



## Biosorption of copper and nickel ions using *Pseudomonas* sp. in single and binary metal systems

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### ABSTRACT

*Pseudomonas* sp. is a common kind of bacteria. In order to confirm whether *Pseudomonas* sp. can be used to remove the heavy metals from wastewater, the study investigated its adsorption capacity in single and Cu<sup>2+</sup>–Ni<sup>2+</sup> binary systems. Experimental parameters affecting the metal uptake by *Pseudomonas* sp. in single system, such as initial solution pH, initial metal concentration, and contact time, were investigated. In single system, the highest adsorption yields of Cu<sup>2+</sup> and Ni<sup>2+</sup> by the *Pseudomonas* sp. were 44.78 mg Cu<sup>2+</sup> g<sup>-1</sup> and 336.84 mg Ni<sup>2+</sup> g<sup>-1</sup>, respectively, at the optimum conditions for each metal. The kinetic and equilibrium experimental data of Cu<sup>2+</sup> and Ni<sup>2+</sup> ions in the single systems could be successfully described by Langmuir and Freundlich isotherms, whereas the adsorption isotherm was better described by a Langmuir model rather than a Freundlich model. In Cu<sup>2+</sup>–Ni<sup>2+</sup> binary systems, the maximum adsorption amount of Cu<sup>2+</sup> and Ni<sup>2+</sup> were 38.62 mg Cu<sup>2+</sup> g<sup>-1</sup> and 323.47 mg Ni<sup>2+</sup> g<sup>-1</sup>, respectively. It obviously showed that the adsorption capacities of the two ions were suppressed, and nickel ion was dominant in the competitive adsorption. Besides, the equilibrium data for the interaction of the metal ions in the binary system could well be described by the Langmuir competitive model. The result gained from these studies indicated that *Pseudomonas* sp. had the potential to remove Cu<sup>2+</sup> and Ni<sup>2+</sup> ions from wastewaters.

**Keywords:** Biosorption; *Pseudomonas* sp.; Competitive; Adsorption binary systems; Langmuir competitive model

### 1. Introduction

Contamination of water sources by heavy metals has been a serious problem to be solved around the world [1,2]. Various industries [3,4], such as electro-

plating, chemical manufacture, leather tanning, oil refining, and especially mining and mineral processing, produce and discharge a larger volume of wastewater polluted by heavy metals. Due to their toxicity and accumulation in the food chain, heavy metals have an adverse impact on the environment and public health [5]. Copper and nickel ions are usually

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encountered together in industrial wastewaters. Although copper is an essential trace element, it can be extremely toxic due to its pro-oxidant activity and cause DNA damage [6,7]. Moreover, the concentration of nickel ion in the solution exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis, and skin dermatitis [8,9]. Additionally, unlike other toxic pollutants, those heavy metals are non-biodegradable [10], so they are not easy to be removed by conventional methods. Usually, conventional methods [11,12] to remove metals from aqueous solutions include chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, solvent extraction, reverse osmosis, membrane technologies, and evaporation recovery. However, due to many reasons, such as the very harsh reaction conditions, high cost, and secondary pollution, the implementation of these methods is limited [13]. Meanwhile, the discharge standard of heavy metals approved by national or international agencies become more and more strict [14,15]. All those reasons have accelerated the search for a cost-effective and environment friendly attractive treatment for metal removal to attain today's toxicity-driven limits [16,17].

In recent years, biosorption presents an attractive alternative to the traditional methods for removing toxic heavy metal from wastewaters [18–22]. Many researches have indicated that biosorption is one of the most applicable technologies and have a potential marketing advantage over other traditional wastewater treatment technologies as it is cheaper and environmental friendly, particularly when natural microorganism is used [19]. Various biomasses such as yeast, fungi, algae, and even extracellular material as exopolysaccharides exhibit high capacity for binding of metals [23–25]. Biosorption of those biosorbents is usually attributed to the presence of biochemical constituents on their cell wall [18]. These biopolymers contain a series of surface functional groups (such as amino, carboxyl, hydroxyl, and sulfate groups) which are responsible for binding of metal ions [26,27].

According to the best of our knowledge, there are not any reports in the literature about the utilization of *Pseudomonas* sp. as a biosorbent to remove heavy metals. *Pseudomonas* sp., a fermentation of Gram-negative bacilli, can use bivalent iron ions as electron donor to denitrify nitrate to nitrogen gas.

In this study, *Pseudomonas* sp. was used as the biosorbent for the removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions from single and binary metals solutions. To explore the adsorption capacities of *Pseudomonas* sp., this study was performed under different conditions. The kinetics and the theoretical isotherm models of bio-

sorption for the two different metal ions were also assessed by the experimental results.

