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The comparison of biosorption characteristics between the two forms of *Aspergillus niger* strain

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ABSTRACT

There is no study and data about aerial mycelium biosorbents for heavy metal removal. In previous investigations, *Aspergillus niger* biosorbents were made of vegetative mycelium, called mycelium pellets, which were obtained from the fermentation of a liquid medium, and usually needed lots of procedures to produce. This work therefore was novel that the mycelium of *Aspergillus niger* were scraped directly from the surface of solid medium (cultivated 7 d) as a kind of biosorbent, called aerial mycelium. In biosorption experiments, aerial mycelium exhibited a short biosorption equilibrium time of 30 min, high copper biosorption capacity (100 mg/g) and high removal efficiency at a pH range of 4.0–6.0. The main Cu^{2+} biosorption mechanism were electrostatic attraction and Cu^{2+} ion exchange with K^+, Na^+, Mg^{2+} and Ca^{2+}, together with chelation with functional groups such as –COOH, $–NH_2$, $–PO_4^{3-}$, and –OH. The biosorption data obtained were well described by the pseudo-second-order kinetic model and the Freundlich isotherm model. In addition, because aerial mycelium can grow on many kinds of moist agro-industrial waste materials, it could be becoming a potential biosorbent in large-scale industrial wastewater treatment.

Keywords: Biosorption; Copper; *Aspergillus niger*; Aerial mycelium; Mycelium pellets

1. Introduction

Fungi biosorbents (yeast, filamentous fungus, and macrofungus) can biosorb metal ions more effectively as the compositions of their cell walls (mannan, glucan, chitin, cellulose, and protein) possess strong negative charges [1]. Some yeast, like *Candida utilis*, has been used to biosorb Cu^{2+} in waste water [2]; and beer yeast has been studied to assess the effectiveness of biosorption for Cu^{2+} [3]. Most filamentous fungi were also able to accumulate metals from wastewater. For example, *Aspergillus niger* was used to biosorb Cu^{2+} in the aqueous solution [4] and *Aspergillus terreus* was applied in a biosorption batch system to study the effects of temperature, pH, biomass dose, and stirring speed on copper removal [5]. In addition, macrofungus, which are common in China, have an effect on the biosorption of heavy metals. The ability of the *Trametes versicolor* biomass for biosorption of Cu^{2+} from aqueous solutions was studied in batch experiments [6].

Aspergillus niger, as one kind of fungus biosorbent, is non-toxic and quite safe [7]. For the past decades, owing to mycelium are easier to acquire from industries and to separate from the liquid medium, researchers have been conducting lots of biosorption studies with *Aspergillus niger*. At first, *Aspergillus niger* was used to biosorb Ni^{2+} [8], After that, pretreated *Aspergillus niger* biomass was found to be a higher biosorption capacity biosorbents [9]; moreover, the equilibrium, kinetic and thermodynamic parameters of biosorption of Cu^{2+} and Pb^{2+} on pretreated *Aspergillus niger* was studied [10]; the comparison of biosorption process of linear and non-linear regression was analyzed [11]. In addition, the biosorption process of Pb^{2+} from aqueous solutions by *Aspergillus niger* was found that followed first-order reaction

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kinetics and the Freundlich model [12]. The chitosan of the *Aspergillus niger* cell wall contributed most to its biosorption capacity [13].

However, all the researchers' biosorbents were mycelium pellets, which acquired from the liquid medium, some collected with centrifugation and used directly [14]. Some mycelium pellets was dried and crushed to powder biosorbents [15]. Obviously, this kind of biosorbents preparation was costly (liquid medium and shaken cultivation) and the procedure was complicated. Aerial mycelium, which grew on the solid medium, can be acquired directly, and most moist agriculture waste can supply the nutrition for fungus growth (although it needs more time to grow than mycelium pellets) [16].This phenomenon suggests that it is unnecessary to undergo a series of complex procedures to produce effective mycelium pellets biosorbents, just collected the aerial mycelium biosorbents directly from the solid medium. Moreover, in the later stage of aerial mycelium growth, a kind of reproductive organ-spores can be produced, which characterized negative zeta potential and lager specific surface area, which may lead to a higher biosorption capacity [17].

Therefore, the main objective of our presented research is to study the biosorption capacity of aerial mycelium under different pH and dosage, while using mycelium pellets as a control. Subsequently, aerial mycelium were systematically studied and observed, using a combination of mathematical modeling, scanning electron microscope (SEM-EDX) and Fourier infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Microorganism and culture medium

Aspergillus niger 98003 was purchased from the Harbin Chun-Rui Corporation.

The liquid martin medium was composed of peptone 5 g, yeast powder 1 g, glucose 20 g, KH_2PO_4 1 g, $MgSO_4$ 0.5 g, and 1 L of deionized water with a pH of 6.4.

The solid martin medium was a mixture of liquid martin medium and 15% agar.

