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Biosorption Efficiency of Chromium (VI) from Aqueous Solution by *Humicola phialophoroides* Bio-filter

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ABSTRACT

The adsorption of Cr^{6+} from aqueous solution using viable biomass, non-viable biomass, HNO_3 and NaOH pretreated biomasses of *Humicola phialophoroides* fungus as adsorbents was studied. The biomass pretreated with NaOH showed the highest Cr^{6+} adsorption capabilities, while maximum Cr^{6+} biosorption of biomass took place in the initial solution at pH more than 8 after 90 minutes. Moreover, the Cr^{6+} was well adsorbed by NaOH treated biomass at high temperature, and desorption of biomass with 0.1 M HNO_3 solution reached 53.74%. Fungus column packed with 15 mL alginate-fungus beads was used to treat 20 mg L^{-1} of Cr^{6+} from aqueous solution. Removal efficiency of Cr^{6+} was 0.99±0.03 mg L^{-1} for flow rate at 5 mL min^{-1}, while it was 0.52±0.06 mg L^{-1} for flow rate at 10 mL min^{-1} with residence time at 15 minutes. Studies have shown that removal efficiency of Cr^{6+} decreases by increasing the residence time. The bio-filter was successfully eluted using 0.01 M HNO_3, with removal efficiency of 31.31% and 32.14% for flow rate at 5 and 10 mL $minute^{-1}$, respectively.

INTRODUCTION

Chromium (Cr) is an essential trace element which is required in small amounts for glucose metabolism for humans and animals, but becomes toxic at higher concentrations. Two natural forms of ionic chromium, i.e. trivalent chromium (Cr^{3+}) and hexavalent chromium (Cr^{6+}) are found in water. Cr^{6+} is used in industrial processes and manufacturing activities, including discharges from stainless steel and pulp mills, whereas Cr^{3+} is naturally occurring, environmentally pervasive and a trace element in human and animals. Cr^{3+} has relatively low toxicity and is a concern in drinking water only at very high levels of contamination, while Cr6+ is much more toxic than Cr^{3+} and poses potential health risks.

Biosorbents derived from suitable biomass can be used for the effective removal and recovery of heavy metal ions from wastewater streams, even at low concentrations. The major advantages of biosorbent materials are inexpensive and can be used to remove heavy metal ions at very low levels. Fungi from their natural habitats are excellent sources of biosorbent. One of the most promising biosorbents is *Humicola phialophoroides* fungus. *H. phialophoroides* is able to grow in the creek sediments from heavy metal contaminate area (Netpae et al. 2015). Recent studies have focused on the potential of Cd^{2+} biosorption by *H. phialophoroides* biomass (Netpae et al. 2014, Netpae 2015), there is no information on the use *H. phialophoroides* for the biosorption of other heavy metals. This research was set out to study the isotherm and kinetic parameters for the biosorption of Cr^{6+} by *H. phialophoroides* biomasses. Moreover, the effects of the flow rate on performance of the Cr^{6+} removal by the biosorbent column were systematically investigated.

MATERIALS AND METHODS

Microorganism: The *H. phialophoroides* was isolated from Mae Tao creek sediments from zinc mine area in Mae Sot District, Tak Province, Thailand. Fungal spores were obtained from a 5 days old culture grown on Potato Dextrose Agar (PDA) at 30±2°C. The spores were collected in 0.01% tween-80 solution.

Preparation of chromium solution: A stock solution of hexavalent chromium was prepared by dissolving potassium dichromate (Merck Company) in deionized water. The solution pH was adjusted using 0.1 M HNO_3 and 0.1 M NaOH at the beginning of the experiment and not controlled afterward.

