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A Comparative Study on Removal Efficiency of Cr(VI) in Aqueous Solution by *Fusarium* sp. and *Myrothecium* sp.

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Abstract Environmental pollution with chromium is due to residues of several industrial processes. Bioremediation is an alternative actually considered to remove Cr (VI) from the environment, using adapted organisms that grow in contaminated places. Have been conducted studies with fungi mechanisms of interaction with chromium, most of which have focused on processes biosorption, characterized it by passive binding of metal components of the cell surface, and bioaccumulation, wherein the metal entry to cells occurs with energy expenditure. The paper presents the results of studies carried out on sorption of chromium (VI) ions from aqueous solutions by *Fusarium* sp. and *Myrothecium* sp. Both biomasses have the ability to take up hexavalent chromium during the stationary phase of growth and as well inactive conditions. *Fusarium* sp. showed 26% of biosorption with active biomass and 64% in inactive biomass; meanwhile, *Myrothecium* sp. obtained 97 and 82%, respectively. Both fungi showed adjust to pseudo-second-order model in active (*Fusarium* sp. R^2 = 0.99; *Myrothecium* sp. R^2 = 0.96) and inactive biomass assay (*Fusarium* sp. R^2 = 0.99; *Myrothecium* sp. R^2 = 0.99). The data of the active biomass test also confirmed to the intraparticle diffusion model (*Fusarium* sp. R^2 = 0.98; *Myrothecium* sp. R^2 = 0.93). The results obtained through this investigation indicate the possibility of treating waste effluents containing hexavalent chromium using *Fusarium* sp. and *Myrothecium* sp.

Keywords Fungal biomass · Fungus · Cr (VI) · Chromium biosorption · *Myrothecium* sp. · *Fusarium* sp.

1 Introduction

In the actuality, the environmental pollution with chromium is due to residues of several industrial processes such as electroplating, leather tanning, nuclear power plant, textile industries, chromate preparation, water cooling, pulp producing, and petroleum refining processes (Park et al. 2004; Srivastava et al. 2015).

Chromium appears to the aqueous system as trivalent and hexavalent forms. Due to higher solubility, hexavalent chromium enters into the living cells more easily and generates reactive oxygen species (ROS), causing severe oxidative injuries to cell constituents (Guria et al. 2014). It is toxic and mutagenic to most organisms and is known to cause eye and skin irritation, corrosion of the skin and respiratory tract, severe diarrhea, ulcers, kidney dysfunction, and probably lung carcinoma in humans (Costa 2003; Ghosh et al. 2016; Gupta et al. 2001; Thacker and Madamwar 2005). Because of toxicity and environmental risk, the permissible discharge level of Cr (VI) from industrial effluents into inland water is only 0.05 mg L1, as recommended by the US Environmental Protection Agency (Guria et al. 2014; US Environmental Protection Agency 1998).

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The physical and chemical methods commonly used to hexavalent chromium removal are a chemical reduction to trivalent chromium followed by precipitation under alkaline conditions, coagulation, removal by reverse osmosis, ion exchange resins, and adsorption on activated carbon. But these methods are highly expensive and also it is ineffective at a lower concentration of metal ions (Park et al. 2004; Samuel et al. 2015a; Sumathi et al. 2005).

Fortunately, there are biological alternatives, like biosorption of heavy metals by biomaterials has been suggested as a potential alternative to the existing physicochemical technologies for detoxification and recovery of toxic and valuable metals from wastewaters (Khambhaty et al. 2009a). Bacteria, fungi, and algae are also promising biosorbents, owing to their abundance and low cost (Ahluwalia and Goyal 2007; Singh et al. 2016). Fungal biomass seems to be a good sorption material, because, it can be produced easily and economically (Aksu and Balibek 2007; Singh et al. 2016). The biosorption of the metal ions is affected by factors other than the specific properties of the surface of the cell wall such as physical–chemical properties of the medium, pH, temperature, presence of nutrients, adsorbent dosage, and equilibrium time (Bayramoglu et al. 2009; Das et al. 2008; Fomina and Michael 2014; Kapoor et al. 1999; Pagnanelli et al. 2003; Vale et al. 2016; Wang et al. 2010).

