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Removal of zirconium from aqueous solution by *Aspergillus niger*

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Abstract. Removal of zirconium from its dilute aqueous solution using *Aspergillus niger* as a dried and living biomass was investigated. Through that, the effect of some operational parameters on biosorption, including pH, temperature, contact time, initial concentration of zirconium and dose of biomass, were studied. Based on the results, it was concluded that the uptake of zirconium by both dried and living biomasses is pH dependent, and maximum uptake was observed in pH = 3.1 for both biomasses. The maximum uptake capacity of the living biomass was obtained at 30°C. However, the biosorption of zirconium by dried biomass was not affected by temperature. The maximum uptake capacity for living and dried biomasses (78.8 mg/g and 142 mg/g, respectively) was obtained at equilibrium time of 120 min and 30 min, respectively. Equilibrium isotherms showed that adsorption of zirconium by living biomass follows the Freundlich model, and the uptake of dried biomass follows the Langmuir model. Kinetic studies showed that both kinds of biomass follow the second order kinetic model.

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1. Introduction

Heavy metals are present in most industrial processes, like mineral activities, metallurgy, and chemical industries, and the release of these metals into the environmen as industrial waste has catastrophic consequences for plant and animal based ecosystems. Most important metals of this kind are: mercury, lead, nickel, arsenic, cadmium, copper, zinc, uranium, zirconium and hafnium. Most of these metals are poisonous and carcinogenic [1]. As these metals are poisonous, health organizations have restricted their presence in industrial waste and their concentrations should not be more than a certain amount.

Zirconium is a shiny and light gray metal with high conductivity, and is commonly used in alloy making, the manufacturing of photoflash bulbs, surgical equipment, and leather tanning [2,3]. However, zirconium is a poisonous metal and smelling zirconium compounds can damage lungs and skin [4]. Many chemical methods, like chemical precipitation, reverse osmosis, resins of ion exchange, membrane processes and adsorption on active carbon, are used to remove these metals from industrial waste [5,6]. These methods are commercially impractical, either because of high operating costs or the difficulty in treating the generated solid waste [7-9]. Chemical precipitation and electrochemical treatments are not very effective, especially when the concentration of metallic ions is less than 100 mg/l [10]. Also, these methods produce a lot of mud, which is removed with difficulty [11], and ion exchange, membrane technologies and active carbon are very expensive [11]. Developing technological and economical methods for the purification of factory effluents has been an important concern for centuries [1]. So, the search for purifying heavy metals by more effective and cheaper methods has led to the

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biosorption method, which has been under study for many decades.

Biosorption is the process of adsorbing heavy metals by adsorption to a biomass in a water solution. This is a controlled non-metabolic omitting process [12]. One of the most important advantages of a biosorbent is its ability to treat large amounts of industrial waste with low concentration [1]. The main advantages of biosorption compared to older treatment methods are: low cost, high efficiency, minimum chemical and bio mud, revival of biosorbence and the ability to recycle metal from the adsorbent [13].

Much research has been undertaken into the effect of operational parameters on the uptake rate of heavy metals by biosorbents [8], but, to the best of our knowledge, a comprehensive study for the uptake of zirconium by biosorbents has not been previously reported.

2. Material and methods

In this work, we focus on some operational parameters, including pH, contact time, temperature, initial concentration of zirconium, and initial dose of biomass on zirconium uptake by dried and living biomass. A survey of Langmuir and Freundlich equilibrium isotherms for the biosorption of zirconium, as well as pseudo first and second order kinetics of both biomasses, was also undertaken.

2.1. Microorganism, growth medium and providing biosorbent

In this study, Fungal *Aspergillus niger* was provided from the Biochemical and Bioenvironmental Research Center (BBRC) culture collection. This strain was cultivated in Potato-Dextrose-Agar (PDA) as a solid growth medium for 7 days and, then, kept at 4°C.

