 °C
Acid soluble	1 mol/L NaAC (pH 5.0)	6 h	25 °C
Fe/Mn bound	0.04 mol/L $NH_2OH{\cdot}HCl$	6 h	96 °C
Organic bound	0.02 mol/L HNO_3 + 30%H_2O_2 (pH 2.0)	3 h	85 °C
	3.2 mol/L NH_4AC in 20% (v/v) HNO_3	0.5 h	25 °C
Residual	Aqua Regia	0.5 h	100 °C

2.3. Metal ion fraction test

Metal ion fraction test was carried out in 50 ml centrifuge tubes following the biosorption experiments (C_o = 100 mg/L, X_o = 1.0 g/L) to extract each chemical species (ionexchangable, acid soluble, Fe/Mn bound, organic bound and residual fraction) from Cr-loaded granules. The detailed extraction procedure in this study is outlined in Table 1, which was based on the reports developed by Tessier et al. [18]. For the metal ion fraction test, 1.0 g pre-dried granules were used.

2.4. Analytical methods

The concentration of Cr^{3+} was measured by flame atomic absorption spectroscopy (AAS Vario 6, Germany). The surface structures and elemental compositions of initial (before biosorption) and Cr-loaded granules were examined by ESEM (FEI QUANTA 200F, Holland) coupled with EDX (EDAX, USA). Infrared spectra of the biomass before and after biosorption were recorded in KBr pellets by a FTIR (Magna-IR750, USA) with the resolution of 2 cm^{-1}. Before analysis, the biomass was freeze-dried and then grounded to a powder.

3. Results and discussion

3.1. Effect of pH

Fig. 2 shows the effect of pH on the Cr^{3+} biosorption at 30 °C with 50 mg/L Cr^{3+} and 1.0 g/L granules. As can be seen, pH played a major role in the biosorption and possibly affected the activity of

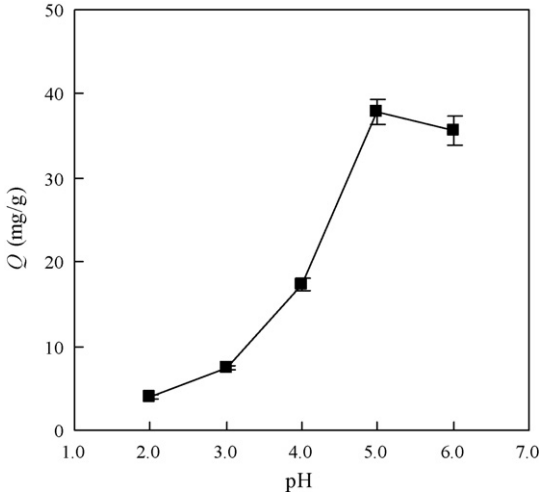

Fig. 2. Effect of pH on the Cr^{3+} biosorption with aerobic granules (C_o = 50 mg/L, X_o = 1.0 g/L, t = 3 h). Error bars are calculated based on triplicate experiments.

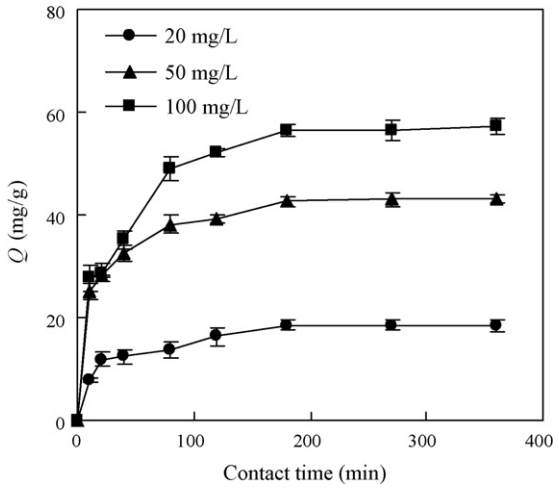

Fig. 3. Effect of contact time and initial Cr^{3+} concentration on the Cr^{3+} biosorption with aerobic granules (X_o = 1.0 g/L, pH 5.0). Error bars are calculated based on triplicate experiments.

