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Chromium(VI) biosorption by dried *Rhizopus arrhizus*: Effect of salt (NaCl) concentration on equilibrium and kinetic parameters

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Abstract

Some industrial wastewaters contain high quantities of salts besides heavy metal ions. The presence of salt ions leads to high ionic strength, which may significantly affect the performance of the biosorption process so the effect of salts on the biosorption of heavy metal ions should be investigated. In this study the biosorption of chromium(VI) from saline solutions on dried *Rhizopus arrhizus* was studied as a function of pH, initial chromium(VI) and salt (NaCl) concentrations in a batch system. The biosorption capacity of *R. arrhizus* strongly depended on solution pH and maximum chromium(VI) sorption capacity of sorbent was obtained at pH 2.0 both in the absence and in the presence of increasing concentrations of salt. Chromium(VI)–salt biosorption studies were performed at this pH value. Equilibrium uptakes of chromium(VI) increased with increasing chromium(VI) concentration up to 250 mg l^{-1} and decreased considerably by the presence of increasing concentrations of salt. At 100 mg l^{-1}, initial chromium(VI) concentration, dried *R. arrhizus* biosorbed 78.0 mg g^{-1} of chromium(VI) in 72 h without salt medium. When salt concentration was raised to 50 g l^{-1}, this value dropped to 64.0 mg g^{-1} of chromium(VI) at the same conditions resulting in 17.9% decrease of biosorption capacity. The equilibrium sorption data were analysed by using Freundlich, Langmuir, Redlich–Peterson and Langmuir–Freundlich (Sips), the two and three parameters adsorption models, using non-linear regression technique and isotherm constants were evaluated depending on salt concentration. The Langmuir–Freundlich (Sips) was the best suitable adsorption model for describing the biosorption of chromium(VI) individually and in salt-containing medium. Pseudo-first-order, pseudo-second-order and saturation type kinetic models described the biosorption kinetics accurately at all chromium(VI) concentrations in the absence and in the presence of changing concentrations of salt. Isotherm and saturation type kinetic constants varied due to the level of salt were expressed as a function of initial salt concentration.

Keywords: Biosorption; *R. arrhizus*; Chromium(VI); Salt; Isotherms; Kinetics

1. Introduction

Chromium, with its great economic importance in industrial use, is a major metal pollutant of the environment. The discharge of effluents by a variety of industries such as textile, dyes and pigments production, leather tanning, electroplating and metal finishing may contain undesirable amounts of chromium(III) and toxic chromium(VI) compounds due to EPA (US Environmental Protection Agency) at concentrations ranging from tens to hundreds of mg l^{-1}. Wastewaters generated by these industries usually contain significant quantities of salts such as sodium chloride, so the effects of these salts on the removal of chromium(VI) should be investigated [1,2].

Biosorption can be defined as sequestering of organic and inorganic species including metals, dyes and odor causing substances using live or dead biomass or their derivatives. This biomass may be bacteria, fungi, algae, sludge from biological wastewater treatment plants, by-products from fermentation industries, seaweeds or agricultural wastes such as rice husk, rice bran and wheat bran. "Biosorption" is used to indicate a number of metabolism-independent processes (physical and chemical adsorption, electrostatic interaction, ion exchange, complexation, reduction, chelation and microprecipitation) taking place essentially on the cell surface. The biosorption capacity of a biomass depends on several factors. It includes type of biomass (species, age), type of sorbates, presence of other competing ions and method of biomass preparation, along with several physicochemical factors (temperature, pH and ionic concentration). Biosorption, if compared with other available technologies such as precipitation, ion exchange, reverse-osmosis and adsorption

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used for the removal of heavy metal ions, presents comparable advantages such as very low cost, competitive performance, availability of known process equipment, recovery of the sorbate and possible regeneration of biosorbent at low cost. Moreover, the biosorption process does not produce chemical sludges (i.e. non-polluting), it could be highly selective, more efficient, easy to operate, and hence, cost effective for the treatment of large volumes of wastewaters containing low pollutant concentrations [2–5].

Although most current research of biosorption is focused on the removal of heavy metal cations, the uptake of toxic metal anionic forms by biomass has become a growing concern in this field. Literature shows that a wide variety of microorganisms, including bacteria, algae and fungi, and agricultural wastes are capable of sorbing chromium(VI) anions [6–30]. Among these microorganisms, fungal biomass seems to be a good sorption material, because, it can be produced easily and economically using simple fermentation techniques with a high yield of biomass and economical growth media. Fungal biomass is also available as a by-product or waste material from various fermentation processes. Furthermore, since dead fungal biomass is of little use and is abundant, it may be good source of biomaterial for the removal of chromium(VI) from industrial wastewaters. Also it is necessary to check the effect of salts on chromium(VI) biosorption by fungal biomass.

The ability of *R. arrhizus* to remove and accumulate heavy metal ions has been recognized and studied to a certain degree for its biosorption capability [6,7,11]. However, the role of salts on metal biosorption by the biomass have not been investigated extensively. In fact, no detailed studies related to this topic have been reported up to date. Hence, the effect of NaCl salt concentration on the biosorption equilibrium and kinetics of chromium(VI) to dried *R. arrhizus* was investigated and compared to single component situation in this study.