The aerobic cultivation of *Aspergillus niger* was carried out in 250 ml Erlenmeyer flasks, covered with cotton containing 100 ml liquid growth medium containing (g/L): glucose, 5; starch, 5; KNO_3, 1; $MgSO_4.7H_20$, 0.5; KH_2PO_4, 1; KCl, 0.5; $FeSO_4.7H_2O$, 0.03; $CuSO_4.5H_2O$, 0.005; $ZnSO_4.7H_2O$, 0.024; $MnSO_4.7H_2O$, 0.002. The pH of the growth medium was set at 4.5. The growth medium was sterilized in an autoclave at 121°C and at a pressure of 1.5 atm for 16 min. After insemination, the cultivation was carried out for 4-5 days at 25°C and 120 rpm (end of exponential phase). After this period, the biomass was separated from the cultivation medium using a Wahtman filter (No. 40) and washed by Double Distilled Water (DDW) several times. This is designated as a "living biomass". Finally, the washed biomass was dried in oven at 60-80°C for 24 h and was powdered by mortar and pestle. The resulted powder was screened through a set of sieves with 100 mesh size for more homogeneity. This powder-like biomass is designated a "dried biomass".

2.2. Solution preparation

All used chemicals in this study were analytical grade. The stock zirconium solution (1000 mg/l) was prepared by dissolving 3.5328 g of $ZrOCl_2.8H_2O$ in 1000 ml DDW. Zirconium solutions of different concentrations were prepared by adequate dilution of the stock solution with DDW. The glassware used was washed by HNO_3 (at boiling point) for 10 min or by sulphochromic acid, 10%, overnight and rinsed several times with DDW.

2.3. Biosorption experiments

Biosorption experiments were carried out in batch mode. All experiments were done in 500 ml polyethylene containers with 100 ml metallic solutions. The pH experiments were performed in 5 pH: 1, 1.5, 2, 2.5 and 3.1 (beyond pH 3.2, zirconium precipitated out in solution). The temperature and contact time were 25°C and 2 h, respectively. The effect of zirconium concentration was studied in the range of 10 to 500 mg/l. The pH value of all solutions was adjusted to the desired value with 1 mol/l NaOH (Merck) and 65% Nitric Acid (Merck). After equilibrium, samples were filtered by a Whatman paper filter (No. 42) and subsequently centrifugated at 5300 rpm for 15 min [14]. The supernatant solution was analyzed for residual metal concentration determination. In experiments with living cells, the separated biomass was dried at 60-80°C for 24 hr in order to determine the weight of dried biomass [15]. The amount of metal uptake capacity, q (biosorbed ion (mg)/dry weight of biomass (g)), was calculated from the following formula:

$$q = \frac{V(C_i - C_f)}{W}. \tag{1}$$

%Removal efficiency was calculated by Eq. (2):

$$\%R = \frac{C_i - C_f}{C_i} \times 100, \tag{2}$$

where C_i (mg/l) corresponds to the initial metal ion concentration, C_f (mg/l) is the final metal concentration in the supernatant solution, W (g) is the dry weight of biosorbent suspended in V (l), volume of the metal solution. From analysis of the zirconium solution in control flasks (C_i), losses due to adsorption to flask walls were found to be negligible.

In this work, all experiments were performed in duplicate, and the average standard deviation between them was less than 5%. The data presented in this paper are the average of the two replications.

Analysis of Variance (ANOVA) was used to determine whether the effect of different conditions on the uptake capacity of zirconium by both living and dried

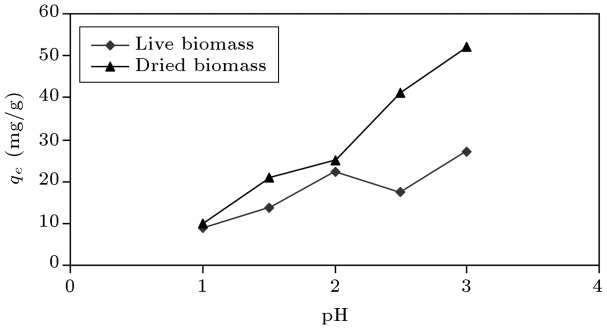

Figure 1. The Effect of pH on biosorption of living biomass and dried biomass; $C_i = 50$ mg/l, $t = 2$ hr, $T = 25°C$, rpm = 120.

biomasses is statistically significant. The significance of differences between uptake capacities under different conditions was analyzed by the Duncan test, as a Post Hoc test.