## 2. Materials and methods

### 2.1. Microorganism and growth conditions

*Pseudomonas* sp. used in the experiments was isolated from the surface sediments of the East Lake in Wuhan. They are rod-shaped, aerobic, and Gram-negative bacteria, which can use bivalent iron ions as electron donor to denitrify nitrate to nitrogen gas.

The isolated bacteria were cryopreserved in solid medium at 4°C. At the beginning of the experiment, the bacteria were transferred to a 500-mL conical flask containing 300-mL ordinary culture medium (1.2 g beef extract, 4.08 g peptone, and 2.0 g NaCl), and shaken at 120 rpm and 28°C for 48 h, then harvested by centrifugation at 9,000 rpm and 4°C for 5 min. The supernatant was discarded, and to eliminate any residue of medium constitution matter, the cells were re-suspended in purified water and centrifuged again 3 times. Washed cells were suspended in distilled water in a proportion of 1:2 (w/v), and this “standard bacteria suspension” was used for subsequent biosorption studies.

### 2.2. Metal solutions standards

The heavy metal solutions were prepared from their chloride salts:  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ . Standard stock solution was prepared in distilled water, slightly acidified with HCl, and sterilized at 121°C for 15 min, then kept at 25°C. The synthetic wastewater solutions were then prepared by diluting the stock standards of concentration  $1,000 \text{ mg L}^{-1}$  of each metal. The glassware was leached in 3 N HCl and rinsed several times with distilled water before using to avoid metal contamination.

### 2.3. Assessing the uptake of heavy metals in single systems

#### 2.3.1. Synthetic metal solutions

Synthetic metal solutions were individually prepared by diluting  $1,000 \text{ mg L}^{-1}$  of chloride salts with deionized water to a desired concentration range. The initial concentration of the metals in the solution and samples after biosorption treatment was determined using UV-vis spectrophotometry (SP-1920, China).

#### 2.3.2. Determination of optimum pH

To evaluate the pH effect, experimental tests were carried out in 250-mL conical flask containing 100 mL

of solution with  $80 \text{ mg Cu}^{2+} \text{ L}^{-1}$  and  $80 \text{ mg Ni}^{2+} \text{ L}^{-1}$ . The pH of the metal solution was adjusted from 2.5 to 9.5 with 0.1 N NaOH or 0.1 N HCl before mixing the microorganism. Standard bacteria suspensions of *Pseudomonas* sp. (2.5 mL containing 1.25 g wet weight) were added to each flask. And the flasks were incubated on rotatory shaker (QYC-200, China) with 120 rpm for 720 min at  $28^\circ\text{C}$ . Then, the mixed solution was centrifuged at 9,000 rpm and  $4^\circ\text{C}$  for 5 min to measure the residual concentrations of the metal ions in these supernatants. At last, the necessary analysis was carried out.

### 2.3.3. Optimum initial ions concentration

The effect of the initial metal ions ( $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ) concentration on biosorption was investigated at pH 4.5 as noted above. For copper ion, various concentrations (10, 50, 80, 100, and  $150 \text{ mg Cu}^{2+} \text{ L}^{-1}$ ) were taken into conical flasks (250 mL) and mixed with 2.5 mL standard bacteria suspensions of *Pseudomonas* sp., while various concentrations of nickel ion were 50, 100, 150, 200, and  $250 \text{ mg Ni}^{2+} \text{ L}^{-1}$ . After that, the mixed solution was shocked on rotatory shaker (QYC-200, China) at  $28^\circ\text{C}$  and 120 rpm for 720 min, which was more than the ample time for adsorption equilibrium, the mixed solution was centrifuged at 9,000 rpm and  $4^\circ\text{C}$  for 5 min, and the residual concentrations of the metal ions in these supernatants were measured using UV-vis spectrophotometry (SP-1920, China). Then, the necessary analysis was carried out.

### 2.3.4. Determination of contact time

The optimum time was carried out at optimum pH by conducting batch biosorption experiments with optimum initial ions concentration of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  and 2.5 mL of standard bacteria suspensions of *Pseudomonas* sp. Then, the flasks were incubated on rotatory shaker (QYC-200, China) with 120 rpm for 720 min at  $28^\circ\text{C}$ . The samples were taken at different time periods and centrifuged for measuring the final ions concentration. Then, the necessary analysis was carried out.