Chromium minimum inhibitory concentration test: Effects of chromium on mass and colour of the spores produced on PDA (10^6-10^7 spores mL^{-1}) were investigated. While, effects of chromium on the biomass growth was measured by weighing dry biomass after 3 days of incubation on a rotary shake flask at 30±2°C at 150 rpm in the Potato Dextrose Broth (PDB). Both culture media were treated with chromium at concentrations of 10, 25, 50 and 100 mg L^{-1}, as compared to that without chromium.

Biomass preparation: The biomass of *H. phialophoroides* was cultivated in PDB, using the shake flask method. Spore

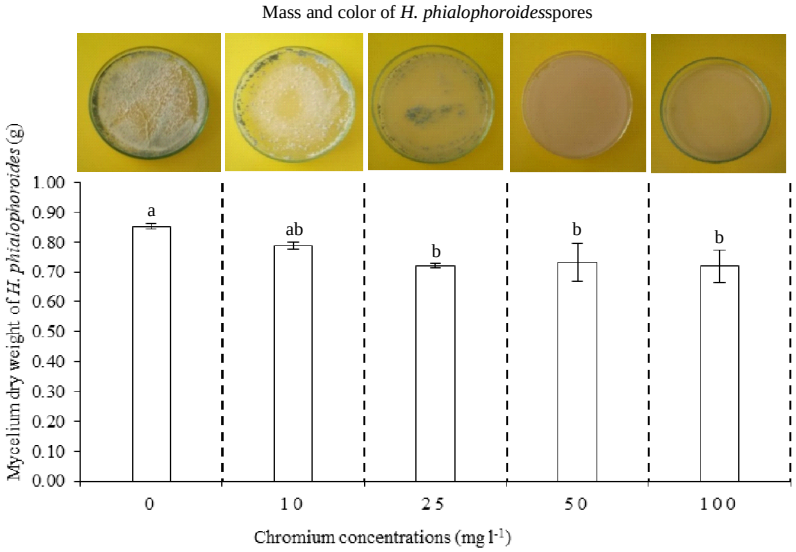

Fig.1: The mass and color of spores and mycelium dry weight of *H. phialophoroides* in media with and without Cr^{6+} at 3 days incubation. Note: Mean of mycelium dry weights followed by the same letter are not significantly different (p<0.05)

suspension (10^8 spores) were cultivated in 50 mL PDB at 30±2°C with shaker at a speed of 150 rpm for 3 days. The viable biomass was harvested by filtration and subjected to successive washings with deionized water. Then non-viable biomass was prepared by autoclaving the viable biomass at 121°C for 20 minutes and then harvested by filtering through a membrane filter and dried at 80°C in an oven for 12 hours. The pretreated biomass prepared by suspending the viable biomass in 10% HNO_3 and 10% NaOH solutions for 30 minutes at 30±2°C. Subsequently, the biomasses were collected and washed with deionized water until the pH of the wash solution was in near pH 7. The pretreated biomass was killed in an autoclave and then harvested by filtering through a membrane filter and dried at 80°C in an oven for 12 hours. Finally, non-viable biomass and pretreated biomass were then ground, using a blender to break cell aggregates into smaller fragments. The biomass was then passed through 100 µm mesh sieves to get particle sizes of less than 0.5-1.0 mm diameter.

Batch isotherm experiments: The equilibrium sorption of the Cr^{6+} ions onto biomass was carried out by contacting 0.1g of the substrate with 50 mL of different concentrations from 0 to 150 mg L^{-1} for 120 minutes on the shaker at a speed of 150 rpm. The amount of metal bound by the biosorbent was calculated as:

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

Where, q is the metal uptake (mg Cr g^{-1} dry wt.), C_i and C_f are the initial and final Cr^{6+} concentrations in the supernatant, respectively (mg L^{-1}), V is the volume of the chromium concentration (mL), and W is the dry weight of the biomass added (g). Linear forms of the isotherm models are also widely adopted to determine the isotherm parameters or the most fitted model for the adsorption system due to the mathematical simplicity. The sorption isotherms of Cr^{6+} was studied by fitting the obtained data to linear forms of the Langmuir (Langmuir 1916), Freundlich (Freundlich 1906) and Temkin (Temkin & Pyzhev 1940) isotherm models (Table 1). The best fit model was selected based on the determination coefficient (R^2).