2.4. Analytical methods

The residual concentration of zirconium in the supernatant solution was determined using an Inductively Coupled Plasma Spectrometer (ICP-OES, GBC 201A).

3. Results and discussion

3.1. The effect of pH on biosorption

By taking a look at Figure 1, it is obvious that increasing pH from 1 to 3.1 leads to an increase in the uptake capacity of zirconium by both living and dried biomasses, and the highest uptake is observed at pH 3.1. Experiments could not be conducted at pH values above 3.2 because of the visual precipitation of zirconium hydroxides at these pH values, which rendered the true sorption studies impossible [2]. Further experiments were conducted at initial solution pH value, 3.1, as an optimal value. Different studies have been conducted on the effect of pH on the biosorption of different metals from their solutions, which showed the significant effect of this factor [2,16,17]. This could be attributed to the effect of pH on the chemical characteristics of both metal and cell surfaces [18,19]. Such an effect of pH on the biosorption of zirconium had also been observed for Candida tropicalis [2]. In fact, the cellular surface of *Aspergillus niger* is polyanionic because of the presence of functional groups, such as carboxyl and phosphate [20], and H^+ can easily connect to these groups. So, H^+ is a rival for metallic ions in connecting to the biomass surface. By increasing the pH value, concentration of H^+ decreases and its effect will be reduced. Thus, functional groups of the cell wall carrying negative charges would be exposed with the subsequent attraction of metallic ions with a positive charge. This would lead to electrostatic attraction between the cations like Zr

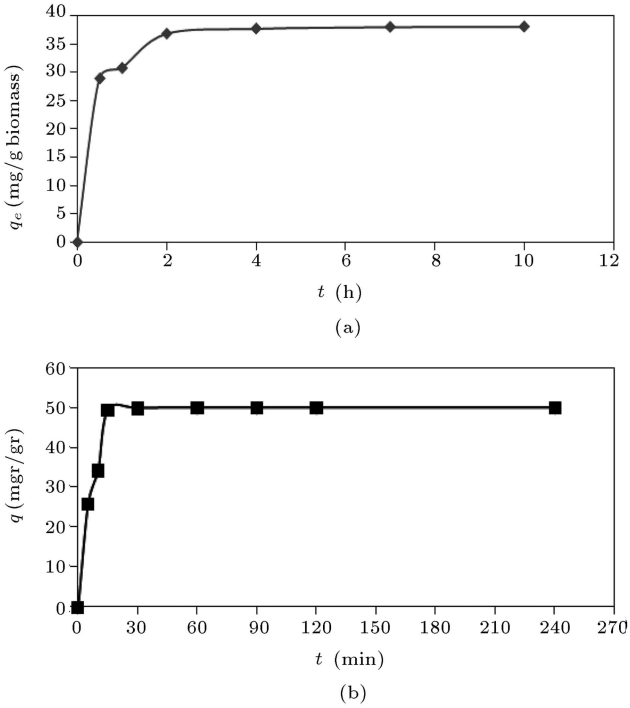

Figure 2. The Effect of contact time on biosorption of (a) living biomass, and (b)dried biomass; $C_i = 50$ mg/l, $T = 25°C$, $V = 100$ ml, rpm = 120.

(IV) and negatively charged binding sites like carboxyl groups [19,21,22].

3.2. The effect of contact time on biosorption

This experiment was undertaken with 50 mg/l zirconium solution and 1 g wet weight for the living biomass and 0.1 g dry weight for the dried biomass, at $T = 25°C$ and pH 3. As shown in Figure 2, increasing contact time results in an increase in the uptake capacity by both living and dried biomasses. This increment continues to reach equilibrium condition. Equilibrium time for living and dried biomasses was estimated to be about 2 h and 30 min, respectively. By looking at Figure 2(a) and (b), it is found that the equilibrium time for dried biomass is less than the needed time for the living biomass. In fact, because of metabolic activity, the living biomass has both metabolic (active) and passive uptake of zirconium [1]. But, dried biomass has just passive uptake, which is faster than the active uptake, and the biosorption process reaches equilibrium faster [1,11,23]. In addition to requiring less time for equilibrium, the uptake capacity of the dried biomass is more than for the living one, which could be attributed to the presence of more active sites on the surface of the dried biomass, due to the physical treatment. The faster biosorptive uptake has significant practical implications in the operation of a bioreactor, where the processes would require less operational time [24]. These results are consistent with the findings of other work [1,22].