### 2.3.5. Isothermal adsorption

In this study, nickel and copper sorption isotherms were obtained by batch biosorption experiments, which were carried out in conical flask (250 mL) at the optimum pH, initial concentration, and contact time at  $28^\circ\text{C}$  with 2.5 mL of standard bacteria suspensions of *Pseudomonas* sp. Samples were taken at different time periods and analyzed for their final metal ion concentrations in the solution. Then, the necessary analysis was carried out.

Metal uptake ( $q$ ) was calculated using balance equation:

$$q = \frac{v(c_o - c_i)}{1000 m} \quad (1)$$

where  $q$  is milligram of metal ion biosorbed per gram of biomass ( $\text{mg g}^{-1}$ );  $c_o$  is initial concentration ( $\text{mg L}^{-1}$ );  $c_i$  is final concentration ( $\text{mg L}^{-1}$ );  $v$  is volume of metal solutions in the flask (mL);  $m$  is weight of biosorbent (g) [28].

### 2.3.6. Equilibrium isotherm models

The Langmuir and Freundlich adsorption isotherms are commonly used to model the biosorption studies based on metal concentration [5,29].

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface [30]. For the Langmuir model, the following equation was used.

$$q = bc_e q_{\max} / (1 + bc_e) \quad (2)$$

where  $q_{\max}$  and  $c_e$  correspond to the milligrams of metal adsorbed per gram of bacterial biomass and the residual metal concentration in the solution at equilibrium, respectively. And  $b$  is the Langmuir constant, which establishes the relationship between sorption and desorption rate.

The Freundlich model assumes a heterogeneous sorption surface [31]. Freundlich isotherm constants were calculated with the equation:

$$q = K_e c_e^n \quad (3)$$

where  $K_e$  and  $n$  are the Freundlich constants characteristic of the system.

Langmuir (Eq. (2)) and Freundlich (Eq. (3)) equation are transformed to the linearized forms by the following equations, respectively [5]:

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m} \quad (4)$$

$$\ln q_e = \ln K_e + \frac{1}{n} \ln C_e \quad (5)$$

### 2.3.7. Competitive biosorption experiments in binary system

The competitive biosorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  was investigated. Based on the biosorption experiments in

single system, experiments were performed in a 250-mL conical flask containing 100 mL of solution with 100 mg Cu<sup>2+</sup> L<sup>-1</sup> and 200 mg Ni<sup>2+</sup> L<sup>-1</sup>, and 2.5 mL standard bacteria suspensions of *Pseudomonas* sp. at 28°C, and shaken at 120 rpm. PH of the solution was adjusted at 4.5 by 0.1N HCl. Samples were taken at different time periods to measure the corresponding concentration of Cu<sup>2+</sup> and Ni<sup>2+</sup>. Besides, based on above experiments results, the effect of the presence of Zn<sup>2+</sup> and Cr<sup>2+</sup> on the biosorption capacities of *Pseudomonas* sp. in binary system was studied. The experiments were carried out in 250-mL conical flask with different concentration of Zn<sup>2+</sup> and Cr<sup>2+</sup>.

### 2.3.8. Binary systems isotherms

To analyze the nature of competition among Cu<sup>2+</sup> and Ni<sup>2+</sup> ions, the Langmuir competitive model [32] was applied to the binary sorption equilibrium data. It is based on the use of single-component adsorption data to describe the behavior of sorption mixtures. Owing to full competition among metals for the binding sites on cell surface, theoretical values of sorption capacity are given by the Eq. (6):

$$q_{L,i} = \frac{q_{\max,i} K_{L,i} C_{\text{eq},i}}{1 + \sum_{j=1}^n K_{L,j} C_{\text{eq},j}} \quad (6)$$

where  $q_{L,i}$  (mmol g<sup>-1</sup>) is the sorption capacity at equilibrium for sorbate “i” and  $C_{\text{eq},i}$  and  $C_{\text{eq},j}$  (mM) are the equilibrium concentrations of sorbates “i” and “j”. The theoretical maximum sorption capacity for sorbate “i”,  $q_{\max,i}$  (mmol g<sup>-1</sup>), and the Langmuir equilibrium constants for sorbates “i” and “j”,  $K_{L,i}$  and  $K_{L,j}$  (L mmol<sup>-1</sup>), were taken from previous work performed on single-component systems, carried out under the same conditions as this one [33]. In a system where the concentrations of the solutes are sufficiently large that surface coverage is substantially complete, the unit term in Eq. (6) may be neglected, and after some algebraic manipulation, the expression can be linearized as shown in Eq. (7) for the binary systems [33],

$$\frac{C_{e,1}}{C_{e,2}q_{e,1}} = \frac{C_{e,1}}{q_{\max,1}C_{e,2}} + \frac{K_{L,2}}{K_{L,1}q_{e,1}} \quad (7)$$

Plots of  $C_{e,1}/C_{e,1}C_{e,2}q_{e,1}C_{e,2}q_{e,1}$  as a function of  $C_{e,1}/C_{e,1}q_{\max,1}C_{e,2}$  would give intercept of  $K_{L,2}/K_{L,1}q_{e,1}$  and a slope of  $1/q_{\max,1}$  for the binary systems.