The bioremediation also is an alternative, using adapted organisms that grow in contaminated places. The biotransformation utilizes the potential of microorganisms to transform metal. This ability, as well as the mechanisms of accumulation, varies with the microbial species or strain, and occur due to binding of the metal ions to functional groups present in the cell wall or on the membrane surface of microorganisms by complexation on the cell surface, ion exchange, physical adsorption, or microprecipitation (Gupta et al. 2000; Veglio and Beolchini 1997).

The objective of this work is to study the biosorption potential of Cr (VI) ions using active and inactive biomass from isolated and characterized metal resistant fungal strains. Along with this, a detailed study was conducted for assessing the biosorption equilibrium employing different sorption kinetics.

2 Materials and Methods

2.1 Isolation and Preparation of Inoculum

Metals resistant strains were isolated from soil. To obtain soil samples, a random sampling was performed, in which 5 subsamples of random points were taken, to obtain a composite sample of the site. The sampling was carried out in Monterrey Nuevo León Mexico. Dilutions of the obtained samples were made and inoculated by surface extension in PDA boxes added with 10 mg/L of Cr (VI), and incubated for 3–7 days at room temperature (26 ± 2 °C). Colonies with fungal characteristics were selected and isolated. The fungi were preserved by periodic reseeding in PDA plates with Cr(VI).

For inoculum of each strain, fungal spores of 14 days growing were removed from plates and put into flasks containing 50 ml Tween 80 (previously sterilized). After was performed a spores count with the Neubauer camera, to obtaining a final concentration of 1×10^6 spores/ml. The fungi were used in two sets of test with Cr (VI): Active biomass and Inactive biomass.

2.2 Biosorption Kinetics

The kinetics studies were carried out by conducting batch biosorption experiments with different conditions of biomass. Samples were taken at different time periods and analyzed for their chromium concentration. All the experiments were repeated three times and the average values have been reported. Also, blank experiments were conducted to ensure that no adsorption was taking place on the walls of the apparatus used.

2.3 Growth Kinetics

Erlenmeyer flasks of 250 ml containing 100 ml of medium (saccharose 40 g/L, K_2HPO_4 5.5 g/L, $MgSO_4$ 0.75 g/L, NH_4Cl 2.5 g/L, citric acid 3 g/L, cysteine 0.5 g/L, yeast extract 1.5 g/L, NaCl 1 g/L, $CaCl_2$ 0.010 g/L) were autoclaved for 15 min at 121 ± 2 °C. Then it were cultivating with 1 ml of inoculum and incubated into a rotatory shaker (200 rpm, 26 ± 2 °C). Samples of the supernatant were taken every 6 h, then every 12 h, and every 24 h until completing 6 days. Samples obtained were spore counts.

2.4 Active Biomass

Erlenmeyer flasks of 250 ml containing 100 ml of medium (saccharose 40 g/L, K_2HPO_4 5.5 g/L, $MgSO_4$ 0.75 g/L, NH_4Cl 2.5 g/L, citric acid 3 g/L, cysteine 0.5 g/L, yeast extract 1.5 g/L, NaCl 1 g/L, $CaCl_2$ 0.010 g/L) were autoclaved for 15 min at 121 ± 2 °C. Then it were cultivating with 1 ml of inoculum, except the control, and incubated into a rotatory shaker (200 rpm, 26 ± 2 °C). In the third day of incubation, was added 5.25 ml of $K_2Cr_2O_7$ (1000 mg/L) to medium to obtain a final concentration of 50 mg/L, and 2 ml samples were taken each 24 h during 144 h. All was done by triplicated for each strain.

2.5 Inactive Biomass

Fungal biomass was produced in 500 ml Erlenmeyer flasks containing 300 ml of medium (saccharose 40 g/L, KH_2PO_4 4 g/L, $MgSO_4$ 0.75 g/L, NH_4Cl 1 g/L, citric acid 3 g/L, cysteine 0.5 g/L, NaCl 1 g/L, $CaCl_2$ 0.1 g/L, Na_2HPO_4 6 g/L), previously sterilized, and it were cultivating 1 ml of inoculum of each strain per flask. It was incubated into a rotator shaker at 200 rpm, temperature room (26 ± 2 °C) per 7 days. Subsequently, the biomass was filtrated, and dried in hot air oven at 50 °C for 3 days and pulverized. In 125 ml Erlenmeyer flasks were added 50 ml of $K_2Cr_2O_7$ (50 mg/L) and 0.5 g of biomass. Control was without biomass. Biosorption experiments were performed in a rotatory shaker (200 rpm, 25 °C). A 1 ml sample from each experiment flask(s) was taken and centrifuged at 6000 rpm for 10 min, each 15 min during 2 h, then each 12 h until 48 h.