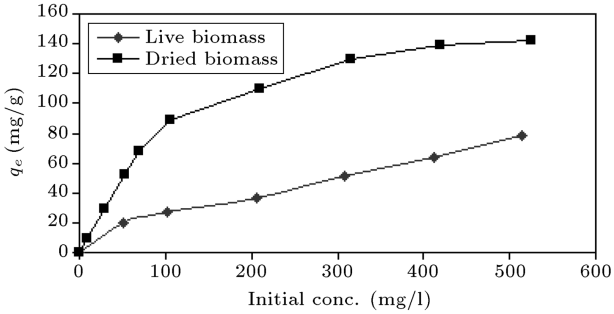

Figure 3. The Effect of initial concentration of Zr on biosorption of living biomass and dried biomass; $t = 2$ hr, $T = 25°C$, pH = 3.1, rpm = 120.

3.3. The effect of initial concentration of metal

Figure 3 displays the uptake capacity of biomass as a function of the initial concentration of metal in the solution. The results revealed that increasing the initial concentration of zirconium causes an increase in the uptake capacity by both dried and living biomasses. This trend was observed in work with other metals [2,25]. Maximum uptake capacity for dried and living biomasses is 78.7 mg/g and 142 mg/g, respectively, which were obtained in the initial concentration of Zirconium 500 mg/l. Akhtar et al. [2] reported maximum uptake by Candida tropicalis in 1000 mg/l zirconium, about 170 mg/g [2].

The increase in the uptake capacity with initial concentration can be attributed to the combined results of the increase in the gradient of concentration between the biosorbent surface and the solution and the possibility of contact between metal ions and biosorbent particles [26,27]. A higher initial metal concentration was reported to have a higher driving force for transporting cations from ambient liquid to the cell surface, resulting in a faster sequestration and higher adsorption capacity [26-30]. On the other hand, by increments in the concentration of zirconium, the possibility of contact between metal ions and biosorbent particles grows, which leads to more metallic uptake [31]. However, comparison between the uptake capacity of zirconium by living and dried biomasses showed the higher uptake capacity of dried biomass, which is more effective in the biosorption of zirconium.

3.4. The effect of temperature on biosorption

The effect of temperature on the uptake of zirconium by dried and living biomasses is shown in Figure 4. This parameter can be very effective in the living biomass because metabolic processes and the production of different enzymes and polysaccharides are dependent on temperature. As shown in Figure 4, increasing temperature from 15 to 30°C leads to an increase in the uptake capacity to 28.8 mg/g. However, using a

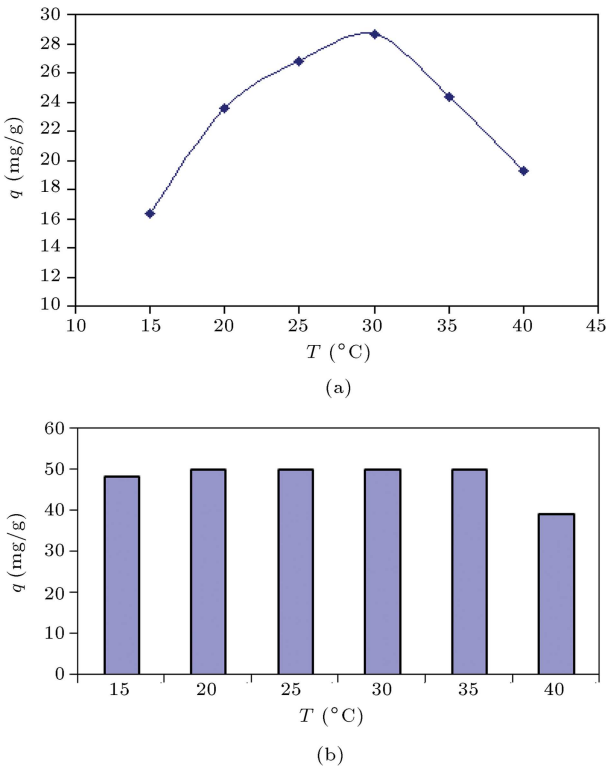

Figure 4. The Effect of temperature on biosorption of (a) living biomass and (b) dried biomass; $C_i = 50$ mg/l, $t = 2$ hr, pH = 3.1, rpm = 120.