the functional groups. At low pH (2.0–3.0), the biosorption process was restricted and biosorption capacity was less than 10.0 mg/g. As the pH increased from 3.0 to 5.0, the biosorption capacity obviously increased and reached the maximum value of 37.8 ± 1.5 mg/g at pH 5.0. When the pH further increased (>5.0), the biosorption capacity began to decrease. This effect of pH on metal uptake could be explained by the different activity of the functional groups and metal chemistry in solution. At low pH (2.0–3.0), protons (H^+) would compete for active sites on the cell of aerobic granules and thus restrict the interaction of metal ions and the biomass [19]. As the pH increased (3.0–5.0), more negative charge functional groups such as carboxyl, amine, hydroxyl, and phosphate groups were exposed as active sites, which could react with metal ions [20]. For pH > 5.0, the chemical precipitation of $Cr(OH)_3$ occurred and then interfered with the biosorption process.

3.2. Effect of contact time and initial Cr^{3+} concentration

Fig. 3 illustrates the effect of contact time and initial Cr^{3+} concentration on the Cr^{3+} biosorption at 30 °C with 1.0 g/L granules. Two-stage of biosorption behavior was observed. At first stage, biosorption capacity sharply increased within the first 20 min due to the rapid surface sorption, which was in agreement with previous studies [21,22]. During the second stage (20–360 min), a slower uptake of Cr^{3+} was observed as a result of free binding sites becoming saturated gradually. Biosorption equilibrium can be achieved at 180 min, after which the increase of biosorption capacity was negligible.

Fig. 3 also showed that the biosorption capacity increased with the increase of initial Cr^{3+} concentration (C_o). For instance, the biosorption capacity increased from 18.6 ± 0.8 mg/g (C_o = 20 mg/L) to 56.5 ± 1.1 mg/g (C_o = 100 mg/L) at 180 min (equilibrium time). The larger biosorption capacity at higher C_o was possibly due to the greater driving force by the pressure gradient ($\Delta C = C_o - C_e$).

3.3. Biosorption isotherms

In the present work, Langmuir and Freundlich isotherms were used to describe the biosorption equilibrium of Cr^{3+} onto aerobic granules.

The Langmuir model describes monolayer sorption which assumes that sorption occur at specific homogeneous sites on the adsorbent. It can be expressed as follows [23]:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{bQ_{max}} \quad (2)$$

where C_e is the equilibrium concentration of Cr^{3+} (mg/L), Q_e is the biosorption capacity of Cr^{3+} at equilibrium (mg/g), Q_{max} is the maximum biosorption capacity (mg/g), b is the constant related to the affinity of the binding sites (L/mg).

The Freundlich model deals with multilayer sorption on heterogeneous surfaces. It can be expressed as follows [24]:

$$\log Q_e = \log k + \frac{1}{n} \log C_e \quad (3)$$

where k and n are the indicators of biosorption density and intensity, respectively.

The Langmuir and Freundlich isotherm constants along with the correlation coefficients can be determined from the relationship between the Q_e and C_e. The results showed that both isotherms were able to describe the biosorption process pretty well with high correlation coefficients ($R^2 > 0.95$), suggesting the mechanism of Cr^{3+} biosorption was complex and various physical and chemical functions were involved. The values of the maximum capacity (Q_{max}) and biosorption affinity (b) determined from Langmuir isotherm were 64.1 ± 1.6 mg/g and 0.12 ± 0.02 L/mg, respectively. The value of $1/n$ (n = 2.83 ± 0.09) lying between 0 and 1 indicated that Cr^{3+} ions were favorably biosorbed by aerobic granules at examined conditions [7].