2.6 Dissolutions

Experiments were performed using synthetic single metal solutions of Cr (VI) prepared from chemical reactants of analytical grade, $K_2Cr_2O_7$. Concentrations varied in each case. Initial pH was adjusted at 4.5 with 0.1 N HCl and 0.1 N NaOH.

2.7 Analytical Method

The metal content was quantified using a Spectrophotometer (Thermo, Evolution 60 S) employing diphenyl carbazide method (DPC) (APHA/AWWA/WEF 1999). All results were analyzed in Excel, obtaining the average and standard deviation.

3 Results and Discussion

3.1 Isolation

Two chromate resistant filamentous fungi were isolated from soil, which were identified by morphological characteristics, macroscopically and microscopically. The first strain coincided with *Fusarium* genus, which showed cottony surface and pink pigmentation colonies, moderate growth, ovals spores and formation of chlamydospores, whereas second strain coincided with *Myrothecium* genus, showed low growth white and cottony surface colonies, dark green conidia collected in large green to blackish wet drops, united conidiophores, and cylinder shape spores (Fig. 1).

3.2 Growth Kinetics

In Fig. 2, we can observe that in both fungi, from 72 h have a higher production of spores, and therefore, production of biomass. Therefore, in the active biomass biosorption test, this time was selected to add the chromium to media.

3.3 Active Biomass

The results obtained in this assay, it is observed that chromium concentration initial for *Myrothecium* sp., was 44.61 mg/L and final concentration (144 h) was 1.30 mg/L. Meanwhile, for *Fusarium* sp., the chromium concentration initial was 49.95 mg/L and the final 36.90 mg/L (Table 1).

Reports of percent removal of chromium mentioned that *Aspergillus niger* var. *tubingensis* strain Ed8 has 94% (Coreno-Alonso et al. 2014), *Aspergillus flavus* has 89.76% (Singh and Bishnoi 2015) and *Beauveria bassiana* has 44% (Gola et al. 2016), while in this study *Myrothecium* sp. and *Fusarium* sp. shows 96% and 26% respectively (Table 1).

Both strains had pellets formation, but there not was measured. *Myrothecium* sp. was more efficient in removing the metal than *Fusarium* sp. Experiments with biomass active in liquid culture help to fungus in the biosorption process. According to Liao et al. (2007), ideal conditions of orbital shaking permit the pellets