2. Mathematical description

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the analysis and design of adsorption systems and provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. One of the difficulties in describing the adsorption equilibrium of metal ions from wastestreams is that wastewaters contain not one, but many components. If mono-component adsorption models could describe the equilibrium of metal ion in the presence of other components, such as salt, the individual isotherm parameters changed due to the level of salt can be related to initial salt concentration and these expressions may be useful to define the equilibrium data in salt-containing solutions. In order to discover the sorption capacity of dried *R. arrhizus* for chromium(VI) in the absence and in the presence of changing concentrations of salt, the experimental data points were fitted to the Langmuir and Freundlich (two-parameter models), Redlich–Peterson and Langmuir–Freundlich (Sips) (three-parameter models) models which are the most frequently used equations in the literature describing the non-linear equilibrium between adsorbed metal ion on the cells (q_{eq}) and metal ion in solution (C_{eq}) at a constant temperature. Two-parameter models are usually preferred since they are simple, give a good description of experimental behavior in a large range of operating conditions, recharacterized by a limited number of adjustable parameters and be easily linearized. However, if two-parameter models cannot fit the data well, three-parameter models needs to be used in this case.

Langmuir sorption model which was originally developed to describe the gas–solid phase adsorption of activated carbon, has traditionally been used to quantify and contrast the performance of different biosorbents and the model serves to estimate the maximum uptake values where they cannot be reached in the experiments. The empirical Langmuir equation which is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules is given by Eq. (1).

$$q_{eq} = \frac{Q^{O} b C_{eq}}{1 + bC_{eq}} \tag{1}$$

where C_{eq} and q_{eq} are the unadsorbed concentration of metal ion (mg l^{-1}) and adsorbed quantity of metal ion per g of biosorbent at equilibrium (mg g^{-1}), respectively. The parameters Q^{o} and b are Langmuir constants related to maximum adsorption capacity and bonding energy of adsorption, respectively, which are functions of the characteristics of the system as well as time [31].

The Freundlich model is the earliest known empirical equation and is shown to be consistent with exponential distribution of active centres, characteristic of heterogeneous surfaces. It is expressed by the following equation:

$$q_{eq} = K_F C_{eq}^{1/n} \tag{2}$$

where K_F and n are the Freundlich constants characteristic on the system. K_F and n are indicators of biosorption capacity and biosorption intensity, respectively. The Freundlich isotherm is also more widely used but provides no information on the monolayer biosorption capacity, in contrast to the Langmuir model [32].

The three-parameter empirical Redlich–Peterson model is widely used as a compromise between Langmuir and Freundlich systems and the non-linear form of the model is given by Eq. (3). It has a linear dependence on concentration in the numerator and an exponential function in the denominator.

$$q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta}} \tag{3}$$

where K_{RP}, a_{RP} and β are the Redlich–Peterson parameters. The exponent β lies between 0 and 1. For $\beta = 1$, Eq. (3) converts to the Langmuir form [33].

Langmuir–Freundlich (Sips) model is another three-parameter empirical model for the representing equilibrium biosorption data (Eq. (4)). It can be considered as a combination of Langmuir and Freundlich equations. This model suggests that the equilibrium data follow Freundlich isotherm at lower solute concentration, and thus, does not obey Henry's law, and follows

Langmuir pattern at higher solute concentration:

$$q_{eq} = \frac{AC_{eq}^{m}}{1 + BC_{eq}^{m}} \quad (4)$$

where A, B and m are the Langmuir–Freundlich parameters. Values for $m \gg 1$ indicate heterogeneous adsorbents, while values closer to or even 1.0 indicate a material with relatively homogenous binding sites. In this case the Sips model is reduced to the Langmuir equation.

On the other hand, three simplified kinetic models including pseudo-first-order [34], pseudo-second-order [35] and saturation type [36] were used to test the biosorption kinetics of chromium(VI) in the absence and in the presence of salt. These three models basically include all steps of adsorption such as external film diffusion, adsorption, and internal particle diffusion, so they are pseudo-models.

The pseudo-first-order rate expression based on solid capacity is generally expressed as follows:

$$\frac{dq}{dt} = k_{1,ad}(q_{eq} - q) \quad (5)$$

where q is the metal ion uptake by unit mass of sorbent at any time (mg g^{-1}), $k_{1,ad}$ is the rate constant of first-order biosorption. After integration and applying boundary conditions, $t = 0$ to $t = t$ and $q = 0$ to $q = q_{eq}$; the integrated form of Eq. (5) becomes:

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_{1,ad}}{2.303}\, t \quad (6)$$

A straight line of $\log(q_{eq} - q)$ versus t suggests the applicability of this kinetic model. The pseudo-second-order equation is also based on the sorption capacity of the solid phase and on the assumption that the sorption process involves chemisorption mechanism and for chromium(VI) both singly and in the mixture is expressed as:

$$\frac{dq}{dt} = k_{2,ad}(q_{eq} - q)^2 \quad (7)$$

where $k_{2,ad}$ is the rate constant of second-order biosorption. For the same boundary conditions the integrated form of Eq. (7) becomes:

$$\frac{t}{q} = \frac{1}{k_{2,ad}\, q_{eq}^2} + \frac{1}{q_{eq}} t \quad (8)$$

If second-order kinetics are applicable, the plot of t/q against t of Eq. (8) should give a linear relationship, from which q_{eq} and $k_{2,ad}$ can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand.