Effect of temperature, pH and contact time on Cr removal by fungus: In order to evaluate the effect of temperature, pH and contact time on the Cr^{6+} uptake, the experiment was conducted in the same manner, except the temperature of chromium solution was changed to 30, 40, 50, 60 and 70°C. The pH of the solution was prepared to be in the range between 3.0 and 8.0 before mixing biomass. The pH was adjusted to the required value with 0.1 M NaOH or 0.1 M HNO_3. The period of contact time was studied up to 180 minutes by using procedure described earlier, samples were collected every 30 minutes.

Chromium desorption experiments: The 0.1 M HNO_3 solution was used to elute Cr^{6+} from both biomass. Following the Cr^{6+} sorption experiments, the Cr-loaded biomass was prepared by centrifugation, washed and returned to 25 mL of the effluent 0.1 M HNO_3 for 30 minutes on a rotary shaker (125 rpm). Chromium concentrations were determined after separating the biomass from eluting agent by filtration.

Column studies: The immobilized cell was highest Cr^{6+} uptake biomass mixed with 4% sodium alginate in a 1:38 ratio

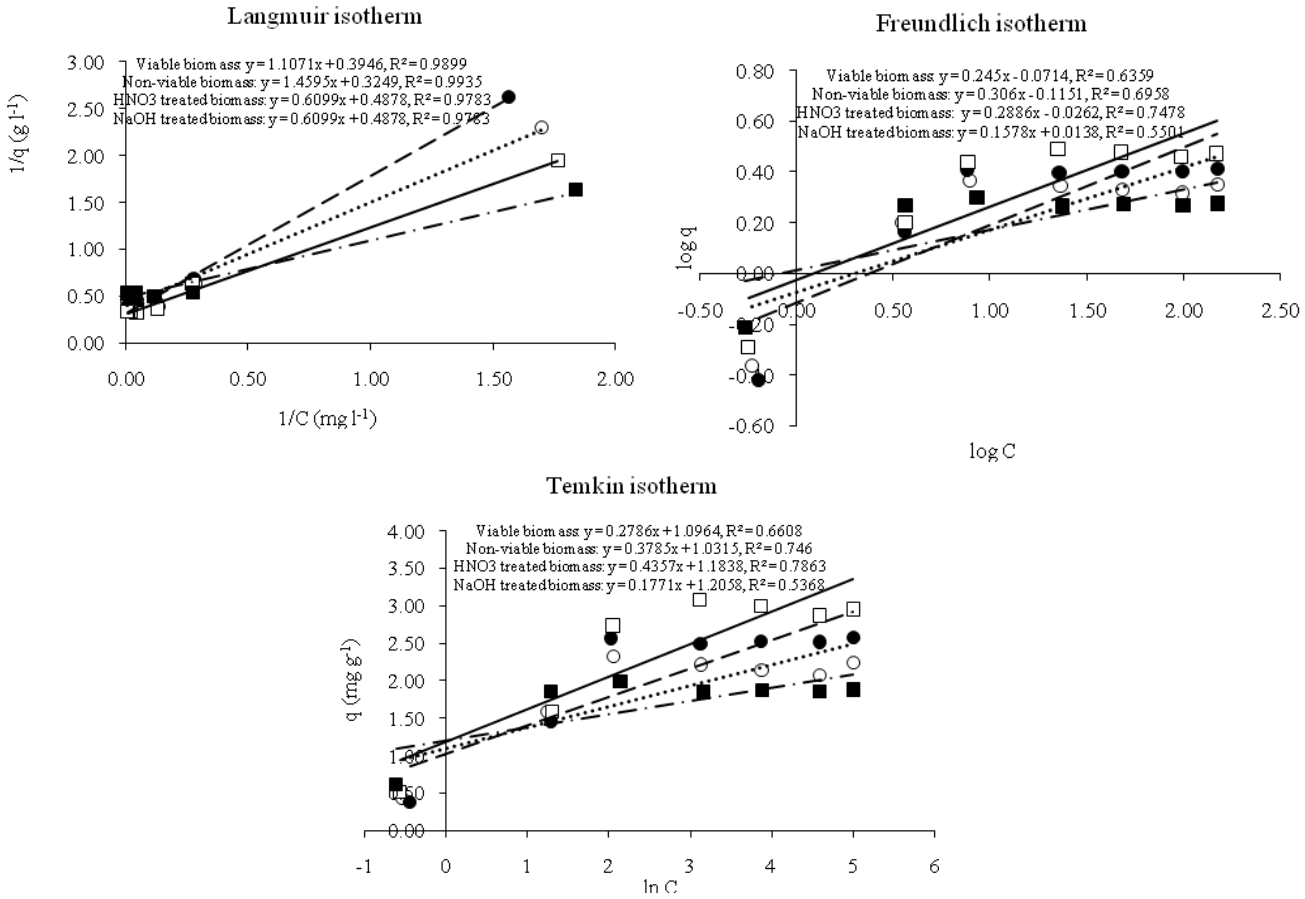

Fig. 2: Adsorption isotherms of Cr^{6+} removal by *H. phialophoroides* : viable biomass (○), non-viable biomass (●), HNO_3 pretreated biomass (□) and NaOH pretreated biomass (■).

used to sorption of Cr^{6+} from synthetic water. The immobilized cells were stacked into glass columns (1.5 cm in diameter) of the bed length in the range of 15 cm. The Cr^{6+} solution at the concentration of 20 mg L^{-1} (pH 7) was continuously pumped upward