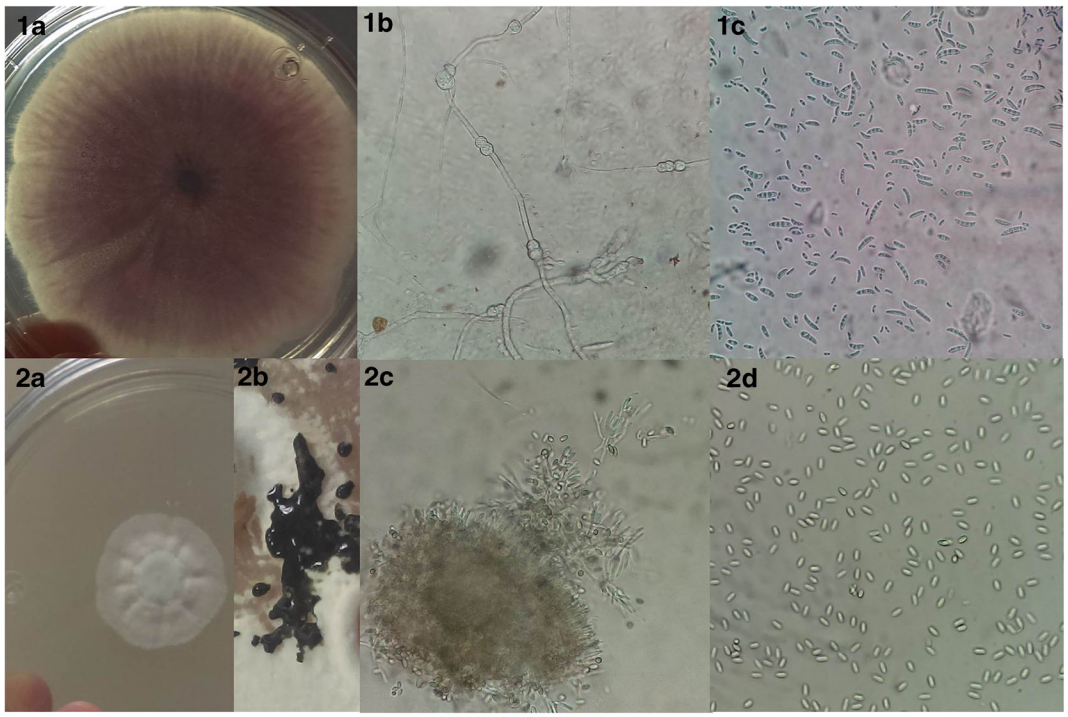

Fig. 1 *1 Fusarium* sp.: *a* Macroscopic morphology, *b* Chlamydospores, *c* Spores. *2 Myrothecium* sp.: *a* Macroscopic morphology, *b* spore cumulus, *c* Conidiophore, *d* spores

formation. This pellets comprised long and fibrous hyphae, randomly arranged in an entangled net, with high biomass density and surface area that improves mass transfer and diffusion of the surrounding metal ions solution into pellets (Moreira et al. 1996; Vale et al. 2016). Therefore, the ions have more chances of contact with the active sites inside the pellet, increasing the capacity of biosorption (Arunakumara and Zhang 2007; Fu and Viraraghavan 2002; Morales-Barrera et al. 2008; Mungasavalli et al. 2007; Vale et al. 2016; Borràs et al. 2008).

3.4 Inactive Biomass

Table 2 shows the capability of chromium biosorption, *Myrothecium* sp. displayed an initial concentration of 49.89 mg/L and after 48 h decreased to 8.90 mg/L; on the other hand, *Fusarium* sp. begin with 56.78 mg/L and fished with 20.15 mg/L.

The biosorption process with inactive biomass, it is allied with the amount of biomass utilized. Vale et al. (2016), mentioned that the amount of adsorbent significantly influenced the extent of metals biosorption,

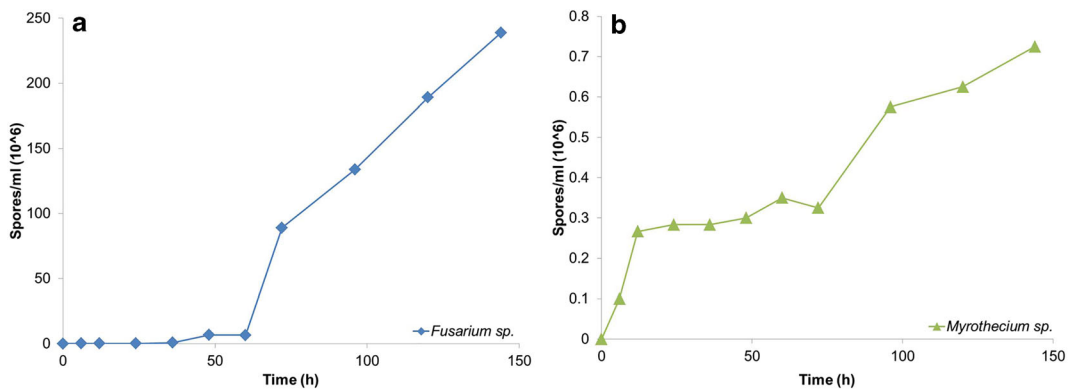

Fig. 2 Counting of spores, **a** *Fusarium* sp. and **b** *Myrothecium* sp., during 6 days of growth in Sabouraud Dextrose broth

Table 1 Cr (VI) biosorption active biomass assay

Time (h)	*Fusarium* sp.		*Myrothecium* sp.	
	[Cr^{+6}] (mg/L)	%removal	[Cr^{+6}] (mg/L)	%removal
0	49.95 ± 1.44	–	42.54 ± 1.31	–
24	43.48 ± 0.87	12.97	26.29 ± 3.43	38.19
48	41.30 ± 1.48	17.32	18.24 ± 3.21	57.13
72	39.06 ± 2.23	21.81	4.56 ± 1.67	89.27
96	37.58 ± 1.11	24.78	1.48 ± 0.00	96.52
120	36.78 ± 0.05	26.38	1.38 ± 0.09	96.76
144	36.90 ± 0.34	26.13	1.30 ± 0.05	96.94