The applicability of saturation type kinetics in modeling the kinetic data was also discussed. The plot of q versus time can be used to find the initial biosorption rate (r_{ad}) by differentiating the plot at $t = 0$ as defined in Eq. (9).

$$\left.\frac{dq}{dt}\right|_{t=0} = r_{ad} \quad (9)$$

From experimental data, it was shown that the initial biosorption rate is proportional to the first power of the initial metal ion concentration at lower bulk metal ion concentrations (first-order kinetics) and at higher metal ion concentrations, the rate becomes independent of initial metal ion concentration (zero-order kinetics). Eq. (10) can be used to describe the rate of biosorption very accurately in both situations. This kind of rate equation is defined as 'saturation type'.

$$r_{ad} = \frac{k_{ad} C_0}{1 + k'_{ad} C_0} \quad (10)$$

where k_{ad} is the first-order rate constant of saturation type biosorption. The zero-order rate constant ($k_{0,ad}$) is expressed as k_{ad}/k'_{ad}. A straight line of $1/r_{ad}$ versus $1/C_0$ suggests the applicability of this kinetic model and k_{ad} and $k_{0,ad}$ can be determined from the slope and intercept of the plot. This model predicts the biosorption behavior over the whole studied concentration range of metal ion at a constant salt level at a constant temperature.

The validity of all models can be checked from the linear plots.

3. Materials and methods

3.1. Microorganism and growth conditions

Rhizopus arrhizus, a filamentous fungus obtained from the US Department of Agriculture Culture Collection was used in this study. The microorganism was grown at 25 °C in agitated liquid media containing malt extract (17 g l^{-1}) and soya peptone (5.4 g l^{-1}). The pH of the medium was adjusted to 6.5–6.8 with dilute H_2SO_4 and NaOH solutions before sterilization.

3.2. Preparation of the microorganism and chromium(VI) and salt solutions for biosorption

After the growth period, *R. arrhizus* was washed twice with distilled water, inactivated using 1% formaldehyde and then dried at 60 °C for 24 h. For the biosorption studies, a weighed amount of dried biomass was suspended in 100 ml of double-distilled water and homogenized in a homogenizer (Janke and Kunkel, IKA-Labortechnick, Ultra Turrax T25, Germany) at 8000 rpm for 20 min and then stored in the refrigerator. At the beginning of biosorption, 10 ml dried biomass suspension was contacted with 90 ml of solution containing a known concentration of chromium(VI) and salt in an Erlenmayer flask at the desired temperature and pH. All the final solutions contained 1.0 g l^{-1} of biosorbent.

Stock chromium(VI) and salt solutions were prepared at 1 and 100 g l^{-1} concentrations dissolving weight quantity of potassium dichromate (Merck) and NaCl (Merck) in double-distilled water, respectively. For single chromium(VI) and binary chromium(VI)–salt mixture studies, desired combinations of chromium(VI) and salt were obtained by diluting stock solutions of these components and mixing them in the test medium. Before mixing with biosorbent solution, the pH of each test solution was adjusted to the required value with H_2SO_4 and NaOH solutions at different concentrations changing from 0.01 to 1.0 M. For this purpose the dilution to 90 ml was not completed to exactly

90 ml, but 85–86 ml in order to be able to add sufficient volume of acid or base solution for desired pH adjustment and than this volume was completed to 90 ml diluted and concentrated H_2SO_4 and NaOH solutions. The ranges of initial concentrations of chromium(VI) and salt prepared from stock solutions varied between 25–250 mg l^{-1} and 10–50 g l^{-1}, respectively.

3.3. Biosorption experiments

Sorption studies were conducted in a routine manner by the batch technique in 250 ml Erlenmeyer flasks containing 100 ml of chromium(VI) or chromium(VI)–salt mixture-bearing synthetic solutions at desired level of each component at the beginning of the adsorption at pH 2.0. The flasks were agitated on a shaker at a 100 rpm constant shaking rate for 3 days to ensure equilibrium was reached. Samples (5 ml) were taken before mixing the biosorbent and the metal ion or metal–salt mixture-bearing solution, at definite time intervals. Before analysis the samples were centrifuged at 4000 rpm for 3 min and the supernatant fraction was analysed for the remaining chromium(VI) ions. Studies were performed at a constant temperature of 25 °C to be representative of environmentally relevant conditions. All the biosorption experiments were repeated twice to confirm the results. The data were the mean values of two replicate determinations.

The uptake of chromium(VI) by unit mass of sorbent at any time (q) was determined from Eq. (11):

$$q = \frac{C_0 - C_{res}}{X} \quad (11)$$

where C_0 is the initial chromium(VI) concentration (mg l^{-1}), C_{res} is the residual (unadsorbed) chromium(VI) concentration at any time (mg l^{-1}) and X is the sorbent concentration (g l^{-1}). C_{res} is equal to C_{eq} and q is equal to q_{eq} at equilibrium.

3.4. Analytical methods

The residual chromium(VI) ions in the biosorption medium were determined spectrophotometrically at 540 nm using diphenyl carbazide reagent in acid solution as the complexing agent for chromium(VI) [37].