2.2. The preparation of mycelium pellets and aerial mycelia biosorbents

2.2.1. Mycelium pellets biosorbents

The liquid martin medium with inoculated *Aspergillus niger* were shaken on a rotary shaker at 150 rpm at 30°C. After 5 d, the mycelium pellets were obtained; then, filtered with a 0.45-um pore size paper. The mycelium pellets were deactivated by heating in an autoclave in a shaker flask at 121°C for 15 min. They were then washed with deionized water. After washing, the collected mycelium pellets were dried at 50°C in an electrically heated blast dry box to a constant weight. The dried mycelium pellets were crushed with grinder and sieved with a standard sieve to obtain the dried mycelium powder.

2.2.2. Aerial mycelium biosorbents

The spore suspension (0.2 ml) of *Aspergillus niger* was smeared on the solid martin medium dishes. After 4 d, the dishes covered with aerial mycelium using the aerial mycelium directly from the dishes were dried at 50°C to a constant weight.

2.3. Biosorption experiment

2.3.1. Comparison of mycelium pellets and aerial mycelium biosorbents

Certain dosages of mycelium pellets and aerial mycelium biosorbents were placed into a 100 mL of $CuSO_4{\cdot}5H_2O$ solution, with an initial Cu^{2+} concentration of 30 mg/L. The pH was 5.3 (without acid or alkaline) and was shaken at 30°C, at 100 rmp for 2 h. The initial concentration of 30 mg/L was chosen since the concentration of most industrial wastewater is under 30 mg/L.

2.3.2. The effect of different initial acidity on mycelium pellets and aerial mycelium biosorption

Mycelium pellets and aerial mycelium biosorbents (0.1 g) were placed into 100 mL of a $CuSO_4{\cdot}5H_2O$ solution with an initial Cu^{2+} concentration of 30 mg/L and with an initial pH value of 2.0, 3.0, 4.0, 5.0 or 5.3 (natural pH) achieved by the addition of HCl. The flasks were shaken at 30°C, at 100 rmp for 2 h to ensure equally distributed pH levels throughout the medium.

2.3.3. Aerial mycelium biosorption kinetics, equilibrium and thermodynamics

In order to depict the process of the biosorption, their kinetics, equilibrium and thermodynamics were studied. For the kinetic studies, Lagergren's first order equation, a pseudo-second-order equation and the intra-particle diffusion equation were used to model the kinetics of copper sorption (from 0 to 180 min) onto the aerial mycelium [18]. Isotherm studies (Langmuir, Freundlich and Tempkin) were conducted with varying initial copper concentration from 10 to 250 mg/L and at a fixed sorbent concentration of 0.1 g/L [19]. The biosorption experiments were also carried out at 298 K, 303 K and 308 K to determine the biosorption thermodynamic parameters [11].

2.3.4. Data processing

The Cu^{2+} solution was filtered through a membrane with a pore diameter of 0.45 um, and was analyzed by inductively coupled plasma mass spectrometry to determine the concentrations of the Cu^{2+} before and after biosorption.

2.3.5. Zeta potential analysis

Aerial mycelium was treated to three kinds: (1) Fresh biosorbent, which acquired from dishes cultivated 4 d; (2) dry biosorbent, which was fresh biosorbent dried at 50°C to a constant weight; (3) inactivation biosorbent, which was fresh biosorbent dried at 160°C over 2 h. Three aerial mycelia and mycelium pellets samples were dispersed in deionized water, and the charge on their surface were tested by Zeta potential meter (ZetaSizer 3000, Malvern Corporation).

2.3.6. FTIR and SEM-EDX characterization

The dried samples (mycelium pellets and aerial mycelium) used for SEM-EDX were mounted on metal stubs and coated with gold for better image contrast. A SU8010 SEM from Japan was used to view the images [20].

FTIR technique was used to characterize the presence of specific chemical groups in the dried biosorbents (mycelium pellets and aerial mycelium). With this aim, the PerkinElmer Spectrum One FTIR spectrometer was used [21].

3. Results and discussion

3.1. Comparison of mycelium pellets and aerial mycelium biosorbents

3.1.1. Biosorption capacity of the two biosorbents

The high biosorption capacity is an important specification of biosorbents and is often affected by reaction conditions, like initial metal concentration, whether they are pretreated or not, and so on [22].

As shown in Fig. 1(a), when the biosorbents were 0.1 g, the maximum biosorption value of aerial mycelium biosorbents was found to be 20.02 mg/g. The maximum biosorption value of the mycelium pellets biosorbents was only 8.14 mg/g. For the two kinds of biosorbents, the aerial mycelia biosorption capability was always higher than mycelium pellets. Regarding the mycelium pellets, in Akar's study at 2006, under the similar conditions, including temperature, dosage and rotating speed, the biosorption capacity was about 6 mg/g [23]. Moreover, *Aspergillus niger* mycelium pellets pretreated with NaOH can improve their biosorption capacity, when the initial concentration was 25 mg/L, a temperature of 25°C, and a pH value of 5.0, the copper biosorption capacity was 7.8 mg/g [24]. So, the Cu^{2+} sorption capacity of mycelium pellets was inferior to the aerial mycelium even when the *Aspergillus niger* was pretreated or modified (Table 1).