Moreover, the biosorption capacity of various microbial biosorbents for Cr^{3+} removal have been investigated in previous studies, including *Spirogyra* spp. (28.2 mg/g, pH 5.0) [7], *Hylocomium splendens* (42.1 mg/g, pH 5.0) [8], *Chlorella miniata* (41.1 mg/g, pH 4.5) [9], *Chlorella sorokiniana* (58.8 mg/g, pH 4.0) [10], *Palmaria palmate* (36.9 mg/g, pH 4.5) [22], blast furnace sludge (9.6 mg/g, pH 7.2) [25], *Pamelina tiliaceae* (52.1 mg/g, pH 5.0) [26], and *Bacillus sphaericus* (6.9 mg/g, pH 5.0) [27]. It was notable that the Cr^{3+} biosorption capacity of aerobic granules in this study (Q_{max} = 64.1 ± 1.6 mg/g, pH 5.0) was higher than that of the other biosorbents mentioned (6.9–58.8 mg/g). Thus, aerobic granules could be considered as an effective biosorbent for the removal of Cr^{3+} from aqueous solution.

3.4. Biosorption kinetics

Three kinetic models of pseudo-first-order, pseudo-second-order, and intraparticle diffusion were used to describe the kinetic data.

The pseudo-first-order and pseudo-second-order models are generally expressed in linearized forms as follows [28,29]:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (4)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{max}^2} + \frac{1}{Q_{max}} t \quad (5)$$

where Q_t is the Cr^{3+} sorption capacity at time t (mg/g), k_1 (1/min) and k_2 (g/mg min) are rate constants of pseudo-first-order and pseudo-second-order, respectively.

The intraparticle diffusion model was used to determine whether intraparticle diffusion was rate limiting for sorption and can be expressed as follows [30]:

$$Q_t = k_p t^{0.5} + C \quad (6)$$

where C is a constant related to the boundary layer thickness and k_p is the intraparticle diffusion rate constant (mg/g $min^{0.5}$).

Table 2 lists the results of kinetic parameters of three models at different C_o. It can be seen from Table 2 that the intraparticle diffusion model had the lowest correlation coefficients ($R^2 < 0.91$), which

Table 2
Kinetic parameters for the biosorption of Cr^{3+} with aerobic granules at different C_o.

C_o	Q'_e	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion	
		k_1	Q_e	R^2	k_2	Q_e	R^2	k_p	R^2
20	184	$(1.4 \pm 0.2) \times 10^{-2}$	11.3	0.94	$(3.3 \pm 0.1) \times 10^{-3}$	17.8	0.98	0.65 ± 0.01	0.85
50	42.7	$(1.7 \pm 0.1) \times 10^{-2}$	21.6	0.96	$(1.8 \pm 0.2) \times 10^{-3}$	44.6	0.99	1.40 ± 0.12	0.91
100	57.1	$(2.0 \pm 0.1) \times 10^{-2}$	46.1	0.97	$(0.8 \pm 0.1) \times 10^{-3}$	59.6	0.99	2.51 ± 0.18	0.89

Errors are calculated based on triplicate analysis.

indicated that the intraparticle diffusion was not the rate limiting during the Cr^{3+} biosorption process. For pseudo-first-order, the calculated values (Q_e) were too low to compare with the experimental ones (Q'_e), suggesting that pseudo-first-order model was not fit for describing the biosorption process even the higher correlation coefficients were achieved ($R^2 > 0.94$).

Pseudo-second-order model described the biosorption process more effectively ($R^2 > 0.98$) and the calculated values (Q_e) matched well with the experimental ones (Q'_e). These results implied that the biosorption of Cr^{3+} with aerobic granules could be best described by the pseudo-second-order model. It also can be noticed that the kinetics rate of pseudo-second-order model was relatively higher ($k_2 > (1.8 \pm 0.2) \times 10^{-3}$ g/mg min) at lower C_o (<50 mg/L), which provided significant practical importance as it would facilitate the process in the treatment of dilute Cr^{3+} contaminated wastewater.