4. Results and discussion

Chromium(VI) biosorption properties of dried *R. arrhizus* were investigated as a function of initial pH, initial chromium(VI) and initial NaCl concentrations. The kinetic and equilibrium results are given as the units of adsorbed chromium(VI) ion quantity in single or salt containing environment per gram of biosorbent at any time (q, mg g^{-1}) and at equilibrium (q_{eq}, mg g^{-1}) and residual chromium(VI) ion concentration in single or salt containing environment at equilibrium (C_{eq}, mg l^{-1}). The adsorption yield is defined as the ratio of sorbed concentration of chromium(VI) ions at equilibrium to the initial chromium(VI) ion concentration for both single and salt containing situations (Ad%).

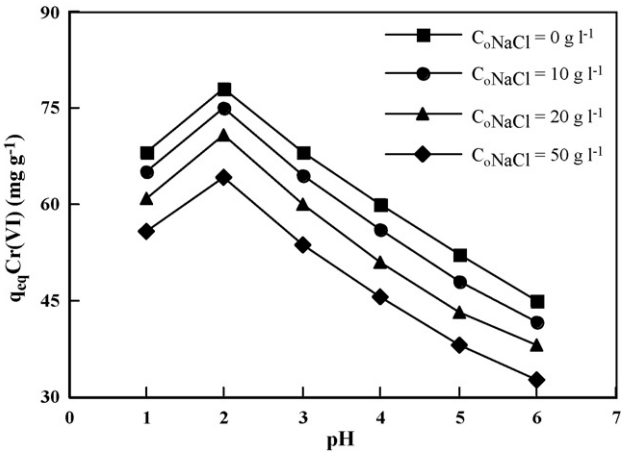

Fig. 1. Effect of initial pH on equilibrium chromium(VI) sorption capacity of dried *R. arrhizus* in the absence and in the presence of increasing concentrations of salt ($C_{0Cr(VI)}$: 100 mg l^{-1}; X: 1.0 g l^{-1}; temperature: 25 °C; agitation rate: 100 rpm).

4.1. Effect of initial pH on chromium(VI) biosorption in the absence and in the presence of increasing concentrations of salt

Earlier studies on heavy metal biosorption have shown that pH was the single most important parameter affecting the biosorption process. To find the suitable pH for the effective biosorption of chromium(VI) ions by dried *R. arrhizus* in single and salt containing media, experiments were performed at different initial pH values (1.0–6.0) and at different initial NaCl concentrations (0–50 g l^{-1}). The variation of equilibrium chromium(VI) uptake with initial pH is given in Fig. 1 at about 100 mg l^{-1} constant metal ion concentration. As seen from the figure, the highest uptake values were found at pH 2.0 and the biosorption of chromium(VI) decreased notably with further increase in pH for all the NaCl concentrations tested.

Solution pH influences both cell surface metal binding sites and metal chemistry in water. At pH values below the isoelectric point (<4.0), the overall surface charge on fungal cells will be positive [38]. It is expected that nitrogen-containing functional groups such as amines or imadazoles in the biomass will also be protonated at acidic pH values. It is known that the dominant form of chromium(VI) at pH 1.0 is the acid chromate ion species ($HCrO_4^-$) and increasing pH shifts the concentration of $HCrO_4^-$ to other forms. At pH 2.0, chromium(VI) behaves as an oxo-anion (CrO_4^{-2} or $Cr_2O_7^{-2}$) in aqueous solution with an overall negative charge. Since there is an increase in sorption of chromium(VI) as pH increased to 2.0 so it may be suggested that probably the CrO_4^{-2} or $Cr_2O_7^{-2}$ are the active forms of chromium(VI), which are being sorbed by the biomass. The binding of chromium(VI) could be occurring either via positively charged ligands on the surface of biosorbent (e.g. amino groups) primarily electrostatically in nature or through the reduction of chromium(VI) to chromium(III) under strongly acidic conditions (pH < 2.5) by contact with the electron-donor groups of the biomass, i.e., groups having lower reduction potential values than that of chromium(VI) (+1.3 V), subsequently

resulting in the binding of chromium(III) to the biomass. Reduction in the biosorption of chromium(VI) at pH value higher than 2.0 is probably due to the change in the overall surface charge on the fungal cells [22,37,39,40].

Salt concentration is proportional to the ionic strength of aqueous solution directly. Ionic strength, besides pH is also one of the important factors that influence the equilibrium uptake. Although the ionic strength or the salinity did not affect the optimum pH of biosorption, influenced the chromium(VI) uptake antagonistically. The chromium(VI) removal decreased with increasing ionic strength of the aqueous solution at all pH values studied as shown in Fig. 1, though the decrease was insignificant at lower ionic strength. But, it was notably at ionic strength greater than 20 g l^{-1}. At pH 2.0, the removal of chromium(VI) decreased from 78.0 to 75.1 mg g^{-1} at 10 g l^{-1} salt containing medium resulted in 3.8% reduction in biosorption capacity. However, chromium(VI) uptake capacity of fungus decreased from 78.0 to 64.0.0 mg g^{-1} with increasing salt concentration up to 50 g l^{-1} resulted in 17.9% decrease in biosorption. This behavior may be due to the inhibition effect of salt on the permeability of cell membrane for chromium(VI) ions and relative competition between chloride and chromate anions on the active centers of fungus [26,37,41]. Biosorption studies of chromium(VI) both singly and in salt containing medium were also performed at the pH value of 2.0.