obtained 99.1% of chromium biosorption with *Aspergillus niger* using 10 g adsorbent/L. In the present study, was tested 0.5 g of biomass in 50 ml, obtaining 82.15% of biosorption for *Myrothecium* sp. and 63.66% for *Fusarium* sp. (Table 2). In literature *Myrothecium verrucaria* shown 67.05% (Karthikeyan and Jayaprakash 2008), *Fusarium solani* 12% (Sen 2012), and *Aspergillus niger* 99% (Ren et al. 2015).This results can be better if be used less amount biomass, because the fungal biomass became swelled up and, at high concentration, the biomass active sites became very close to each other, causing an electrostatic interaction among these sites, which generates a shield, known as "shell effect," that hinders further occupation by the metal ions (Vale et al. 2016).

Table 2 Cr (VI) biosorption inactive biomass assay

Time (h)	*Fusarium* sp.		*Myrothecium* sp.	
	[Cr^{+6}] (mg/L)	%removal	[Cr^{+6}] (mg/L)	%removal
0	56.78 ± 0.50	–	49.89 ± 0.54	–
0.5	23.68 ± 0.65	58.28	20.33 ± 1.91	59.24
0.75	24.68 ± 0.45	56.53	25.81 ± 4.06	48.26
1	17.78 ± 1.17	68.68	20.20 ± 0.81	59.51
1.25	18.27 ± 4.08	67.83	12.68 ± 0.38	74.58
1.5	24.56 ± 0.85	56.74	16.90 ± 1.23	63.23
1.75	31.90 ± 0.77	43.82	19.07 ± 1.81	61.77
2	28.83 ± 2.57	49.23	19.29 ± 1.18	61.33
12	24.38 ± 4.14	57.06	13.60 ± 1.59	72.73
24	24.98 ± 2.23	56.01	12.01 ± 2.03	75.92
36	24.99 ± 2.78	55.99	9.01 ± 2.30	81.94
48	20.15 ± 1.66	64.52	8.90 ± 1.50	82.15

3.5 Effect of Contact Time

Figure 3 depicts the effect of contact time on the adsorption of Cr(VI) ions behavior of both active and inactive biomass used.

The plots of inactive biomass could be split into three different stages: the first (0–2 h), which indicates the instantaneous adsorption of ions, suggesting rapid external diffusion and surface adsorption; the second (2–12 h) shows a gradual equilibrium; the third indicate the equilibrium state (12–48 h). The behavior of active biomass was distinct because was gradually reached equilibrium and the time was longer.

3.6 Kinetics of Adsorption

The prediction of adsorption rate gives important information for designing batch adsorption systems. The dynamics and mechanism of adsorption can be understood by evaluating the kinetic data. Table 3 shows different kinetic models used in this study.

The kinetic parameters were obtained by fitting the pseudo-first, pseudo-second and intraparticle diffusion equations to the experimental data (Table 4). According to the correlation coefficients (R^2) exported, the best fitting was for the pseudo- second order equation using inactive biomass, while the pseudo-first order and intraparticle diffusion equations presented lower coefficients in the same tests. Likewise, it is observed that in adsorption tests with active biomass, intraparticle diffusion is favored for both biomasses. There are inactive biomass of fungi that shown affinity to pseudo-first-order model like *Aspergillus niger* (R^2 = 0.95, k_1 = 190.83) (Khambhaty et al. 2009b), *Ceratocystis paradoxa* MSR2 (R^2 = 0.97, k_1 = 0.102) (Samuel et al. 2015b), *Aspergillus niger* MSR4 (R^2 = 0.98, k_1 = 0.11) (Samuel et al. 2015a), *Aspergillus niger* (R^2 = 0.95, k_1 = 0.0009) (Vale et al. 2016); and active biomass *Aspergillus flavus* (R^2 = 0.97, k_1 = 0.23) (Singh and Bishnoi 2015).