In the above several experiments, to avoid confusion between biosorption and possible metal precipitation, a control test without microorganisms was performed for each sample in parallel.

## 3. Results and discussion

### 3.1. Effect of pH on metal adsorption

Many researchers [34,35] have reported that pH of the aqueous solution influences cell surface metal-binding sites [36], so pH is considered as an important factor which could affect the adsorption capacity of metal ions from solutions. As depicted from this Fig. 1(a), the maximum biosorption efficiency of Cu<sup>2+</sup> and Ni<sup>2+</sup> was occurred at same pH value (pH 4.5).

The results indicated that the biosorption capacities reached its maximum at pH 4.5, but when beyond the optimum pH, the biosorption capacities started to decrease. This phenomenon could be explained using the fact that, at lower pH, the amount of positive charge (protons) increased on the sites of biomass surface [37,38], which outcompeted the metal ions for the available active sites. When the pH increased, the proton concentration decreased and the biomass surface existed more negatively charge [39]. The biosorption of the positively charged metal ions increased till reaching their maximum biosorption around pH 4.5 for Cu<sup>2+</sup> and Ni<sup>2+</sup>. The decrease of the biosorption efficiency at higher pH values (4.5–7.5) might be attributed to the formation of anionic hydroxide complexes, which decreased the dissolved metal concentration in solution, and their competition with the active sites. Moreover, because the neutral or alkaline solution is not suitable for *Pseudomonas* sp., so the biosorption efficiency of Cu<sup>2+</sup> and Ni<sup>2+</sup> was limited at a very low level under this environment, especially for Cu<sup>2+</sup>.

### 3.2. Effect of initial metal concentrations

The initial metal concentration is also an important influencing factor. Biosorption efficiency of Ni<sup>2+</sup> and Cu<sup>2+</sup> by the *Pseudomonas* sp. at different metal concentration during 24 h was shown in Fig. 1(c) and (d). The concentration of Cu<sup>2+</sup> was varied from 10 to 150 mg Cu<sup>2+</sup> L<sup>-1</sup> at the optimum pH, while the concentration of Ni<sup>2+</sup> varying from 50 to 250 mg Ni<sup>2+</sup> L<sup>-1</sup> with the optimum pH at the same condition. The results presented in Figs. 2 and 3 indicated that the maximum biosorption efficiency of Cu<sup>2+</sup> and Ni<sup>2+</sup> was 14.38 and 84.72%, respectively.

Fig. 1(c) and (d) indicated that the biosorption capacities increased with the increasing of initial Cu<sup>2+</sup> and Ni<sup>2+</sup> concentrations up to 100 mg Cu<sup>2+</sup> L<sup>-1</sup> and 200 mg Ni<sup>2+</sup> L<sup>-1</sup>, respectively. When beyond the optimum initial concentration, the biosorption capacities became to decrease.

Before the optimum initial concentration, from the point of molecular kinematics, the increasing initial ion concentration increased the collision probability