This phenomenon of high biosorption capacity of aerial mycelium suggests that it is unnecessary to undergo a series of complex procedures to produce effective mycelium pellets biosorbents. Aerial mycelia used were collected directly from the solid martin medium. In addition, we found that the *Aspergillus niger* strain can grow on most kinds of moist agricultural and forestry residues like rice and corn stalks to produce abundant aerial mycelium, without any added nutrition. So, the usage of aerial mycelium is an innovative method that can significantly increase biosorption capacity.

3.1.2. Effect of biosorbents dosage

The biosorbents dosage also affects copper biosorption (Fig. 1(a)). The ability of biosorption of Cu^{2+} declines as the dosage of mycelium pellets and aerial mycelium increase. The lower the biosorbents concentration, the higher the attached uptake. This phenomenon is due to static electricity reaction, the distance between the biosorbents are bigger, and a larger number of metal can be biosorbed [24,26].

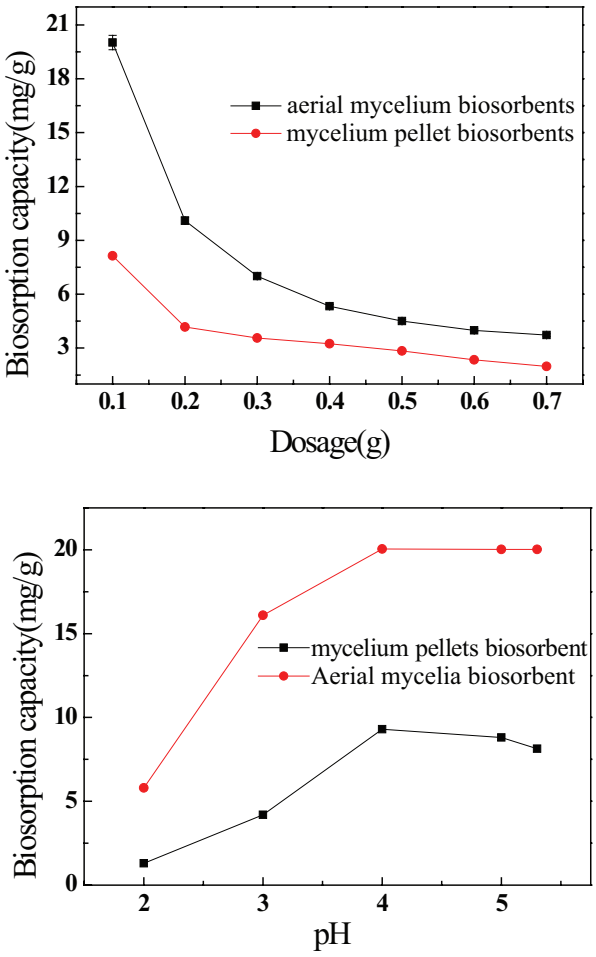

Fig. 1. (a) The comparison of Cu^{2+} biosorption capacity between mycelium pellets and aerial mycelium biosorbents under different biosorbent dosages. (b) Effect of pH values on the biosorption by mycelium pellets and aerial mycelium biosorbents.

3.2. Effect of pH values on the biosorption of Cu^{2+} by mycelium pellets and aerial mycelium biosorbents

Biosorption is a complex process [27], which depends on several factors [28], such as pretreatment, initial concentration and pH. Biosorption solution pH influences both cell surface metal binding sites and the metal chemistry in water. *Aspergillus niger* contained an abundance of chitin–chitosan units and a reasonable amount of protein and amino acids like histidine, serve as a matrix of –COOH and $–NH_2$ groups, which is essentially a weak acid [29]. As can be seen in Fig. 1(b), under such condition (100 mL of $CuSO_4.5H_2O$ solution, an initial Cu^{2+} concentration of 30 mg/L, shaken at 30°C, at 100 rmp for 2 h), when the pH was between 2 and 4 (Fig. 1(b)), Cu^{2+} sorption of the two biosorbents increased rapidly as the pH rose. When the pH value ranged between 4 and 6, there was no significant increase or decrease in Cu^{2+} sorption by aerial mycelium, which implied that Cu^{2+} biosorption reaction was adaptable to a wide range of pH levels. This result corresponds with Omorogie's research in 2012 [20]. However, the biosorption by mycelium pellets was decreased a little, which

Table 1
Comparison of the biosorption capacity for Cu^{2+} by different forms of *Aspergillus niger* in different conditions