4.2. Effect of initial chromium(VI) concentration on chromium(VI) biosorption

Initial concentration provides an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases. Hence, a higher initial concentration of chromium(VI) will increase the biosorption rate. Such an effect was clearly demonstrated in Table 1. The equilibrium sorption capacity of fungus increased with increasing initial chromium(VI) concentration in both single chromium(VI) and chromium(VI) and salt containing situations. In the absence of salt, when the initial chromium(VI) concentration increased from 25 to 250 mg l^{-1} approximately, the loading capacity increased from 23.2 to 108.9 mg g^{-1} due to the increase in the number of ions competing for the available binding sites on the biomass surface. The uptake of chromium(VI) reached a plateau at 250 mg l^{-1} showing the saturation of binding sites at higher concentration levels. The initial chromium(VI) concentration also remarkably influenced the biosorption yield as shown in Table 1 in both single chromium(VI) and salt containing situations. Chromium(VI) removal yield was the maximum at the lowest concentration of chromium(VI) (25 mg l^{-1}) due to higher number of active sites attained than at higher concentrations of chromium(VI).

4.3. Effect of salt concentration on chromium(VI) biosorption

Table 1 illustrates the effect of salt concentration (or ionic strength) on the removal of chromium(VI) ions by dried *R. arrhizus* at different initial chromium(VI) concentrations. The

Table 1
Effects of initial chromium(VI) and salt concentrations on the equilibrium uptakes and adsorption yields of chromium(VI) (initial pH: 2.0; *X*: 1.0 g l^{-1}; temperature: 25 °C; agitation rate: 100 rpm)

C_{0NaCl} = 0 g l^{-1}			C_{0NaCl} = 10 g l^{-1}			C_{0NaCl} = 20 g l^{-1}			C_{0NaCl} = 50 g l^{-1}		
$C_{0Cr(VI)}$ (mg l^{-1})	q_{eq} (mg g^{-1})	Ad%	$C_{0Cr(VI)}$ (mg l^{-1})	q_{eq} (mg g^{-1})	Ad%	$C_{0Cr(VI)}$ (mg l^{-1})	q_{eq} (mg g^{-1})	Ad%	$C_{0Cr(VI)}$ (mg l^{-1})	q_{eq} (mg g^{-1})	Ad%
25.2	23.2	92.1	25.0	22.4	88.0	25.0	20.5	82.0	25.5	18.4	72.2
50.8	46.0	90.6	51.6	44.2	85.7	50.6	40.9	80.8	50.5	34.8	68.9
100.3	78.0	77.8	100.2	75.0	74.9	99.2	70.8	71.4	101.2	64.0	63.2
149.8	95.2	63.6	150.2	92.0	61.2	151.0	87.0	57.6	150.5	79.1	52.6
201.1	105.2	52.3	200.6	101.4	50.5	201.1	95.0	47.2	199.6	85.9	43.0
252.3	108.9	43.2	251.5	104.8	41.7	249.6	99.2	39.7	250.4	90.0	35.9

results clearly demonstrate that in the absence of salt, the fungus showed excellent ability for the chromium(VI) biosorption. Moreover, the uptake of chromium(VI) ions was not significantly affected by the low concentration of salt. However, increasing the salinity up to 50 g l^{-1} led to a significant decrease of the amount of metal removed from aqueous solution and percent removal efficiency. When studied with 25 and 250 mg l^{-1} initial chromium(VI) concentrations, as salt concentration increased from 0 to 10 g l^{-1}, equilibrium chromium(VI) uptakes lessened only from 23.2 to 22.4 mg g^{-1} and only from 108.9 to 104.8 mg g^{-1}, respectively. The uptakes of chromium(VI) varied by less than 3.4% and 3.8% for 25 and 250 mg l^{-1} initial chromium(VI) concentrations, respectively. However, as the concentration of salt increased from 0 to 50 g l^{-1}, the amount of chromium(VI) adsorbed by dried *R. arrhizus* and chromium(VI) removal yield diminished from 23.2 to 18.4 mg g^{-1} and from 92.1 to 72.2%, respectively, for 25 mg l^{-1} initial chromium(VI) concentration. When studied with 250 mg l^{-1} chromium(VI) uptake decreased from 108.9 to 90.0 mg g^{-1}, while the percent removal efficiency decreased from 43.2 to 35.9% with increasing salt concentration from 0 to 50 g l^{-1}. The reductions in chromium(VI) uptake were 20.7 and 17.4% for 25 and 250 mg l^{-1} initial chromium(VI) concentrations, respectively for this case. But even at 50 g l^{-1} of salt, the biosorbent still has high uptake capacity and the dried *R. arrhizus* has been used to efficiently remove chromium(VI) from aqueous solution with higher salt concentration.