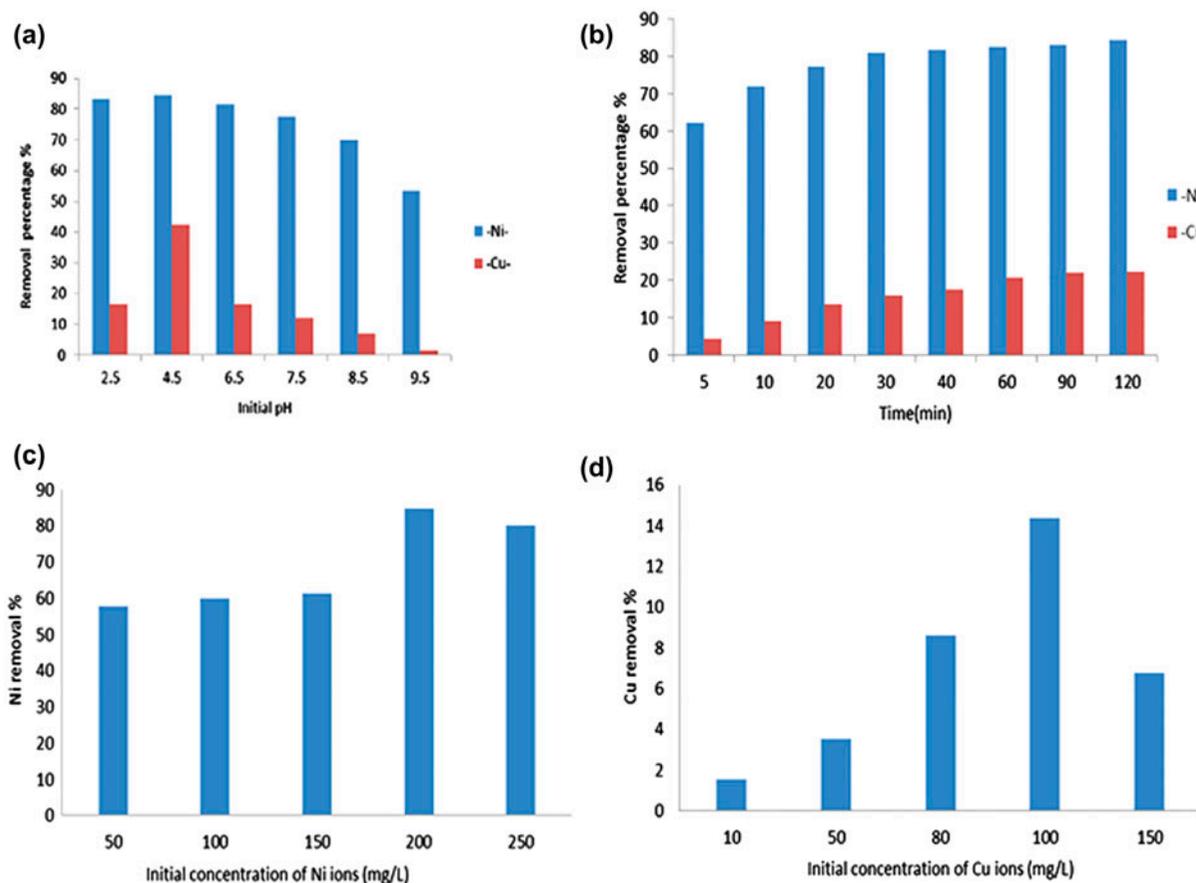


Fig. 1. The influence of different factors for each ion in the single systems: (a) Effect of pH on the biosorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> by *Pseudomonas* sp.; (b) Effect of contact time on the biosorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> by *Pseudomonas* sp.; (c) Effect of initial concentration on the biosorption of Ni<sup>2+</sup> by *Pseudomonas* sp.; (d) Effect of initial concentration on the biosorption of Cu<sup>2+</sup> by *Pseudomonas* sp.

between ions and *Pseudomonas* sp. bacteria, which to some extent improved the adsorption potential of the bacteria. This behavior was attributed to the fact that, initially, all binding sites on the biomass surface were vacant resulting in high metal biosorption in low initial metal concentrations [40]. Moreover, the high metal concentration could provide a driving force to overcome mass transfer resistance between the biosorbent and biosorption medium [41], so higher biosorption capacities were obtained at higher initial concentrations for Cu<sup>2+</sup> and Ni<sup>2+</sup>. However, the initial ion concentration continued to increase, the biosorption of metal was decreased because of a few active sites were available on the surface of the *Pseudomonas* sp. [40]. Besides, another reason for the decreasing of biosorption might be that high initial ion concentration could inhibit the physiological activities of the bacteria; thus, the adsorption process was not completed successfully. So when beyond the optimum initial con-

centration, the biosorption efficiency decreased with initial ion concentration increasing.

### 3.3. Effect of contact time

The contact time was chosen as the variable in the biosorption experiments to investigate its effect on the biosorption Cu<sup>2+</sup> and Ni<sup>2+</sup> by *Pseudomonas* sp. According to the general regular of microbial adsorbent adsorption which shows that adsorption is rapid at the first half, in this study, sampling time was 5, 10, 20, 30, 40, 60, 90, and 120 min, respectively. The results of the experiment were shown in Fig. 1(b), which revealed a two-stage kinetic process [26]: a rapid initial adsorption in the first 5 min, followed by a longer period of much slower uptake.