higher temperature, to 40°C, resulted in a lower uptake capacity compared to when the biosorption was done at 30°C. Akhtar reported the same trend in the removal of zirconium by Candida tropicalis and maximum uptake was observed at 30°C [2].

The increase in uptake at the increased temperature may be due to either a higher affinity of sites for the metal ions or an increase in the binding sites on the relevant biomass [32]. However, overgrowth in temperature can cause the destruction of some sites and a consequent reduction in the uptake capacity [33]. Regarding dried biomass, as seen from Figure 4(b), by increasing temperature from 15°C to 20°C, an increment in uptake capacity is observed, but, this increment is not clear in the range of 20-35°C. At higher temperature (40°C), reduction in uptake capacity is observed. The results are consistent with the results of Aksu et al. [34], which shows that temperature in the range of 20-35°has little effect on biosorption.

3.5. The effect of dose of biomass on uptake capacity and removal efficiency

Figure 5 shows the effect of biomass dosage on both uptake capacity and removal efficiency. Different doses of biomass were 0.5, 1, 1.5 and 2 g/100 ml (wet weight) for living biomass, and 0.05, 0.1, 0.15, 0.2 and 0.25 g/100 ml (dry weight) for dried biomass. It is observed that for both kinds of biomass, increasing the amount

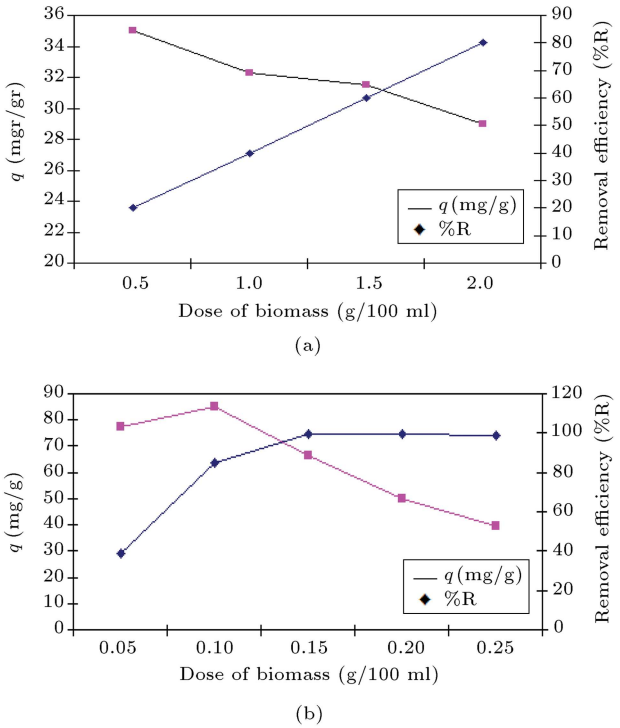

Figure 5. The Effect of biomass dosage on biosorption of (a) living biomass, and (b) dried biomass; $C_{i\ \text{dried}} = 100$ mg/l, $C_{i\ \text{living}} = 50$ mg/l, $T = 25^{\circ}$C, $t = 2$ hr, rpm=120.

of biomass leads to an increase in removal efficiency ($\%R$) and a decrease in uptake capacity (q). For the living biomass, increasing the amount of biomass from 0.5 g/100 to 2 g/100 ml resulted in a decrease in uptake capacity from 35 mg/g to 28.6 mg/g. However, removal efficiency increased from 20% to 80%. Regarding dried biomass, by increasing the dose of biomass from 0.05 g/100 ml to 0.1 g/100 ml, the uptake capacity increased from 77 mg/g to 85 mg/g, but, after 0.1 g/100 ml, reduction in the uptake capacity was observed. In fact, maximum uptake capacity was obtained in a dose of 0.1 g/100 ml. On the other hand, by increasing the amount of biomass, removal efficiency increases too, and in doses of 0.15 g/100 ml, almost all the metal is removed. The decrease in the values of uptake capacity with the increase in the dose of biomass has been explained by various researchers who have hypothesized that high biomass dosage leads to the formation of cell aggregates, thereby, reducing the effective biosorption area [17,35-37], and an increase in biomass concentration leading to interference between binding sites [37,38].