into the column. At room temperature (30±2°C), the Cr^{6+} loading rates were 5 and 10 mL min^{-1}, while the residence time of Cr^{6+} solution inside the column was 15, 30, 45,60, 90, 180 and 300 min, respectively. The Cr^{6+} elution was carried out with 0.1 M HNO_3 solution at a flow rate 5 mL min^{-1} for 30 minutes. Samples were collected from the effluent to measure the residual Cr^{6+} concentrations.

Atomic absorption analysis: The samples of Cr^{6+} were measured by atomic absorption spectrophotometer (Perkin Elmer model PinAAcle 900T) by using the flameless method of graphite system.

Statistical analysis: All the experiments were triplicated. Mean values were used in the analysis of data by using the analysis of variance (one-way ANOVA) and Post Hoc. Duncan test (p<0.05).

RESULTS AND DISCUSSION

Minimum inhibitory concentrations of Cr^{6+}: Effects of chromium on the spores and mycelium produced are presented in Fig. 1. The results show that spore and mycelium of *H. phialophoroides* can resist against Cr^{6+} concentration until 25 mg L^{-1}. This indicates that the tolerant species have the mechanisms and physiological adaptation to resist the higher Cr^{6+} concentrations and so avoid its toxic effect response to the concentrations of the Cr^{6+} ions. As found in other researches, phenotypes of hypersensitivity to Cr^{6+} are produced as a result of alteration of the vacuolar ATPase and vacuolar structures or by alteration of proteins that protect the oxidative effect of Cr^{6+} as the alkyl hydroperoxide reductase (Gharieb & Gadd 1998, Nguyen-Nhu et al. 2002).