The decrease in biosorption ability of microorganism with increasing salt concentration may be a result of biosorption mechanisms. Salt concentration could markedly influence the biosorption presumably due to the competition between chloride ions (present in salt used to change the ionic strength of solution) and chromium(VI) species for the same binding sites on the biosorbent surface. Another reason is that ionic strength increases, the activity of biosorbent (active sites) and metal activity decreases, so the adsorptive capacity of biosorbent decreases. According to surface chemistry theory, when two phases, e.g., fungal and metal species in aqueous solution, are in contact, they are bound to be surrounded by an electrical double layer owing to electrostatic interaction. If the adsorption mechanism is significantly by the electrostatic attraction, variations in background electrolyte concentration would remarkably influence the sorbent–sorbate interactions involving the electrostatic interaction and adsorption decreases with increase in ionic strength. Some inorganic anions existing in the solution such as chloride may also form complexes with metal ions, and therefore, affect the adsorption process adversely [26,37,40].

4.4. Biosorption kinetics of chromium(VI) in the absence and in the presence of increasing concentrations of salt

It must be remembered that the two important physicochemical aspects for parameter evaluation of the sorption process as a unit operation are the kinetics and the equilibria. Kinetics of sorption describing the solute uptake rate which in turn governs the residence time of sorption reaction is one of the important characteristics defining the efficiency of sorption. Hence,

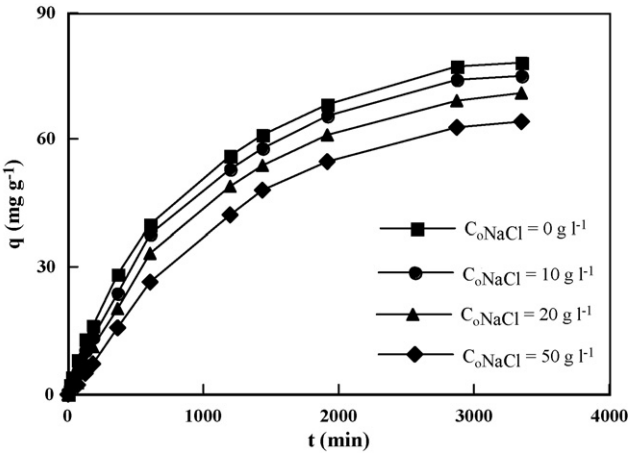

Fig. 2. Biosorption curves of chromium(VI) in the absence and in the presence of increasing concentrations of salt ($C_{0Cr(VI)}$: 100 mg l^{-1}; *X*: 1.0 g l^{-1}; temperature: 25 °C; agitation rate: 100 rpm).

the kinetics of chromium(VI) removal both individually and in salt containing medium has been carried out to understand the behavior of the dried *R. arrhizus*. For this purpose, biosorption capacity (q) was plotted as a function of time for 100 mg l^{-1} initial chromium(VI) concentration at varying salt concentrations (Fig. 2). The time and salt concentration dependent, similar shaped biosorption curves were obtained. The adsorption of chromium(VI) increased with increasing contact time at all salt concentrations studied and decreased with increasing salt concentration. It was observed that chromium(VI) uptake was maintained with a high constant rate for the initial 10–12 h due to an increased number of vacant sites available at the initial stage for biosorption, and thereafter, it proceeded at a slower rate and finally attained saturation. The plots show that the contact time required to reach equilibrium was very long and equilibrium occurred within 60 h and the equilibrium time was independent of salt concentration. Based on these results, the contact time was fixed at 60 h for the rest of the batch experiments to make sure that equilibrium was reached in all cases.

4.5. Application of kinetic models in the absence and in the presence of increasing concentrations of salt

The sorption data were also analysed in terms of pseudo-first-order, pseudo-second-order and saturation type kinetics.

The first-order rate constant ($k_{1,ad}$) and q_{eq} values were determined from the plots of linearized form of the pseudo-first-order model (Eq. (6)) at all chromium(VI) and salt concentrations studied for the initial 30 min (data not shown) and are presented in Table 2 along with the corresponding regression coefficients. The first-order rate constants decreased slightly with increasing the initial concentration of chromium(VI) and increased with increasing the salt concentration. As seen from the table, besides very high regression coefficients (>0.995), experimental q_{eq} values agreed very well with q_{eq} values obtained from Lagergren plots. This indicated that pseudo-first-order kinetic model describes the kinetics adequately in the concentration ranges studied.

Table 2
Comparison of the pseudo-first and pseudo-second-order kinetic constants obtained at different initial chromium(VI) concentrations in the absence and in the presence of increasing salt concentrations (initial pH: 2.0; X:1.0 g l^{-1}; temperature: 25 °C; agitation rate: 100 rpm)