Regarding the observed trend for removal efficiency ($\%R$), it can be concluded that by increasing the dose of biomass, more binding sites are available for the same amount of Zr cations [31]. Similar results on the effect of biomass dosage on the uptake capacity and removal efficiency of metal ions have been reported for various microorganisms [31].

3.6. Equilibrium models

There are many theoretical and empirical models for surveying the equilibrium of the biosorption process. Among these models, Freundlich and Langmuir models are more known. The Langmuir isotherm is valid for monolayer adsorption and is described by the following equation [39,40]:

$$q_e = \frac{q_m b C_e}{1 + bC_e}, \tag{3}$$

where q_m (mg/g biomass) is the maximum adsorption capacity, b is the affinity of the binding sites, C_e (mg/l) is the equilibrium concentration of Zr in solution and q_e (mg/g biomass) is the amount of adsorption.

The linear form of the model is:

$$\frac{1}{q_e} = \frac{1}{bq_{\max} C_e} + \frac{1}{q_{\max}}. \tag{4}$$

The Freundlich equation, which is an empirical model, is usually presented as Eq. (5) [2]:

$$q_e = k_F C_e^{1/n}, \tag{5}$$

where k_F and n are the Freundlich constants related uptake capacity and intensity, respectively [39]. This formula can be transformed as follows:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e. \tag{6}$$

Some authors explain that the Langmuir isotherm corresponds to a dominant ion exchange mechanism, while the Freundlich isotherm shows adsorption-complexation reactions that take place in the adsorption process [41,42]. Figure 6(a) and (b) show the Langmuir isotherm for living and dried biomasses, respectively. The R^2 value for living and dried biomasses is 0.9093 and 0.994, respectively. The R^2 values show that the Langmuir isotherm is more suitable for dried biomass (especially at low concentrations of zirconium), but it cannot fit the data related to living biomass.

The model parameters, q_m and b, are presented in Table 1. As can be seen, q_m from the Langmuir model for dried biomass is 142.86, which is close to the real value (142).

Figure 6(c) and (d) shows the Freundlich isotherm for living and dried biomass, respectively. The determination coefficients (R^2) for living and dried biomass are measured as 0.964 and 0.805, respectively. According to these values, the Freundlich model is only suitable

Table 1. Parameters of Langmuir and Freundlich isotherm models for living biomass and dried biomass.

Biomass	Langmuir		Freundlich	
	b	q_m	n	k_f
Live cell	0.011	68.97	1.871	2.706
Dried cell	0.762	142.86	4.114	38.65