Cr^{6+} uptake on H. phialophoroides biomass: Table 2 shows the uptake mechanism of Cr^{6+} with viable, non-viable and two types of pretreated biomasses of *H. phialophoroides* at 30±2°C with the concentration between 0 to 150 mg L^{-1}. A further increase in Cr6+ concentration in solution did not

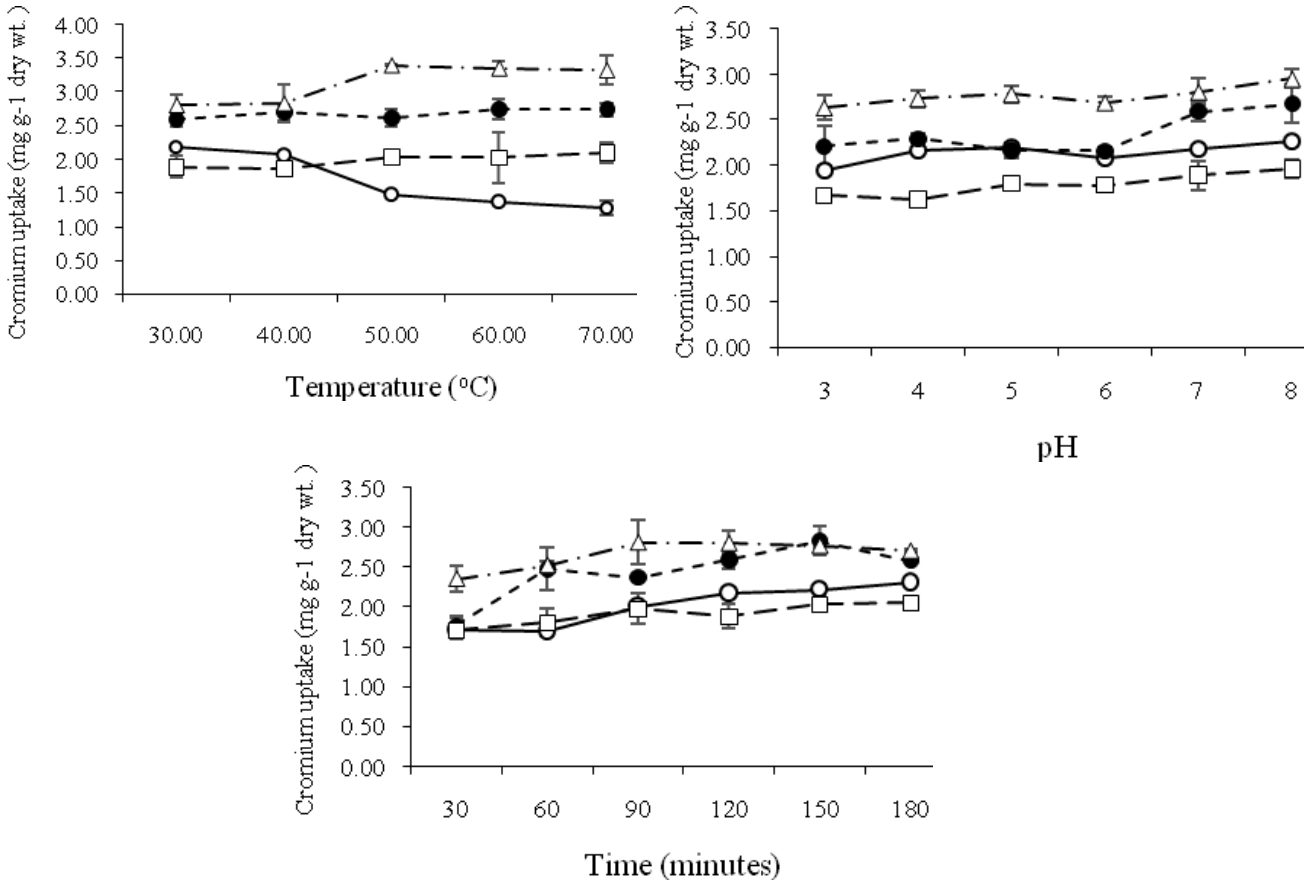

Fig. 3: Effect of pH (a) temperature (b) and contact time (c) on Cr^{6+} removal by *H. phialophoroides* : viable biomass (○), non-viable biomass (●), HNO_3 pretreated biomass (□) and NaOH pretreated biomass (Δ).