3.5. ESEM and EDX analysis

ESEM and EDX were used to investigate the metal interaction with the biomass before and after Cr^{3+} biosorption. The results are shown in Fig. 4.

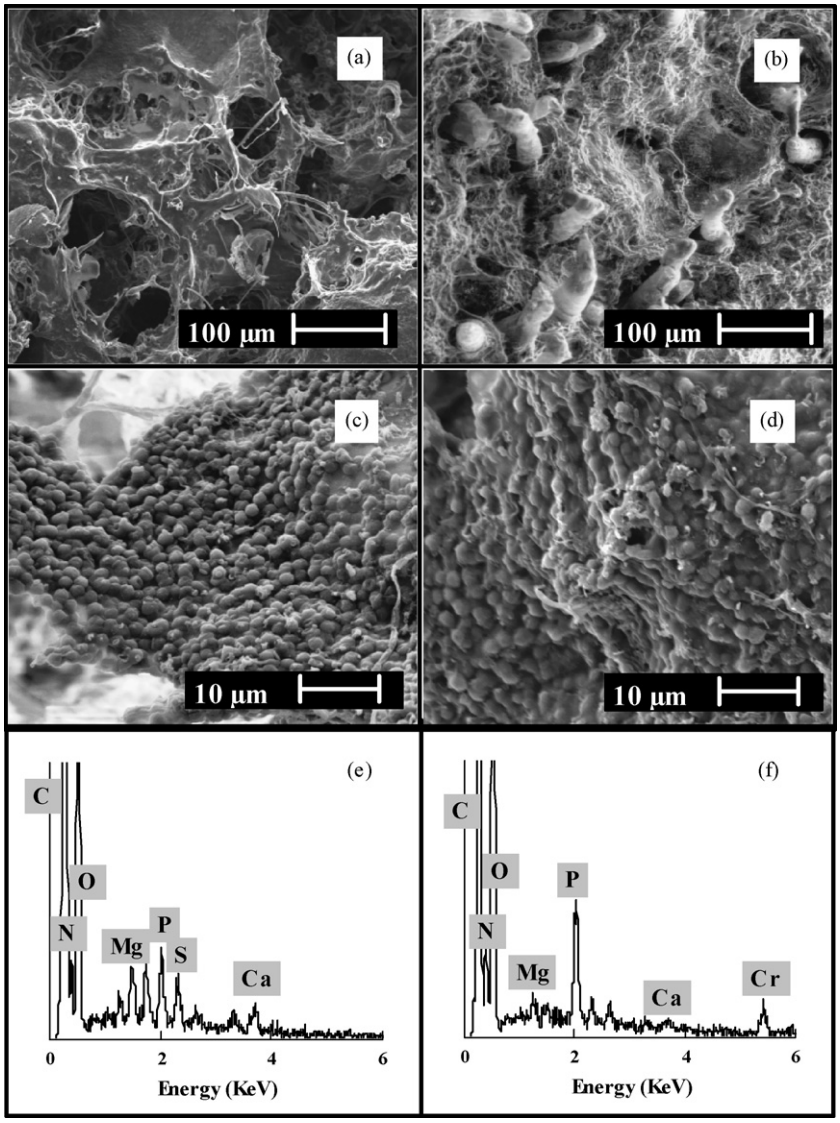

Fig. 4. The surface of (a) initial granules and (b) Cr^{3+}-loaded granules at low magnification (×800); the microorganism of (c) initial granules and (d) Cr^{3+}-loaded granules at high magnification (×5000); EDAX spectrum of (e) initial granules and (f) Cr^{3+}-loaded granules.