Biosorbent	Initial Cu^{2+} concentration (mg/L)	pH	Biomass dosage (g/L)	Cu^{2+} uptake (mg/g)	Reference
NaOH pretreated mycelium pellets	250	5	1	28.7	[10]
PVA-immobilized mycelium pellets	30	5.5	1	8.9	[25]
Mycelium pellets	30	5.5	1	5.8	[25]
Mycelium pellets	30	5.3	1	8.1	Present study
Aerial mycelia	30	5.3	1	20.02	Present study
Spores	30	5.3	1	27.3	Present study

indicated that the best pH of mycelium pellets biosorbent was 4. In addition, the natural pH of 30 mg/L Cu^{2+} was 5.3, which means that in the actual treatment of Cu^{2+} waste water, it is not necessary to adjust the pH. The best pH was similar to Akar's study 2006, where the biosorbents were *Aspergillus flavus*, and the most effective initial pH was about 5 during the biosorption process [23]. When the pH was 1, H_3O^+ ions in the solution were at a high concentration and the Cu^{2+} ions had to compete with them for biosorption sites. The other reason for this was that the functional groups were more protonated, which led to a rejection of the Cu^{2+}. As the pH increased to 5.3, the Cu^{2+} biosorption capacity also increased to its peak. This can be attributed to the increase in negative charge on the biosorbent surface and the reduction of H^+ ions which compete with Cu^{2+} for biosorption sites in the solution.

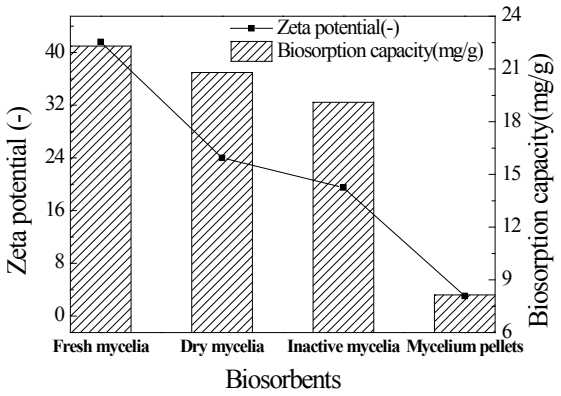

Fig. 2. Zeta potential and Cu^{2+} biosorption capacity of the mycelium pellets and aerial mycelia biosorbents.

3.3. Zeta potential analysis

The zeta potential stands for the charge of the sample surface, as can be seen in Fig. 2, all the samples were negative charge gel, and with the decrease of the absolute value of zeta potential, the biosorption capacity of samples was also decreased, this phenomenon indicated that the biosorption process was related to the electrostatic attraction. In addition, aerial mycelium were more negative than mycelium pellets, which mean that compared with mycelium pellets, aerial mycelium can attract more positive ions, and therefore have better biosorption capacity.

3.4. SEM-EDX of aerial mycelium and mycelium pellets

Figs. 3(a)–(e) display the SEM micrograph of aerial mycelium and mycelium pellets before and after the copper biosorption.

Figs. 3(a) and (b) depict the aerial mycelium before and after copper biosorption. From Fig. 3(a), we can see some smooth tubes, which are aerial mycelium, and some scattered particles, which are spores. After biosorption, the vegetative mycelium were distorted and have twisted slightly out of shape. Figs. 3(c) and (d) were the mycelium pellets before and after the biosorption, and as can be seen in Fig. 3(c), vegetative mycelium have the characteristics of being like a flat network; it has a regular shape and the surface is not rough. After biosorption as seen in Fig. 3(d), the structure was destroyed and the shape has been totally changed. In addition, Figs. 3(b) and (d) indicate that the copper resistance of aerial mycelium was greater than mycelium pellets.

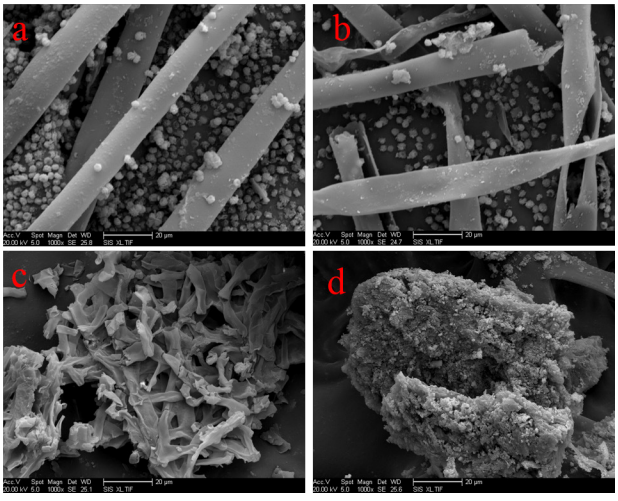

Fig. 3. (a) and (b) Aerial mycelium before and after biosorption; (c) and (d) Mycelium pellets before and after biosorption.

From the four pictures, we can see that morphology and structure of aerial mycelium is totally different with mycelium pellets, even though they grow in the same medium (one is liquid medium, and other is solid) and absorbed the same nutrients. The *Aspergillus niger* strain in a liquid medium can form mycelium pellets (Figs. 3(c) and (d)); however, on solid medium, aerial mycelium will be formatted (Figs. 3(a) and (b)), and in the later stage of aerial mycelia

Table 2
Element content of aerial mycelium and mycelium pellets

Biosorbents	Aerial mycelium	Mycelium pellets
C	65.73	58.41
N	13.67	19.45
O	15.46	16.92
P	02.53	2.11
K	00.83	1.09

growth, a type of reproductive organ-spore can be produced. Spores, characterized by the strong power to resist external hostile environmental conditions, have a small diameter, about 2 um, and there are many small bumps and wrinkles on the surface of the spores, which means that they have a large specific surface area. In addition, TEM demonstrated that the spores of *Aspergillus niger* were typically characterized by negative zeta potentials over a wide range of pH values, which may lead to high ability of biosorption [30].