Salt concentration (g l^{-1})	C_0 (mg l^{-1})	$q_{eq,exp}$ (mg g^{-1})	First-order kinetic model			Second-order kinetic model		
			$k_{1,ad}$ ($\times 10^3$ mg l^{-1})	$q_{eq,cal}$ (mg g^{-1})	R^2	$k_{2,ad}$ ($\times 10^4$ g mg^{-1} min^{-1})	$q_{eq,cal}$ (mg g^{-1})	R^2
0	25.2	23.2	6.91	22.5	0.967	6.25	24.3	0.997
	50.8	46.0	4.38	44.7	0.940	5.90	48.3	0.998
	100.3	78.0	4.15	75.9	0.971	5.18	80.4	1.000
	149.8	95.2	2.99	93.2	0.983	4.47	96.0	1.000
	201.1	105.2	2.53	104.0	0.966	3.76	104.2	1.000
	252.3	108.9	1.38	113.2	0.984	3.05	110.7	1.000
10	25.0	22.4	7.71	19.7	0.914	7.24	22.0	1.000
	51.6	44.2	5.54	39.0	0.965	6.21	44.7	1.000
	100.2	75.0	4.38	72.5	0.954	5.16	78.0	1.000
	150.2	92.0	3.22	87.0	0.993	4.51	93.6	1.000
	200.6	101.4	2.78	101.0	0.939	3.46	100.2	1.000
	251.5	104.8	1.57	107.2	0.971	3.11	102.7	0.998
20	25.0	20.5	8.13	19.8	0.922	7.48	21.9	1.000
	50.6	40.9	6.12	38.0	0.940	6.54	38.5	1.000
	99.2	70.8	4.51	71.0	0.954	5.47	67.0	1.000
	151.0	87.0	3.59	93.2	0.970	4.48	86.4	1.000
	201.1	95.0	2.97	97.0	0.920	3.15	93.4	0.993
	249.6	99.2	1.63	104.0	0.967	3.24	96.0	0.999
50	25.5	18.4	8.29	20.5	0.920	7.72	18.7	1.000
	50.5	34.8	6.23	30.5	0.940	6.40	34.5	1.000
	101.2	64.0	4.69	63.1	0.930	5.58	63.5	1.000
	150.5	79.1	3.67	85.4	0.970	4.42	81.9	1.000
	199.6	85.9	3.05	91.0	0.980	2.89	90.4	1.000
	250.4	90.0	1.78	109.0	0.951	3.18	93.1	1.000

Using Eq. (8), t/q was plotted against t and second-order adsorption rate constants ($k_{2,ad}$) and equilibrium uptake values (q_{eq}) were determined from the slope and intercept of the plots (data not shown). The values of the parameters $k_{2,ad}$ and q_{eq} and of corresponding correlation coefficients are also presented in Table 2. The results indicated that second-order rate constants were also affected by both the initial chromium(VI) and salt concentrations and diminished with increasing chromium(VI) concentration. The correlation coefficients obtained greater than 0.993 and the adequate fitting of theoretical and experimental q_{eq} values for all chromium(VI)–salt combinations suggest the applicability of second-order kinetic model based on the assumption that the rate limiting step may be the chemisorption in explaining the kinetics of biosorption for the entire sorption period.

The saturation type kinetic model was also applied to the experimental data at changing salt concentrations to describe the batch biosorption kinetics over the whole concentration range of chromium(VI) studied. The values of k_{ad} and $k_{o,ad}$ were determined from the plots of linearized form of the saturation type kinetic model at all salt concentrations (data not shown). The plots indicated that such saturation type kinetic expression is also so valid to the present system ($R^2 > 0.997$ for all temperatures). Table 3 shows that both the biosorption rate constants were affected with increase in salt concentration and decreased notably with increasing salt concentration.

These suggest that the biosorption of chromium(VI) at changing salt concentrations may be best described by the pseudo-second-order and pseudo-first-order kinetics, following saturation type kinetic model, with fairly high correlation coefficients.

As the saturation type kinetic model described the batch biosorption kinetics over the whole concentration range of chromium(VI) studied and the kinetic parameters of this model also changed due to the level of salt, a regression method was used to obtain a functional relationship between kinetic constants of saturation type kinetic model and salt concentration in order to predict the kinetic constants of chromium(VI) biosorption in an undefined salted aqueous solution. The expressions of kinetic constants as a function of initial salt concentration were presented in Table 4. As expressed in the table, the sat-

Table 3
Effect of salt concentration on the saturation type kinetic constants (initial pH: 2.0; X: 1.0 g l^{-1}; temperature: 25 °C; agitation rate: 100 rpm)

Salt concentration (g l^{-1})	k_{ad} ($\times 10^2$ l g^{-1} min^{-1})	k_{0ad} ($\times 10^3$ l mg^{-1})	R^2
0	7.04	4.51	0.993
10	6.23	3.90	0.995
20	5.91	3.58	0.995
50	5.33	3.16	0.996

Table 4
Functional relationship between the saturation type kinetic constants and salt concentration

$k_{ad} \times 10^2 = 0.001C^2_{0NaCl} - 0.074C_{0NaCl} + 7.00$	$R^2 = 0.988$
$k_{0ad} \times 10^3 = 0.001C^2_{0NaCl} - 0.061C_{0NaCl} + 4.49$	$R^2 = 0.996$

uration type kinetic parameters of chromium(VI) biosorption decreased following a second-order polynomial function of salt concentration with very high linear regression coefficients of determination.

4.6. Application of equilibrium models in the absence and in the presence of increasing concentrations of salt

The non-linearized adsorption isotherms of chromium(VI) in the absence and in the presence of increasing concentrations of salt is shown in Fig. 3. Equilibrium chromium(VI) uptake increased with increasing initial chromium(VI) concentration up to 250 mg l^{-1}. The curvilinear relationship between the amount of chromium(VI) adsorbed per unit weight of biomass and the residual chromium(VI) concentration at equilibrium suggests that saturation of cell-binding sites occurred at the higher concentrations of this metal ion. The equilibrium uptake of chromium(VI) decreased regularly with increasing salt concentration. The inhibitory effect of salt on the equilibrium chromium(VI) uptake was dominant at higher salt concentrations.