*Pseudomonas* sp. showed higher adsorption efficiency for Cu<sup>2+</sup> in the first 30 min, especially in the first 5 min. The main adsorption process was done

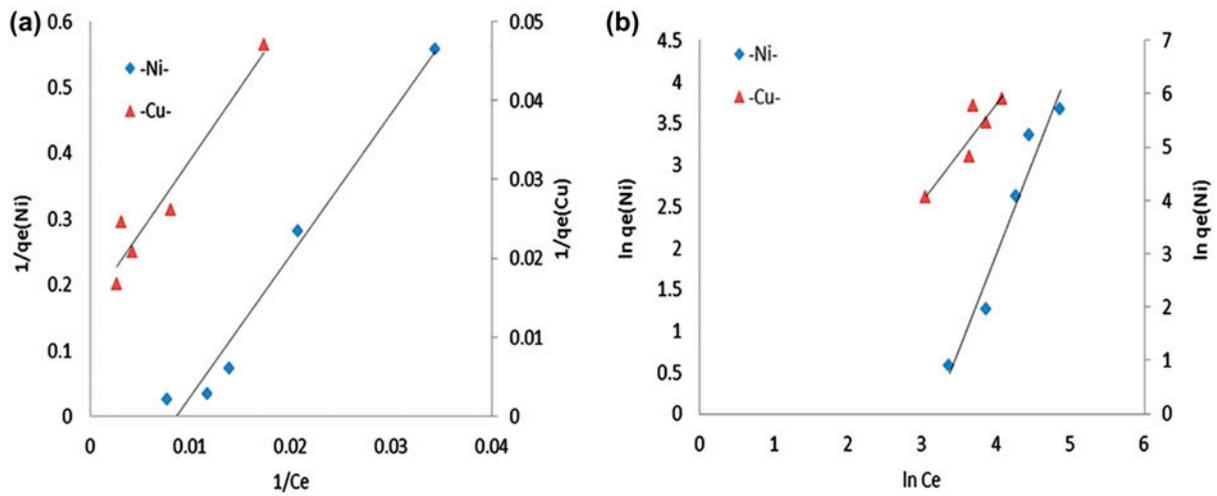


Fig. 2. Equilibrium isotherm models in the single systems: (a) Langmuir plots for the adsorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ; (b) Freundlich plots for the adsorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ .

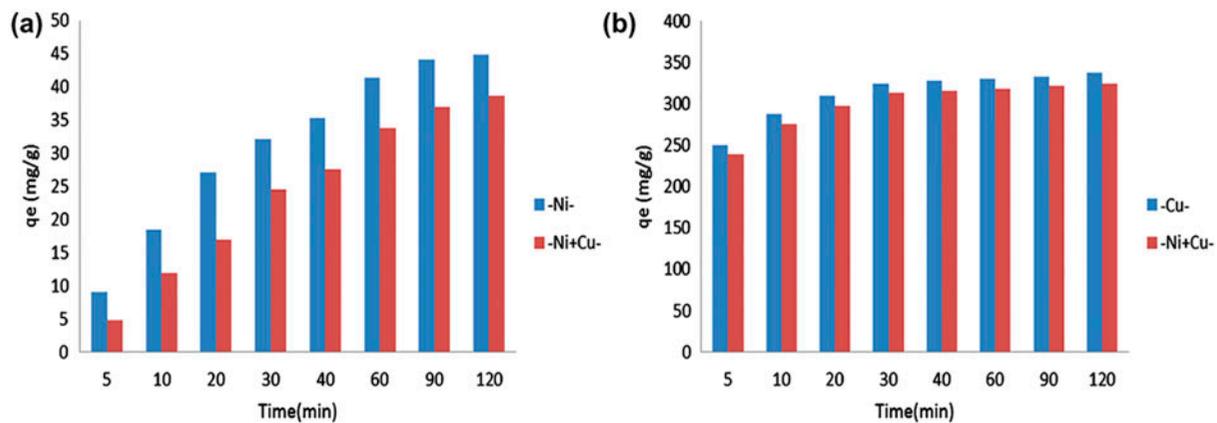


Fig. 3. Competitive biosorption experiments in binary system: (a) The difference of binary for  $\text{Ni}^{2+}$  in the single system and the binary system; (b) The difference of binary for  $\text{Cu}^{2+}$  in the single system and the binary system.

during this period. As time went on, the adsorption efficiency of *Pseudomonas* sp. decreased, and after 40 min, the adsorption process was basically completed and reached equilibrium. The plot of removal efficiency at different contact times for  $\text{Ni}^{2+}$  was similar to that of  $\text{Cu}^{2+}$ . But the maximum removal efficiency for  $\text{Ni}^{2+}$  was observed after 60 min. The adsorption process accorded with the general rule of adsorption.

### 3.4. Isothermal biosorption and adsorption kinetics

In order to further investigate the biosorption mechanism of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , the biosorption isotherm models were used to characterize the interaction of concentrations of metal ions in solution ( $c_e$ ;  $\text{mg L}^{-1}$ )

with the amount of adsorbed metal ions on adsorbent ( $q_e$ ;  $\text{mg g}^{-1}$ ) at equilibrium. Based on the previous experiments, the isothermal biosorption was conducted with different initial concentrations of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  at pH 4.5 and  $28^\circ\text{C}$  for 60 min. And the experimental data of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  biosorption were analyzed using the Langmuir and Freundlich.