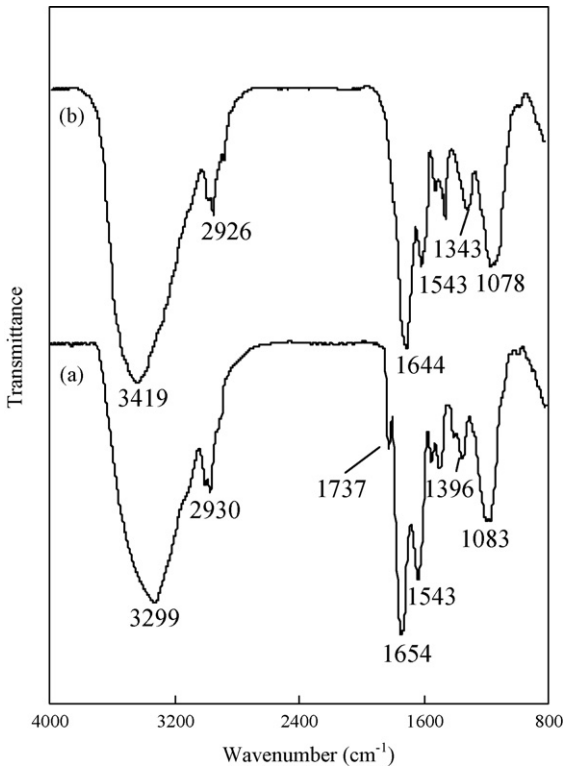

Fig. 5. FTIR spectrum of (a) initial granule; (b) Cr^{3+}-loaded granule (resolution = 2 cm^{-1}, C_o = 100 mg/L).

A lot of cavities (Fig. 4a) and coccoid bacteria (Fig. 4c) were present on the coarse surface of the granule before Cr^{3+} biosorption. After contacting metal ions, the surface of biomass became more compact with the presence of some particles (<70 μm) (Fig. 4b) and the coccoid bacteria appeared somewhat wrinkled (Fig. 4d). These findings could be the result of metal complexation or chemical precipitation involved in the Cr^{3+} biosorption. Similar result was previously reported by Akar and Tunali, who investigated the Cd^{2+} and Cu^{2+} removal from aqueous solution using fungi *Botrytis cinerea* [31].

The EDX analysis showed that the presence of C, N, O, Mg, Ca, P, and S on the surface of the biomass before biosorption (Fig. 4e). These elements could derive from polysaccharides and proteins of the cell wall of the biomass. After Cr^{3+} biosorption, Cr peak was detected, while the Ca and Mg peaks decreased (Fig. 4f). These results implied that the ion exchange was involved in the Cr^{3+} biosorption. Furthermore, the increase of P after biosorption (Fig. 4f) could be due to the release of phosphatide inside the cell membrane, and the phosphatide might also contribute to the biosorption of Cr^{3+}.

3.6. FTIR spectral analysis

The FTIR spectra of the initial and Cr-loaded granules were taken to identify the functional groups involved in the Cr^{3+} biosorption (Fig. 5). The FTIR spectrum of initial granules displayed a number of absorption peaks (Fig. 5a), which can be identified based on the reports in previous studies [25,32]. The strong bands in the region of 3000–3500 cm^{-1} reflected N–H and O–H stretching vibrations, showing the presence of hydroxyl and amine groups on the biomass surface. The peak at 2930 cm^{-1} is the indicator of alkyl chains C–H stretching vibration. The carboxylic groups gave rise to two bands: C=O asymmetrical stretching band at 1737 cm^{-1} and a symmetrical stretching band at 1396 cm^{-1}, respectively. A distinct band at 1654 cm^{-1} was the result of C=O and C–N (amide I) stretching vibration. The amide II band was a combination of N–H bending and C–N stretching at 1543 cm^{-1}. The band at 1080 cm^{-1} may be attributed to the P–O vibration.