As shown in Table 2, the elements of aerial mycelium and mycelium pellets are similar, as they have similar chemical component, in addition, the content sequence is C > N > O > P > K, which are caused by the constituents of *Aspergillus niger* chitin, glucan, mannan, and little protein and lipids [13].

The C content of aerial mycelium is higher than mycelium pellets; this difference may be caused by spores, which are characterized by having thick cell walls made of chitin that is a kind of hexose. The biosorption capacity of the fungus was dependent on species and age as well as on the chemical composition of the cell walls [13] and thus we can conclude that spores may related to the higher biosorption capacity.

3.5. FTIR of mycelium pellet and aerial mycelium

The aerial mycelium and mycelium pellets before and after biosorption were shown in Fig. 4. The IR spectrum of the mycelium pellets appear to be a little different from the aerial mycelium. Mycelium pellets have two extra bands, peaking at 1,379 and 1,312 cm^{-1}, which were for C-H and C-N; and aerial mycelium also has two additional functional groups C–H and C=O, which have characteristic absorption peaks at 2,855 and 1,740 cm^{-1}, respectively. Both C–N and C=O were stretching the vibration of the glucan and chitin, which are the major cell wall constituents. The relative difference in the band intensity corresponds to the difference in the concentration of respective functional groups associated with the band. Therefore, a conclusion maybe deduced that the function group and chemical constituents of the cell walls were not the main reason differences of biosorption between aerial mycelium and mycelium pellets. The determining factor was the size. Because of the small size of the spores, the surface area contacts with copper had become lager.

As can be seen from Fig. 4, the peak observed at 2,926 was indicative of the C–H group [15]. The wave at 1,740 cm^{-1}, a shoulder was observed which may be due to a carbonyl group of unionized carboxylates. The esterification of carboxylate functionalities present in the cell walls of *Datura innoxia* results in a decrease in metal uptake by as much as 40%. Carboxylate groups are important in metal

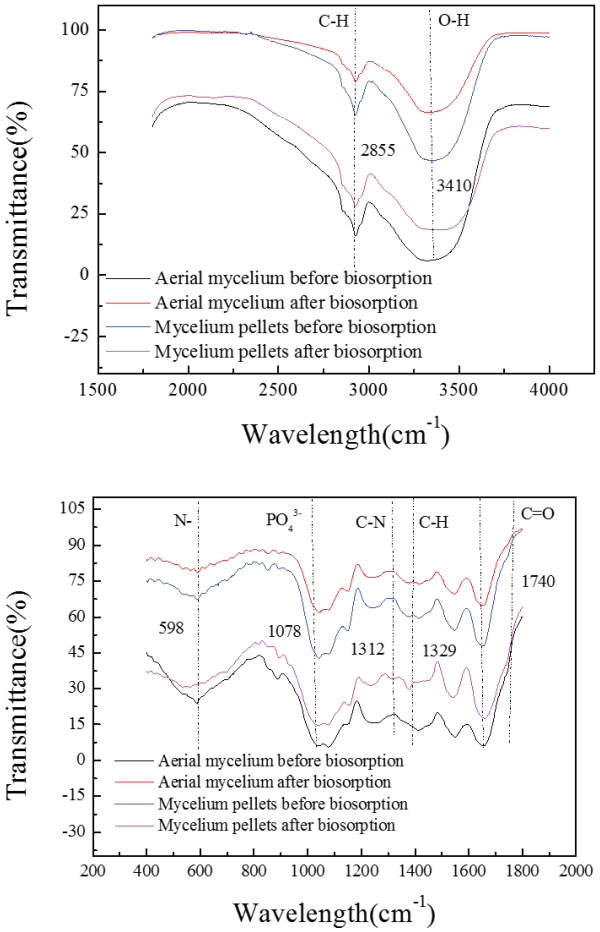

Fig. 4. FTIR spectra of mycelium pellets and aerial mycelium.

ion adsorption for this specific biomaterial [31]. Moreover, Mukhopadhyay in 2008 also observed the same shoulder at 1,725 cm^{-1} for *A. niger* [9]. The peak present at 1,655 cm^{-1} was the result of C=O stretching with N–H deformation and was indicative of an amide band (amide 1). The band present at 1,549.5 cm^{-1} indicated the presence of amide 2 and which resulted from N–H deformation. These two amide bands were also observed by Guibal in 1995 [32]. The biosorption wavelength at 1,317.74 cm^{-1} can be attributed to the C–N stretching vibration of the chitin–chitosan and protein fractions.