The Intraparticle Diffusion Equation The model for intraparticle diffusion developed by Mckay and Poots (1980) was used to establish the mechanism of sorption. The model is given as

$$C_s = k_i t^{1/2} + C_i \quad (1)$$

where C_s is the amount of Cr(VI) adsorbed at time t, k_i (mg L^{-1} $min^{-0.5}$) is the intraparticle diffusion rate

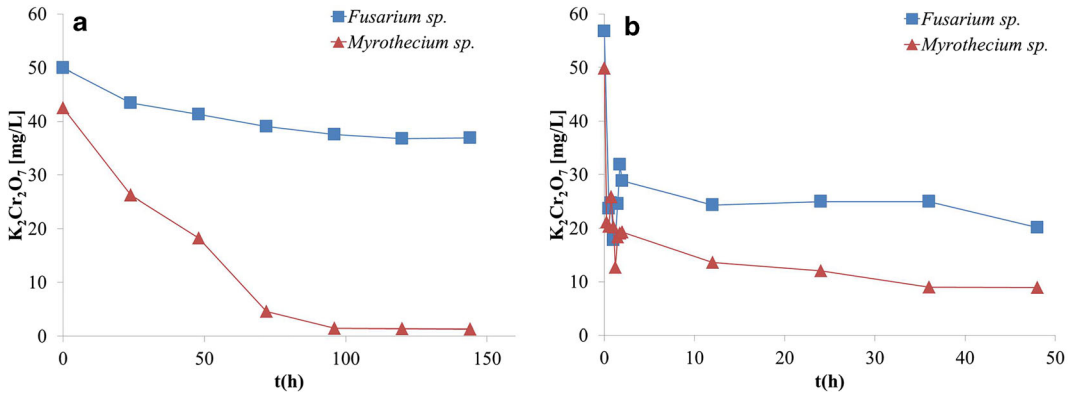

Fig. 3 Effect of contact time on adsorption of Cr(VI) onto **a** active and **b** inactive biomass (pH = 4.5, 50 mg/L ion concentration, T = 25 °C, 150 rpm)

constant and C_i is the boundary layer thickness. The slope of the linear part of the curve (i.e., C_s Vs $t^{0.5}$) gives the initial rate of sorption, (here taken between 72 h in *Myrothecium* sp. and 96 h in *Fusarium* sp. before equilibrium was reached; (Fig. 4), controlled by intraparticle diffusion k_i, while the C_i value is lower in *Myrothecium* sp. active, which means that the sorption process is carried out more efficiently (Table 4). While the others studies shows intraparticle diffusion in *Aspergillus niger* (R^2 = 0.666, k_i = 0.977) (Khambhaty et al. 2009b), *Ceratocystis paradoxa* MSR2 (R^2 = 0.89, k_i = 1.39) (Samuel et al. 2015b), *Aspergillus niger* MSR4 (R^2 = 0.80, k_i = 1.78) (Samuel et al. 2015a), with the linear regression coefficient R^2 low.

The Pseudo-Second-Order Equation If the rate of sorption is a second order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as (Shek et al. 2009):

$$\frac{dC_s}{dt} = k(C_e - C_s)^2 \tag{2}$$

where C_e and C_s are the metal concentration at equilibrium and at time t adsorption by biomass, respectively, (mg/g) and k is the rate constant of pseudo-second-order sorption, (L/mg/min). For the boundary conditions $C_s = 0$ to $C_s = C_s$ at $t = 0$ to $t = t$; the integrated form of equation becomes:

$$\frac{1}{C_e - C_s} = \frac{1}{C_e} + kt \tag{3}$$

This is the integrated rate law for a pseudo-second order reaction. The equation can be rearranged to obtain:

$$C_s = \frac{t}{\frac{1}{kC_e^2} + \frac{t}{C_e}} \tag{4}$$

This linear form:

$$\frac{t}{C_s} = \frac{1}{kC_e^2} + \frac{1}{C_e}t \tag{5}$$

Eq. (5) does not have the problem of assigning as effective. If pseudo-second order kinetics is applicable, the plot of t/C_s against t of Eq. (5) should give a linear relationship, from which C_e and k can be determined from the slope and intercept of the plot (Fig. 5) and there is no need to know any parameter beforehand.