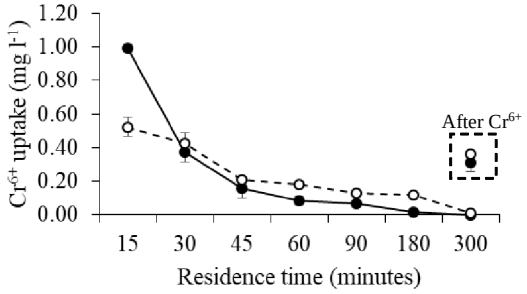

Fig. 4: The effects of residence time and elution on removal efficiency of Cr^{6+} for immobilized column: flow rate at 5 mL min^{-1} (●), and 10 mL $minutes^{-1}$ (○).

show any significant increase in metal uptake rate. The uptake of Cr^{6+} increased with concentration from 1 to 10 mg L^{-1} for most of the biomass types. Only for biomass pretreatment by NaOH, the Cr^{6+} uptake increased as the Cr6+ concentration was increased from 1 to 25 mg L^{-1}. These results indicated that biomass pretreatment by NaOH had a highest Cr^{6+} adsorption capacity among the biomasses studied. Many researchers reported that relatively high initial concentration of Cr^{6+} could accelerate biosorption (Samuel et al. 2015, Subbaiah et al. 2008). The initial concentration might provide an important driving force which overcomes all mass transfer resistance of metal ions between the aqueous and solid phase was attained, resulting in a collision between the metal ions and sorbents.

Isotherm assessment: Langmuir, Freundlich and Temkin adsorption isotherms were employed to determine the preference of one to another. Plot for the nonlinear Langmuir, Freundlich and Temkin equations are shown in Fig. 2, while Table 3 gives the values of the isotherm constants. A high correlation coefficient (R^2) was represented for the best isotherm. The q_m is the maximum amount of Cr^{6+} sorbed, and K_L is an equilibrium constant representing the affinity between the fungi biomass. The values of correlation coefficients for all models indicated that the studied process fitted better to the Langmuir equation, which means that

Table 1: Linear isotherm models forms in this study.

Isotherm models	x-axis	y-axis	Linear form
Langmuir	1/q	1/C	$1/q = (1/q_m K_L)(1/C) + 1/q_m$
Freundlich	log q	log C	$\log q = 1/n \log C + \log K_F$
Temkin	Q	lnC	$q = BlnA + BlnC$

Where,

C = the equilibrium concentration (L g^{-1})
q = the amount of metal ions adsorbed (mg g^{-1})
q_m = the maximum monolayer coverage (mg g^{-1})
K_L = the Langmuir constant (L mg^{-1})
K_F = the Freundlich constant related to the adsorption capacity
A = the Temkin isotherm equilibrium binding constant (L g^{-1})
B = a constant related heat of sorption (j mol^{-1}) by $B = RT/b_T$
b_T = the Temkin isotherm constant
R = the universal gas constant (8.314 $Jmol^{-1}K^{-1}$)
T = the temperature at 298 K

Table 2: Uptake mechanism of Cr^{6+} by *H. phialophoroides* biomasses.