Comparing the biosorbents before and after biosorption, there were some shifts of the peaks, from 1,740 to 1,743; and 1,655 to 1,653; 1,549.5 to 1,548; and also from 2,926 to 2,855. Moreover, it was noted that the peaks in the region of the lower wavelength (<700 cm^{-1}) for aerial mycelium and mycelium pellets without copper appeared to contain multiple biosorption peaks as compared with that of loaded aerial mycelium and mycelium pellets with copper; this could be attributed to the interaction between copper species and N-containing bioligands [33]. These results showed that functional groups such as carboxyl (–COOH), amide (–NH_2), phosphate (–PO_4^{3-}), and hydroxide (–OH) were responsible for metal sequestering by the fungal biomasses.

3.6. Biosorption kinetics of Cu^{2+} by aerial mycelium

The biosorption kinetics reflected the relationship between the sorption rate and sorption time [18]. During the first 30 min, the sorption rate increased at a rapid speed; after that, the increase of Cu^{2+} sorption began to slow down and then stabilized at 120 min as it reached equilibrium.

For liner simulation, as shown in Table 3, the pseudo-second-order equation was better ($R^2 = 0.997$) than the Lagergren-first-order ($R^2 = 0.931$) and intra-particle diffusion ($R^2 = 0.722$) to simulate the dynamic Cu^{2+} sorption process by aerial mycelium. Moreover, the theoretical maximum biosorption capacity (17.8 mg/g in Table 3) inferred from the pseudo-second-order equation (26.31 mg/g in Table 3) was closer to the detected experimental value (24.1 mg/g in Table 3). The data which fit in the pseudo-second-order equation (Fig. 5(b)), meaning that there was a chemical process such as chelation and ion exchange as we obtained a series of data in the liquid after Cu^{2+} biosorption, and the contents of Ca^{2+}, K^+, Mg^{2+}, and Na^+ were 0.67, 16.20, 2.77 and 1.32 mg/g, respectively. Sepehr's study in 2012 had similar results, and his biosorbents were *Aspergillus niger*, where his process fit in both the pseudo-first-order and pseudo-second-order model (both of them $R^2 > 0.90$). Furthermore, the pseudo-second-order model was a little more adaptable in describing this process than the pseudo-first-order model [34]. In addition, intra-particle diffusion should be the rate-controlling step if the lines were to pass through the origin, together with the parameters R^2, which demonstrated that the intra-particle diffusion was not the rate-controlling step [11].

The non-linear method was also used to simulate the process of biosorption kinetics, because each of these transformations (linear methods) changes the original error distribution (for better or worse) [35], as the Fig. 5(d) shown, pseudo-second-order equation ($R^2 = 0.998$) depicted the process better than the Lagergren-first-order ($R^2 = 0.868$) and the intra-particle diffusion equation ($R^2 = 0.757$), and a paired sample *t*-test was applied to the data to test the biosorption model' simulation. The results show that both pseudo-second-order equation ($p = 0.776$) and Lagergren-first-order ($p = 1$) were better than intra-particle diffusion equation ($p = 0.034$) to

Table 3
Simulation of sorption kinetic equations and corresponding parameters (linear)

$q_{e\,exp}$ (mg/g)	Lagergren-first-order			Pseudo-second-order			Intra-particle diffusion		
	$q_{e\,cal}$ (mg/g)	k_1 (min)	R^2	$q_{e\,cal}$ (mg/g)	k_2 (g/mg/min)	R^2	C (mg/g)	K_i (g/mg/min)	R^2
24.1	17.823	0.04	0.931	26.3	0.004	0.997	1.5	7.26	0.722