The pseudo-second-order rate constant k_2, the calculated C_e value and C_s the corresponding linear regression coefficient value R^2 are given in Table 4. At all initial biomass conditions, the linear regression coefficient values were higher. The higher values confirm that the adsorption data are well represented by pseudo-second order kinetics and supports the assumption behind the model that the

Table 3 Kinetic parameter for the adsorption of Cr(VI)

Kinetic model	Equation used
Pseudo-first order	$lnC_s = \ln C_e - k_1 t$
Pseudo-second order	$\frac{t}{C_s} = \frac{1}{C_s} + \frac{1}{C_s}t$
Intraparticle diffusion	$C_s = k_i t^{1/2} + C_i$

Table 4 Kinetic constants for adsorption of Cr(VI) onto both active and inactive biomass

Biomass	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
	k_1	R^2	C_e	k_2	R^2	C_e	k_i	R^2	C_i
Myrothecium active	0.0033	0.8693	16.9404	0.0002	0.9643	62.9839	3.8020	0.9315	0.0397
Myrothecium inactive	0.0034	0.7794	30.1773	0.0446	0.9993	40.9576	1.9985	0.8534	28.2801
Fusarium active	0.0025	0.9271	6.4056	0.0014	0.9952	17.3365	1.0023	0.9769	1.9085
Fusarium inactive	0.0008	0.1847	24.9997	0.0646	0.9941	27.7265	0.1803	0.0988	25.3936

adsorption is due to chemisorptions (Khambhaty et al. 2009b; Mungasavalli et al. 2007; Vale et al. 2016). This finding coincides with that already reported: *Colorius versicolor* ($R^2 = 0.985$, $k_2 = 5.12 \times 10^{-5}$) (Sanghi et al. 2009), *Aspergillus niger* ($R^2 = 0.99$, $k_2 = 5.3 \times 10^{-5}$) (Khambhaty et al. 2009b), *Ceratocystis paradoxa* MSR2 ($R^2 = 0.99$, $k_2 = 1.23$) (Samuel et al. 2015b), *Aspergillus niger* MSR4 ($R^2 = 0.99$, $k_2 = 1.68$) (Samuel et al. 2015a), *Aspergillus niger* ($R^2 = 0.998$, $k_2 = 5.52$) (Vale et al. 2016).

Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups, and surface area.

4 Conclusions

The results of this work indicated that both fungi presented abilities for chromium biosorption. The experiments performed revealed that active biomass of *Myrothecium* sp. had a higher potential for Cr(VI) removal than his inactive biomass and both biomasses of *Fusarium* sp.

In terms of the sorption kinetic experiments, the results of three sorption parameter systems were substituted to three kinetic models which were the intraparticle diffusion, pseudo-first order, and pseudo-second order. The pseudo-second-order kinetic model fitted best among the other kinetic models tested, thereby describing the