Chromium concentrations (mg L^{-1})	Cr^{+6} uptake (mgCr g^{-1} dry wt.)			
	Viable biomass	Non-viable biomass	HNO_3 pretreated biomass	NaOH pretreated biomass
0	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}
1	$0.44\pm0.00b^{b}$	0.38 ± 0.01^{b}	0.61 ± 0.03^{b}	0.52 ± 0.01^{b}
5	1.60 ± 0.02^{cde}	1.47 ± 0.04^{c}	1.85 ± 0.02^{def}	1.58 ± 0.07^{cd}
10	2.33 ± 0.05^{hij}	2.58 ± 0.01^{jkl}	1.98 ± 0.15^{efgh}	2.73 ± 0.10^{klm}
25	2.22 ± 0.12^{fghij}	2.51 ± 0.28^{ijk}	1.84 ± 0.26^{def}	3.07 ± 0.27^{m}
50	2.15 ± 0.03^{fghi}	2.53 ± 0.37^{ijk}	1.87 ± 0.35^{defg}	2.99 ± 0.32^{m}
100	2.08 ± 0.20^{fgh}	2.53 ± 0.26^{ijk}	1.85 ± 0.33^{def}	2.86 ± 0.32^{klm}
150	2.25 ± 0.12^{ghij}	2.58 ± 0.42^{jkl}	1.88 ± 0.19^{defg}	2.95 ± 0.44^{lm}

Note: For a Cr uptake, mean concentrations followed by the same letter are not significantly different ($p<0.05$)

Table 3: Isotherms parameters models for Cr^{6+} adsorption onto the *H. phialophoroides* biomasses.

Isotherms	Viable biomass	Non-viable biomass	HNO_3 pretreated biomass	NaOH pretreated biomass
Langmuir				
q_m (mg Cr g^{-1}dry wt.)	2.53	3.08	2.05	3.17
K_L (L mg^{-1})	0.44	0.47	0.29	0.30
R^2	0.99	0.99	0.98	0.99
Freundlich				
K_F (mg g^{-1}) (L $mg^{-1})^{1/n}$	0.85	0.77	1.03	0.94
N	4.08	3.27	6.34	3.47
R^2	0.64	0.70	0.55	0.75
Temkin				
A (L g^{-1})	51.18	15.26	905.40	15.13
B	0.28	0.38	0.18	0.44
R^2	0.66	0.75	0.54	0.79

Table 4: Desorption of Cr^{6+}on biomasses of *H. phialophoroides* used with 0.1 M HNO_3.

Biomass	Cr^{6+} uptake (mg Cr g^{-1}dry wt.)		Removal efficiency (%)
	Before desorption	After desorption	
Viable biomass	2.18 ± 0.01	1.59 ± 0.29	72.94
Non-viable biomass	2.60 ± 0.11	1.56 ± 0.08	60.00
HNO_3 pretreated biomass	1.89 ± 0.16	1.46 ± 0.04	77.25
NaOH pretreated biomass	2.81 ± 0.15	1.51 ± 0.04	53.74

the biosorption of Cr^{6+} onto chemically modified biomass of *H. phialophoroides* was a monolayer onto a surface containing finite number of identical sites. This model does not permit transmigration of the adsorbate in the plane of the surface (Perez Marín et al. 2007). The values of maximum monolayer adsorption capacity of *H. phialophoroides* biomasses were 2.53, 3.08, 2.05 and 3.17 mg Cr g^{-1} dry wt. for viable biomass, non-viable biomass, HNO_3 treated biomass and NaOH treated biomass, respectively. This value is higher than many of fungal biomasses such as, *Trichoderma viridae* (El-Kassas & El-Taher 2009), *Pleurotus ostreatus* (Javaid & Bajwa 2007), but lower than *Aspergillus niger* (Vale et al. 2016 and Chhikara et al. 2010) and *Phanerochaete chrysosporium* (Nikazar et al. 2008).

Effect of temperature on biosorption: Temperature exposure on Cr^{6+} uptake in *H. phialophoroides* biomasses is presented in Fig. 3a. It was slightly higher for Cr^{6+} uptake curve in non-viable biomass and 2 pretreated biomasses after 60°C. The Cr^{6+} uptake in biomass pretreated by NaOH of *H. phialophoroides* was greater than 3.36±0.09 mg Cr g^{-1} dry wt. after 60°C ($p < 0.05$), while the Cr^{6+} uptake in viable biomass was lower in temperature higher than 50°C. Temperature can affect the stability of cell wall as well as its configuration and can also cause ionization of chemical moieties. These factors may simultaneously affect the binding sites of fungal biomass causing reduction in Cr^{6+} uptake (Iram & Abrar 2015).