It appears from Fig. 5b that different functional groups would be responsible for biosorption of Cr^{3+}. After biosorption of Cr^{3+}, the band at 1737 cm^{-1} disappeared and the band at 1396 cm^{-1} shifted to 1343 cm^{-1}. This result suggested that the carboxyl groups were involved in the binding of Cr^{3+}. The broad overlapping region for N–H and O–H stretching was significantly shifted from 3299 to 3419 cm^{-1}, which indicated that amino and hydroxyl groups were responsible for the Cr^{3+} biosorption with aerobic granules. The peak at 1654 cm^{-1} of initial granules, corresponded to the amide I band from proteins shifted to the 1644 cm^{-1}, revealing the complexation of Cr^{3+} with the functional groups from proteins. Moreover, the band at 1083 cm^{-1} shifted to the lower wavenumber of 1078 cm^{-1}, which could be attributed to the interaction of Cr^{3+} and phosphate groups.

3.7. Metal ion fraction test

The metal ion fraction test gives an approximation of the metal distribution into different chemical fractions [33,34] and thus generally reflects different categories of mechanism such as ion exchange, chemical precipitation, and complexation process [35]. In the present study, the contribution of each biosorption mechanism is determined from the result of the metal ion fraction test, given in Fig. 6. Among five extracted species, the organic-bound fraction was largest with the value of 60.3%. This could be due to the effect of metal metal complexation process which involved abundant negatively charged functional groups on the cell wall of biomass. Moreover, the result of FTIR analysis in Section 3.6 confirmed that functional groups such as carboxyl, amino, hydroxyl, and phosphate played an important role in the metal complexation. Therefore, the metal complexation could be expected to be the dominant mechanism for Cr^{3+} biosorption with aerobic granules. On the other hand, the exchangeable fraction (metals that can be released by ion-exchange process) [36] and acid soluble fraction (metals which are precipitated with carbonate) [36] were relatively small with the value of 18.7 and 11.2%, respectively. This result indicated that ion exchange and chemical precipitation was probably only had a minor effect on the overall Cr^{3+} biosorption. Similar results have also been

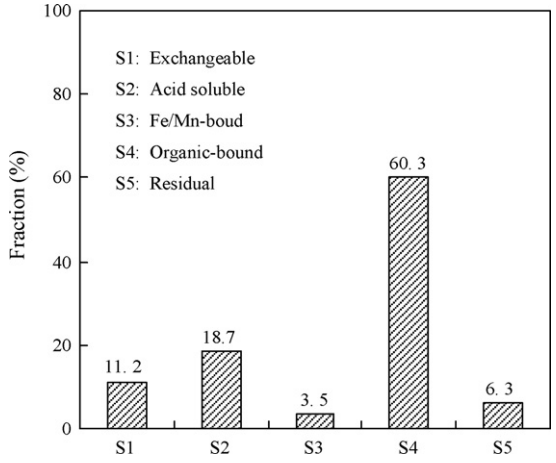

Fig. 6. The percentage of each species extracted from Cr-loaded granules (C_o = 100 mg/L).

reported regarding the Cr^{3+} biosorption by a microalgal isolate *C. miniata* [9].

4. Conclusions

This study investigated the feasibility of aerobic granules as a novel effective biosorbent for Cr^{3+} removal. The main conclusions can be drawn as follows:

(1) The Cr^{3+} biosorption capacity increased with the increasing of pH value from 2.0 to 6.0. When pH was 5.0 (C_o = 50 mg/L), a maximum biosorption capacity of 37.8 ± 1.5 mg/g was achieved.
(2) Both Langmuir and Freundlich models described the biosorption process well. The maximum biosorption capacity obtained from Langmuir model was 64.1 ± 1.6 mg/g.
(3) The Cr^{3+} biosorption process showed two distinct stages and the pseudo-second-order kinetic model gave a reasonable description of the biosorption. Moreover, the biosorption capacity increased with the increase of initial Cr^{3+} concentration.
(4) ESEM, EDX, and FTIR analyses revealed that metal complexation, chemical precipitation, and ion-exchange mechanisms were involved in the Cr^{3+} removal. Further analysis by a metal ion fraction test demonstrated that metal complexation could be the dominant mechanism of biosorption.

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