Adsorption equation parameters were obtained from experimental data using Eqs. (4) and (5). The results and correlation coefficients were presented in Fig. 2 and Table 1. By comparing the constants and correlation coefficients  $R^2$  (Table 1), it could be seen that the Langmuir model was more suitable for the experimental equilibrium sorption data than the Freundlich model.

Table 1  
Langmuir and Freundlich parameters for the biosorption of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions by *Pseudomonas* sp.

Model	Metal	$q_{\max}$ (mmol g <sup>-1</sup> )	$b$ (Lmmol <sup>-1</sup> )	$K_f$ (Lmmol <sup>-1</sup> )	$1/n$	$R^2$
Langmuir	Ni <sup>2+</sup>	2.207	0.439	–	–	0.9755
	Cu <sup>2+</sup>	0.057	0.539	–	–	0.9296
Freundlich	Ni <sup>2+</sup>	–	–	0.83	0.046	0.9477
	Cu <sup>2+</sup>	–	–	0.23	0.551	0.8358

### 3.5. Competitive biosorption experiments in binary system

In reality, wastewater usually contains several metals [42]. The presence of more than one metal in wastewater can affect biosorption because of many reasons [30,43], such as the number of metals competing for binding sites, the metal concentrations, and the nature of the biosorbent. In order to analyze the competitive effect and selectivity of the biomass for metal ions, the isothermal biosorption in binary system was conducted. The results of the biosorption in the binary Cu<sup>2+</sup>–Ni<sup>2+</sup> systems by *Pseudomonas* sp. were shown in Fig. 3. The experiments results indicated that in binary systems, copper and nickel sorption were both inhibited, but the extent of inhibition of the former metal was greater than that of the latter.

Since most of the functional groups present on the cells wall were non-specific, this suppression in biosorption indicated a degree of overlap in the binding sites, which resulted in a competition on the active sites of the sorbent. Besides, chemical interactions between these metals as well as with the biomass might also result in suppression in biosorption. Moreover, since heavy metal could inhibit the biological activity, in binary system, the presence of copper ion and nickel ion might had much more significant in biological activity than that in single systems, which also might be one reason for the suppression of copper and nickel uptake in the binary systems.

As shown in the Fig. 4, there was a reduction in Cu<sup>2+</sup> and Ni<sup>2+</sup> uptake in the presence of either Zn<sup>2+</sup> or Cr<sup>2+</sup> in binary system, and the metal adsorption decreased in trimetal systems as showed in bimetal systems. Meanwhile, high concentrations of Zn<sup>2+</sup> or Cr<sup>2+</sup> would have a strong suppression of copper and nickel uptake in the binary systems. Reduced metal adsorption in trimetal system as compared to that in bi-metal system could be ascribed to crowding of all the metal ions in solution and saturation of binding sites in constant biomass concentration, leading to enhanced magnitude of competition between metal ions for binding sites [44].

### 3.6. Application of the Langmuir competitive model to binary system

The graphs plotted using Eq. (7), and the adsorption parameters obtained were shown in Fig. 5 and Table 2. The binary combinations fitted the Langmuir competitive model with  $R^2 > 0.993$ . These results indicated that the equilibrium data for the interaction of the metal ions in the binary system could well be described by the Langmuir competitive model. This implied that there was competitive interaction in the sorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> ions. Besides, the  $K_{L,2}/K_{L,1}$  parameter ratios for Ni–Cu and Cu–Ni binary systems were 0.46 and 1.43, respectively. Since the  $K_{L,2}/K_{L,1}$