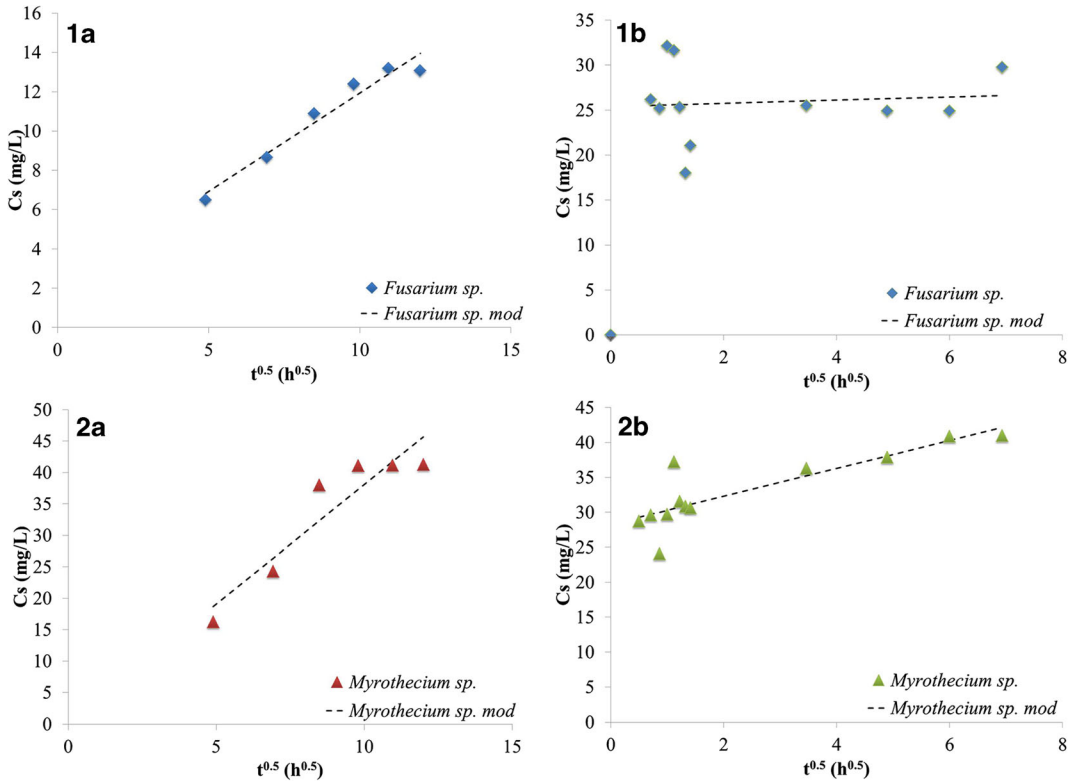

Fig. 4 Adjust to intraparticle diffusion model for **a** active biomass and **b** inactive biomass, by *1 Fusarium* sp.; *2 Myrothecium* sp.

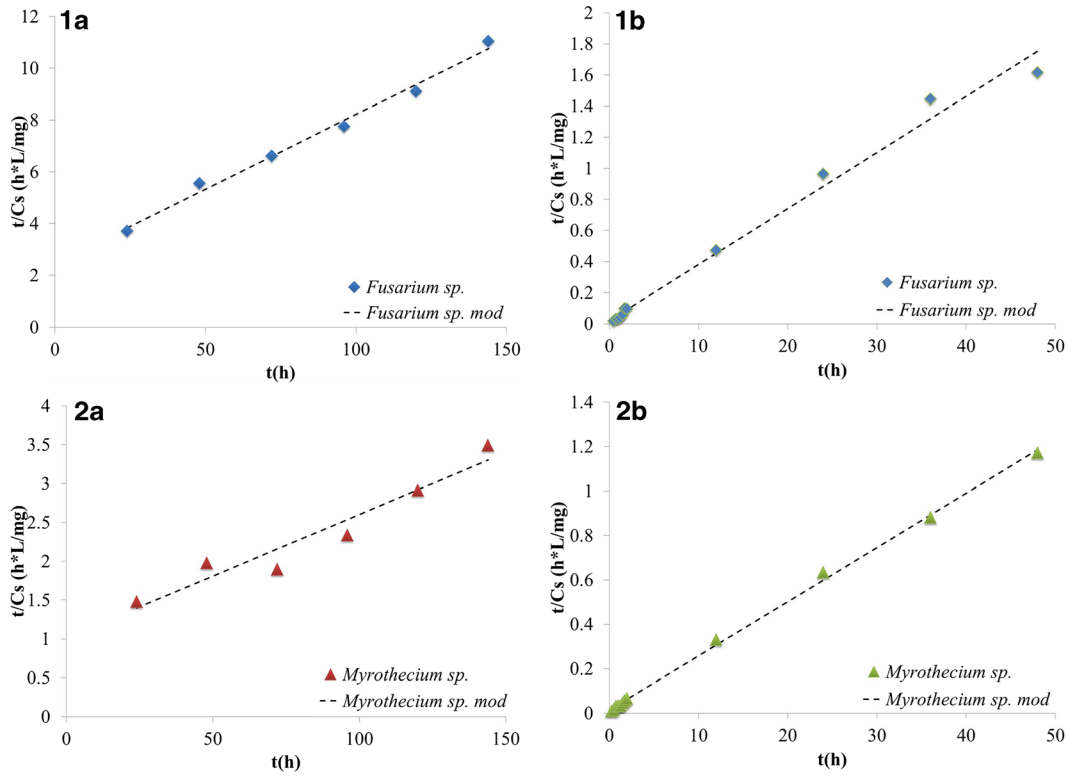

Fig. 5 Adjust to pseudo-second-order for **a** active biomass and **b** inactive biomass, by *1 Fusarium* sp.; *2 Myrothecium* sp.

mechanism of Cr(VI) biosorption as a chemisorption process. The data obtained in active biomass showed that an intraparticle diffusion process occurs, although this is not the limiting step in the sorption of chromium. The fitting pseudo-second order model indicates that a superficial biosorption process occurs rejecting a biotransformation of chromium (VI) to chromium (III), which is confirmed due to no change the color of the sample.

The adsorption kinetics is systematically studied to explore the interaction mechanism between metal ions and absorbent. The findings of the study indicate that biosorption is a promising technology for removal of heavy metal especially chromium.

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