Effect of pH on biosorption: The efficiency of Cr^{6+} removal was strongly dependent on pH (Fig. 3b). Maximum removal of Cr^{6+} was found to be at high pH, while at low pH, protons compete with Cr^{6+} for most of the binding sites on the biosorbent surface. Binding attraction decreases as the surface of the biosorbent becomes more positively charged, as suggested by Abdul-Talib (2013).

Effect of contact time on biosorption: The effect of contact time on biosorption of Cr^{6+} by *H. phialophoroides* biomasses was studied under optimal condition (Fig. 3c). Although the adsorption capacity was different, the Cr^{6+} uptake by all *H. phialophoroides* biomasses had rapidly increased up to 90 minutes and tend to remain constant afterward as well. This indicated that initially the presence of abundant vacant binding sites become saturated after these sites were occupied. Remaining vacant binding sites might also be difficult to occupy due to repulsive force between the solute molecules of the solid and bulk phase (Mathivanan & Rajaram 2014).

Desorption: A summary of the Cr^{6+} removal of the *H. phialophoroides* biomasses after desorption by 0.1 M HNO_3 is provided in Table 4. The Cr^{6+} uptake was decreased by about 72.94%, 60.00%, 77.25% and 53.74% for viable biomass, non-viable biomass, HNO_3 treated biomass and NaOH treated biomass, respectively. The desorption might be due to the increase of the concentrations of competing H_3O^+. It is also possible that the physical structure of the biomass becomes damaged by HNO_3 (Sun et al. 2010).

Removal of Cr^{6+} in immobilized column experiments: Removal efficiency of Cr^{6+} at 20 mg L^{-1} concentration from aqueous solution was 0.99±0.03 mg L^{-1} for flow rate at 5 mL min^{-1}, while it was 0.52±0.06 mg L^{-1} for flow rate at 10 mL min^{-1} at residence time of 15 min. Studies have shown that removal efficiency of Cr^{6+} decreases by increasing residence time. The column was successfully eluted using 0.01 M HNO_3, with removal efficiency of 31.31% and 32.14% for flow rate at 5 and 10 mL min^{-1}, respectively (Fig. 4). This result agrees with Alrasool Ali (2013), who found that removal efficiency depends on the residence time between the metal ions and biomass biosorbent surface, and the flow rate of metal solution through the biosorbent column influences metal removal efficiency as it affects the contact time. These results showed that immobilized *H. phialophoroides* biomass treated with NaOH can be used repeatedly for removal of Cr^{6+} from aqueous solutions.

CONCLUSIONS

The adsorption equilibrium of Cr^{6+} sorption at low concentration can be described by Langmuir isotherm model. The values of maximum monolayer adsorption capacity of *H. phialophoroides* biomasses was 2.53, 3.08, 2.05 and 3.17 mg Cr g^{-1} dry wt. for viable biomass, non-viable biomass, HNO_3 treated biomass and NaOH treated biomass, respectively. Maximum Cr^{6+} biosorption of biomass pretreated with NaOH took place at initial solution at pH more than 8 after 150 minutes. Moreover, the Cr^{6+} was well adsorbed by NaOH treated biomass at high temperature. Desorption experiments indicated that the desorption of NaOH treated biomass with 0.1 M HNO_3 solution reaches 53.74%. Removal efficiency of 20 mg L^{-1} of Cr^{6+} by column packed with 15 mL alginate-fungus beads was 0.99±0.03 and 0.52±0.06 mg L^{-1} for flow rate at 5 and 10 mL min^{-1}, respectively. Residence time at 300 minutes, it was 0.00±0.02 and 0.01±0.01 mg L^{-1} for flow rate at 5 and 10 mL min^{-1}, respectively.

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