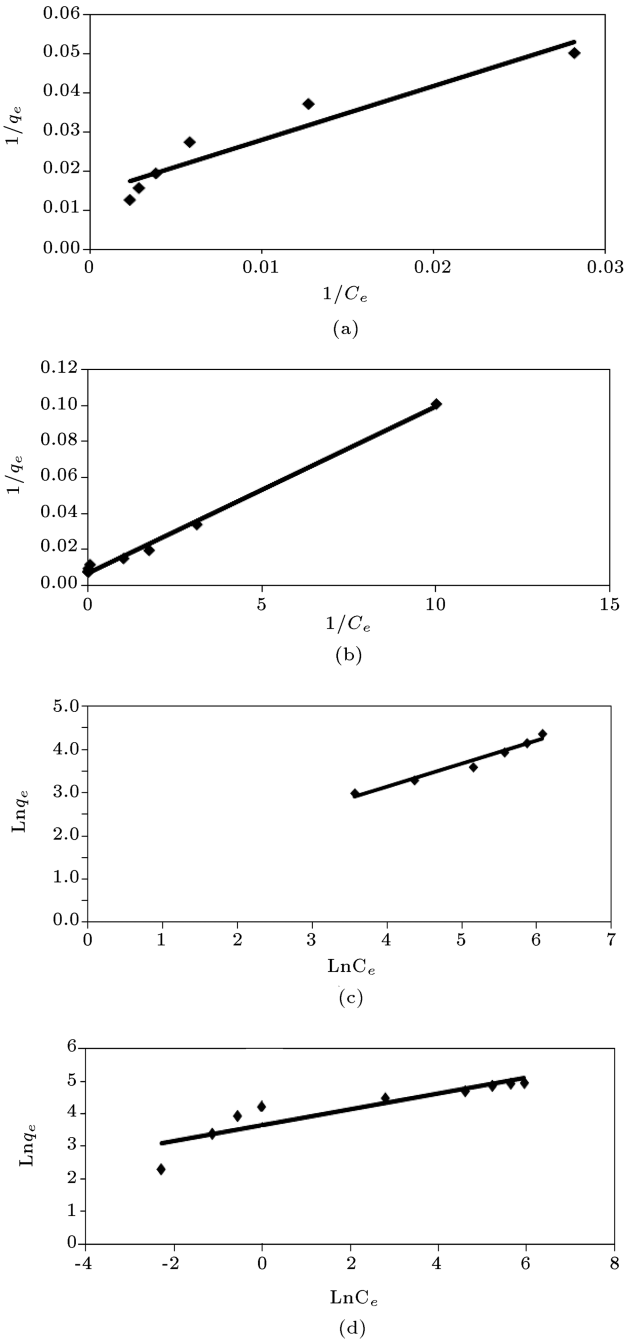

Figure 6. Langmuir isotherm for (a) living biomass, and (b) dried biomass. Freundlich isotherm for (c) living biomass, and (d) dried biomass.

for living biomass. By considering the wide range of concentrations and the complexity of the adsorption process of living biomass, the inability of this model to fit the data of living biomass was predictable. Table 1 shows the parameters of Langmuir and Freundlich isotherms obtained from experimental data.

3.7. Kinetic models

In this section, the Zr (IV) adsorption kinetic on *A.niger* is surveyed. To discover the controlling mechanism of biosorption, pseudo-first-order [43] and pseudo-second-order models [44] were used to interpret the experimental data, assuming that measured concentrations are equal to cell surface concentrations. The pseudo-first-order model considers that the rate of occupation of sorption sites is proportional to the number of unoccupied ones. This model is as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \tag{7}$$

where q_t and q_e are the sorption capacity at time t and at equilibrium, respectively, and k_1 is the pseudo-first order rate constant.

The linear form of this model is shown in Eq. (8):

$$\log(q_e - q_t) = \log q_e - \frac{k_l t}{2.303}. \tag{8}$$

The pseudo-second-order model considers that the rate of occupation of sorption sites is proportional to the square of the number of unoccupied sites. This model is as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \tag{9}$$

where k_2 is pseudo-second order rate constant. After integration and applying boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$; the integrated form of Eq. (9) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + (\frac{1}{q_e})t. \tag{10}$$

The values of k_2 and q_e can be obtained from the intercept and the slope of Eq. (10), respectively.

Figure 7(a) shows the first order kinetic model for living biomass. The R^2 value for the first order kinetic was 0.955. By considering the results, the values of the parameters of the first order kinetic (q_e and k_1) are 11.038 mg/g and 0.0131, respectively. Figure 7(b) shows the second order kinetic for living biomass. In this mode, q_e, k_2 and R_2 are 38.76 mg/g, 2.515 $\times 10^{-3}$ and 0.9998, respectively. By considering this value of R^2, it can be concluded that second order model fits the experimental data of living biomass appropriately. This result can be obtained from comparing the value of q_e from the model (38.76 mg/g) and the experiment (38.05 mg/g).

Figure 7(c) and (d) shows first and second order kinetics for dried biomass, respectively. By considering this figure, for the second order model, q_e and k_l are 68.9 mg/g and 0.255, respectively. Also, R^2 was 0.928 for this model, which is not large enough for fitting data (i.e. the first order kinetic is not suitable for surveying adsorption behavior with dried biomass). For the second order model, values of q_e, k_2 and R^2 are 50.76 mg/g, 9.004 and 0.9995, respectively.