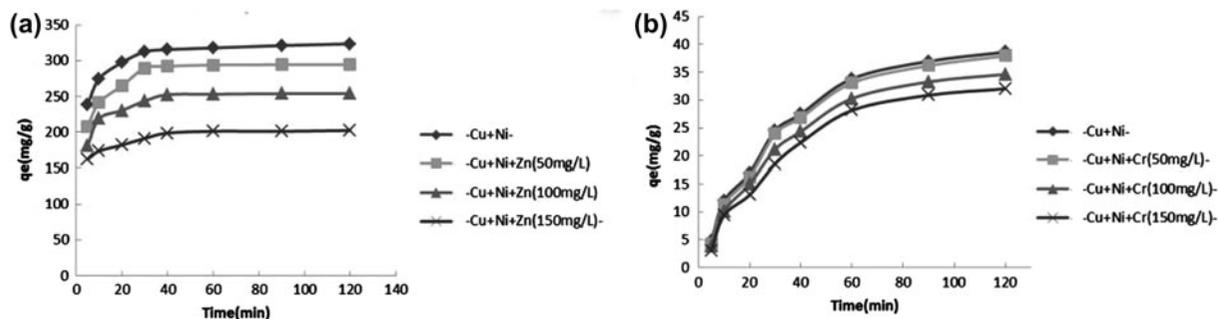


Fig. 4. Effect of the presence of other ions in binary system: (a) Effect of the presence of Zn<sup>2+</sup> on the adsorption of Cu<sup>2+</sup> and Ni<sup>2+</sup>; (b) Effect of the presence of Cr<sup>2+</sup> on the adsorption of Cu<sup>2+</sup> and Ni<sup>2+</sup>.

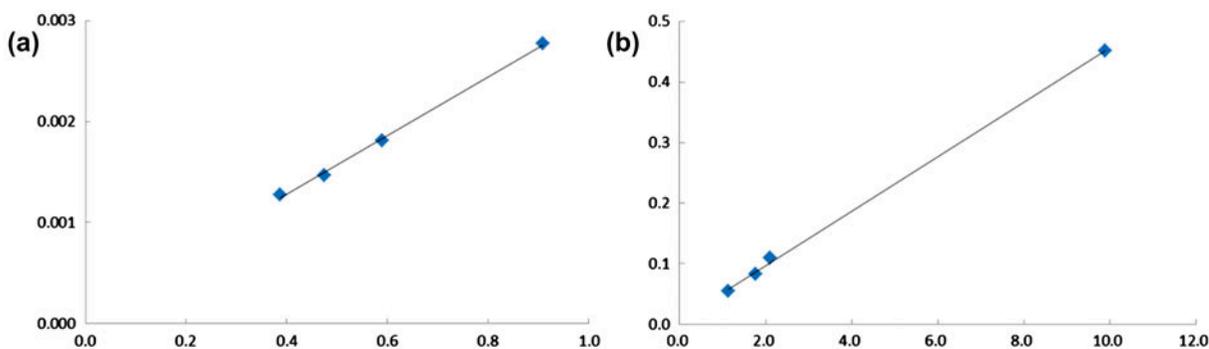


Fig. 5. Competitive Langmuir model plots for the binary sorption: (a)  $\text{Cu}^{2+}$  sorption in the presence of  $\text{Ni}^{2+}$ ; (b)  $\text{Ni}^{2+}$  sorption in the presence of  $\text{Cu}^{2+}$ .

Table 2

Competitive Langmuir model parameters for the biosorption of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions by *Pseudomonas* sp.

System	Metal ion (+interferent)	$q_{\max}$ (mg/g)	$K_{L,2}/K_{L,1}$	$R^2$
Binary	Ni–Cu	293.132	0.46	0.9937
Binary	Cu–Ni	28.371	1.43	0.9933

parameter indicates the heat of adsorption, therefore order of heat of adsorption based on the magnitudes of the  $K_{L,2}/K_{L,1}$  ratios was found to be  $\text{Ni} > \text{Cu}$ .

According to these results, *Pseudomonas* sp. could be used as an effective and alternative biomass for the removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from wastewater, especially the removal of  $\text{Cu}^{2+}$ , due to its high biosorption capacity, being of natural and cost-effective biomass.

#### 4. Conclusions

In this study, *Pseudomonas* sp. was used as an adsorbent for the removal of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ . Data presented in this study confirmed the sorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  on *Pseudomonas* sp. was significantly affected by pH, contact time, and initial metal concentration, and the maximum uptake  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  were  $336.84 \text{ mg Ni}^{2+} \text{ g}^{-1}$  and  $44.78 \text{ mg Cu}^{2+} \text{ g}^{-1}$  under each favorable conditions in single systems, respectively. This study also revealed that the Langmuir isotherm was more suitable than Freundlich isotherm for the biosorption by *Pseudomonas* sp. In binary system, there existed the competitive adsorption for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , so  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  sorption were both inhibited, and the extent of inhibition of the former metal was greater than the latter. Besides,  $\text{Cu}^{2+}/\text{Ni}^{2+}$  binary systems showed good fitting to the Langmuir competitive model. So the sorption of both metals ions could be

based on the assumption of the Langmuir model on the cyanobacterium surface. Consequently, this adsorbent had a great potential for removing of metals ions as an eco-friendly process. In order to further study, the adsorption mechanism of *Pseudomonas* sp., much work is underway.

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