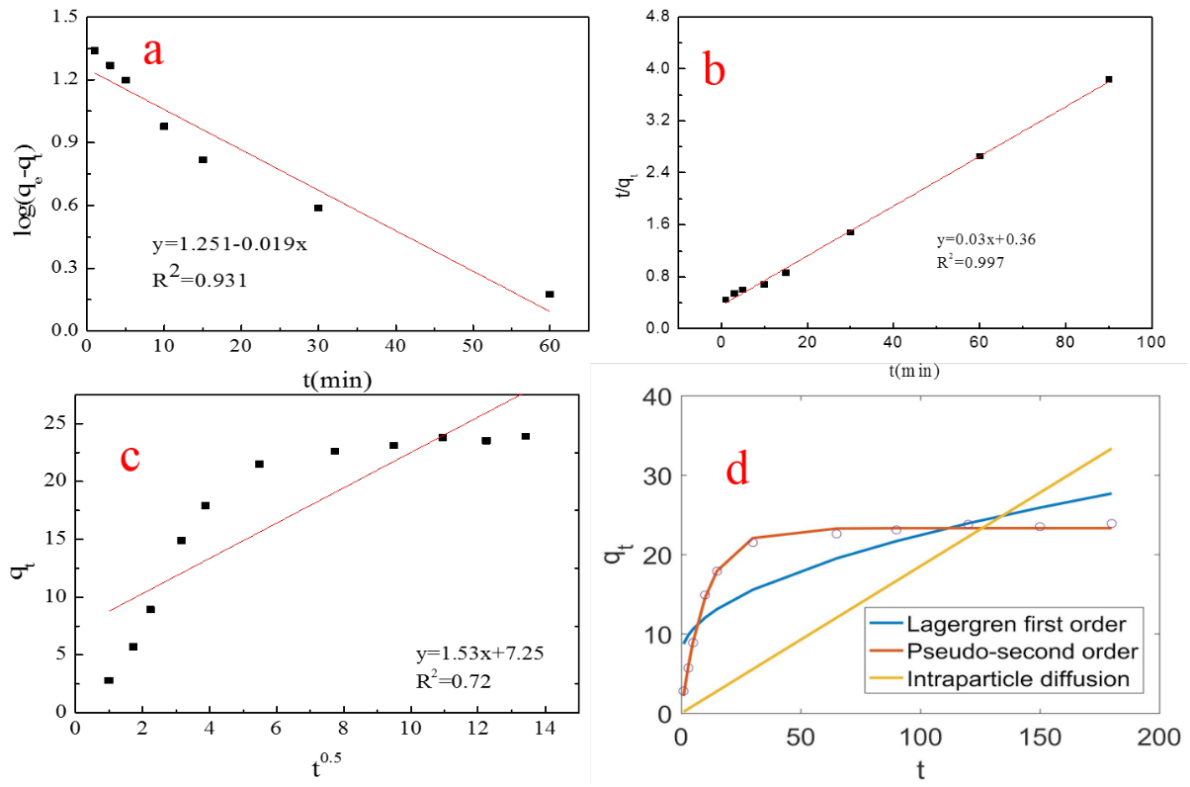

Fig. 5. (a)–(c) Linear simulation of kinetics: Lagergren first order, pseudo-second-order and intra-particle diffusion; (d) non-linear simulation of kinetics.

simulate the dynamic of the biosorption process, because $p < 0.05$ indicates that calculated data are significantly different from the experimental results.

3.7. Isotherm biosorption of Cu^{2+} by aerial mycelia

The sorption isotherm model described the relationship between sorption capacity and equilibrium concentration as seen in Fig. 6.

For linear method, the biosorption data obtained under the optimum conditions were well described by the Freundlich isotherm model than Langmuir and Tempkin (Fig. 6 and Table 4), since the Freundlich model assumes the biosorbents surface was heterogeneous and the biosorption process was multilayer, so there was a heterogeneous distribution of available active sites onto the aerial mycelium [36].

In addition, the non-modified biosorption models describe the individual isotherm parameters under 303 K, as the Fig. 6(d) shown, Freundlich model ($R^2 = 0.998$) simulated the process better than the Langmuir ($R^2 = 0.994$) and the Tempkin models ($R^2 = 0.961$), and a paired sample *t*-test was applied to the data to test the biosorption model simulation. The results show that Freundlich model ($p = 0.81$), Langmuir model ($p = 0.41$) and Tempkin model ($p = 0.96$) can simulate the dynamic of the biosorption process well, since $p < 0.05$ indicates that there is no significantly different between the two samples. Therefore, this biosorption process can be well simulated by these three models with the non-linear method, which was accordance with the results of linear method, as all of them $R^2 > 0.9$.

3.8. Thermodynamic model of Cu^{2+} biosorption by aerial mycelium

In order to understand the impact of temperature, spontaneity and feasibility of this adsorption system with aerial mycelium, there is need to calculate and evaluate the various thermodynamic parameters of this process [20]. As shown in Table 5, the negative values of ΔG° indicated the spontaneous