As can be seen, R^2 is close to 1, which shows that

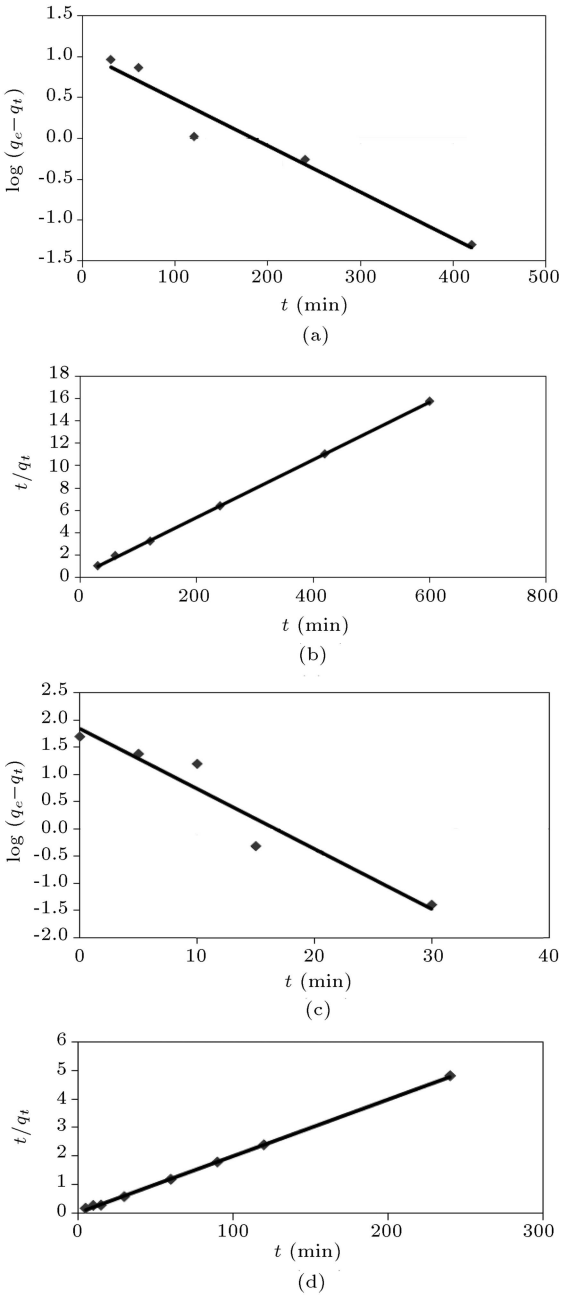

Figure 7. (a) First order kinetic for living biomass. (b) Second order kinetic for living biomass. (c) First order kinetic for dried biomass. (d) Second order kinetic for dried biomass.

the second order model fits data appropriately. The amounts of parameters for both first order and second order kinetic models are presented in Table 2.

4. Conclusion

In this study, *Aspergillus niger* was used in 2 forms; living biomass and dried biomass, for removing zirconium from aqueous solutions. General results suggest that dried biomass is more appropriate than living biomass, because it reaches equilibrium faster and has more uptake capacity under different situations. The maximum uptake capacity by dried biomass was in concentrations of 500 mg/l of zirconium, pH = 3.1, biomass dosage 0.1 g/100 ml ($q_{\max,\exp}$=142 mg/g). Adsorption by living biomass follows the equilibrium isotherm of Freundlich and the second order kinetic model. The Longmuir model appropriately fits the adsorption data of dried biomass and shows that dried biomass adsorbs zirconium in a one layer mode. Also, dried biomass follows the second order kinetic model. The results indicate that *A.niger* can be used as an efficient biosorbent for removal of Zr (IV) from wastewater.

Table 2. Parameters of first and second order kinetics for living biomass and dried biomass.

Biomass	First order		Second order	
	K_1	q_e	K_2	q_e
Live cell	0.013	11.04	0.003	38.7
Dried cell	0.255	68.9	0.009	50.76

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