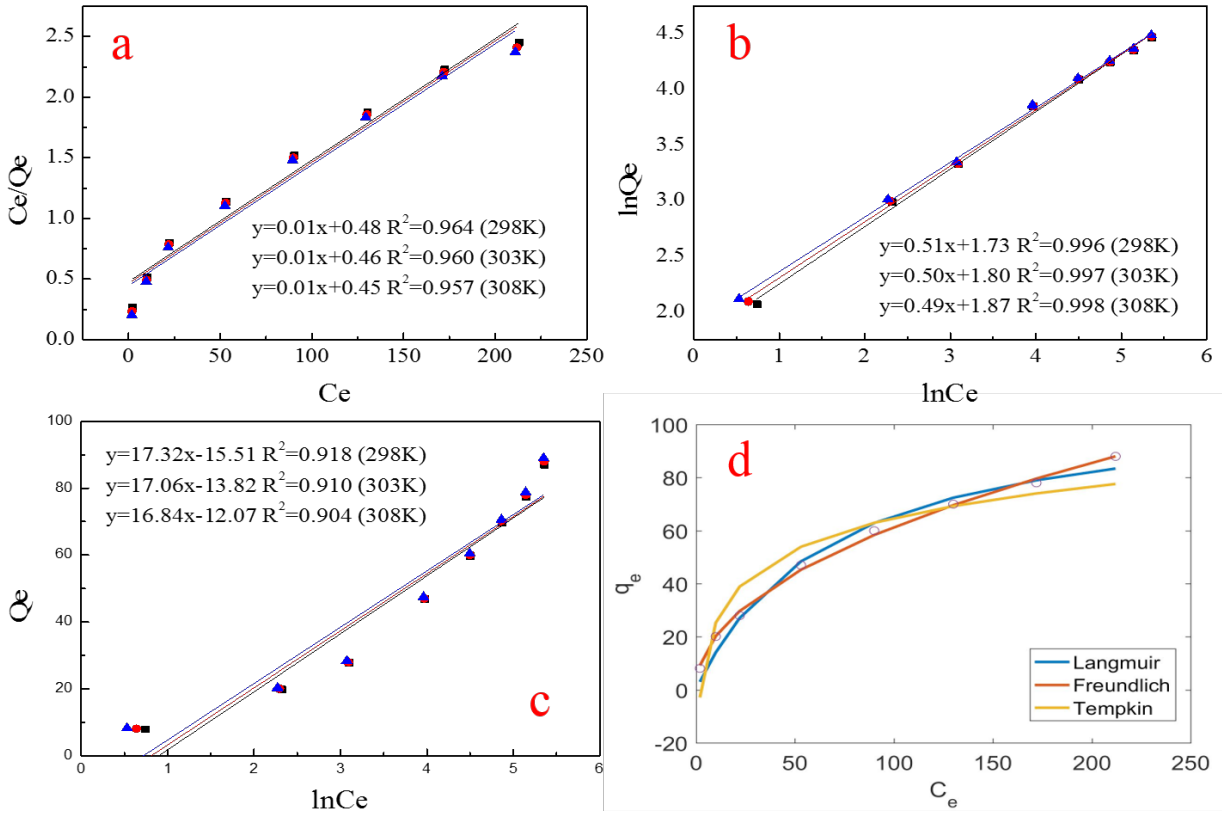

Fig. 6. (a)–(c) Linear simulation of isotherm: Langmuir, Freundlich and Tempkin; (d) non-linear simulation of isotherm.

Table 4
Simulation of isotherm sorption models and corresponding parameters (linear method)

Temperature (K)	Langmuir			Freundlich			Tempkin		
	q_{max} (mg/g)	b (L/mg)	R^2	K (L/mg)	n	R^2	B_T	K_T	R^2
298	100	0.159	0.964	5.64	1.96	0.996	17.32	2.44	0.918
303	100	0.168	0.960	6.05	2.0	0.997	17.06	2.24	0.910
308	100	0.173	0.957	6.48	2.04	0.998	16.84	2.04	0.904

Table 5
Thermodynamic parameters for the biosorption at different temperature

ΔG° (KJ/mol)			ΔH°	ΔS°	R^2
298	303	308	(KJ/mol)	(J/mol·k)	
–4.56	–4.42	–4.35	10.77	0.02	0.939

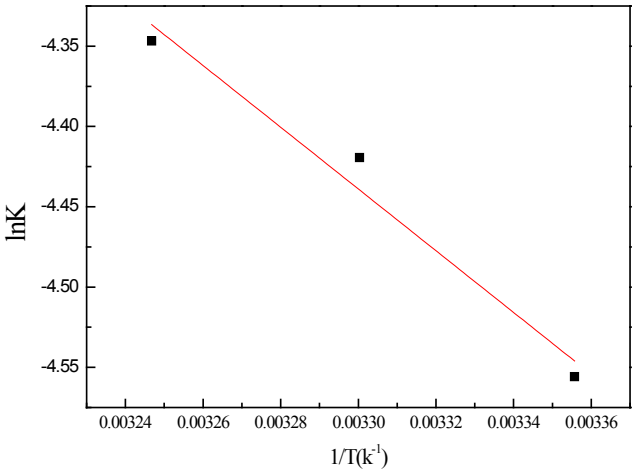

Fig. 7. Plot of ΔG versus 1/T for the estimation of thermodynamic parameters for biosorption of Cu^{2+} by aerial mycelium.

nature of the adsorption process. Positive value of ΔS° showed the increasing randomness at the solid–solution interface during the adsorption process. The positive values of ΔH° suggested the endothermic nature of the adsorption interaction [6].

4. Conclusions

The biosorption characteristics of *Aspergillus niger*, aerial mycelia were studied for Cu^{2+}. In the same reaction conditions, the biosorption capacity of spores (27.3 mg/g) and aerial mycelium (20.08 mg/g) were much better than mycelium pellets (8.14 mg/g). The pseudo-second-order and Freundlich biosorption models described the biosorption of Cu^{2+} onto aerial mycelium very well. Thermodynamic study indicates the biosorption process was spontaneous and endothermic. The results of SEM-DEX and FTIR showed that the high biosorption capacity of aerial mycelium was attributed to the spores, which are characterized by small size, loose surface, and strong stress resistance. This research promotes a theory that *Aspergillus niger* spores are one kind of natural large biosorption capacity material.

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