For the investigation of salt effect on chromium(VI) biosorption, the Langmuir, Freundlich, Redlich–Peterson and Langmuir–Freundlich equations were applied to the equilibrium data obtained from single chromium(VI) and chromium(VI)–salt biosorption systems. The corresponding Langmuir, Freundlich, Redlich–Peterson and Langmuir–Freundlich (Sips) parameters at different salt levels obtained by nonlinear regression analysis were listed in Table 5 along with the average percentage errors and linear regression coefficients. The values of average percentage errors and linear regression coefficients were the criteria for the selection of the most suitable isotherm model. The average

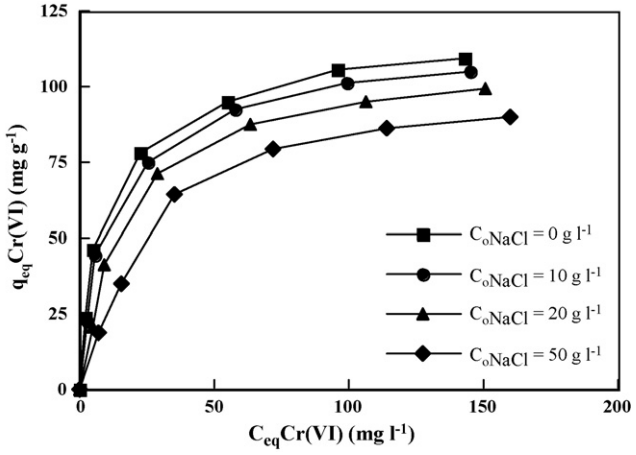

Fig. 3. Non-linearized adsorption isotherms of chromium(VI) in the absence and in the presence of increasing salt concentrations.

Table 5
Effect of salt concentration on the Freundlich, Langmuir, Redlich–Peterson and Langmuir–Freundlich adsorption constants of chromium(VI) biosorption (initial pH: 2.0; X: 1.0 g l^{-1}; temperature: 25 °C; agitation rate: 100 rpm)

Salt concentration (g l^{-1})	Freundlich model			
	K_F [(mg g^{-1}) (mg l^{-1})$^{-1/n}$]	n	ε (%)	R^2
0	22.67	2.91	13.5	0.983
10	19.38	2.72	14.0	0.981
20	13.69	2.35	12.7	0.987
50	8.59	2.02	8.3	0.990

Salt concentration (g l^{-1})	Langmuir model			
	Q^o (mg g^{-1})	b (l mg^{-1})	ε (%)	R^2
0	114.9	0.119	4.8	0.995
10	112.4	0.090	4.8	0.995
20	109.9	0.059	3.8	0.998
50	107.5	0.034	6.4	0.993

Salt concentration (g l^{-1})	Redlich–Peterson model				
	a_{RP} [(l $mg^{-1})^{\beta}$]	K_{RP} (l g^{-1})	β	ε (%)	R^2
0	0.154	16.45	0.994	3.4	0.997
10	0.060	6.94	0.999	6.7	0.993
20	0.046	5.29	0.999	1.7	0.999
50	0.040	4.24	1.000	2.7	0.998

Salt concentration (g l^{-1})	Langmuir–Freundlich model				
A (l^m mg^{1-m} g^{-1})	B (l $mg^{-1})^m$		m	ε (%)	R^2
0	18.12	0.152	1.014	0.8	1.000
10	6.45	0.057	1.027	1.3	0.999
20	4.92	0.045	1.042	0.2	1.000
50	4.68	0.040	0.093	2.4	0.998

percentage error between the experimental and predicted values are calculated using Eq. (12). In Eq. (12), the subscripts 'exp' and 'calc' show the experimental and calculated values and N the number of measurements.

$$\varepsilon\,\% = \frac{\sum_{i=1}^{N}(q_{eq,i,exp} - q_{eq,i,calc})/q_{eq,i,exp}}{N} \times 100 \qquad (12)$$

On the basis of average percentage errors and linear regression coefficients in Table 5, the three-parameter Langmuir–Freundlich (Sips) model best described the chromium(VI) sorption isotherm data compared to other models examined. The model fitted the experimental data with a lower average percentage error in the range 0.8–2.4 and a higher linear regression coefficient in the range 0.998–1.000 suggesting that the monolayer, homogeneous sorption in single- as well as salt added binary-systems. The relatively lower percentage errors also indicated that both the two-parameter Langmuir and three-parameter Redlich–Peterson models were also very suitable for describing the biosorption equilibrium of chromium(VI) by the fungal cells in all cases. The other two-parameter model of Freundlich exhibited a poor fit to the biosorption data of chromium(VI) with an average percentage error more than 8.3.

Adsorption model constants the values of which express the surface properties and affinity of the biosorbent can be used to compare the adsorptive capacity of dried *R. arrhizus* for chromium(VI) due to the salt level.

The estimated coefficients of Freundlich model (K_F and n) for chromium(VI) sorption from single chromium(VI) and chromium(VI)–salt containing solutions are listed in Table 5. The n is an empirical parameter that varies with the degree of heterogeneity and is related to the distribution of bonded ions on the sorbent surface. In general, $n > 1$ illustrates that adsorbate is favorably adsorbed on an adsorbent, corresponds to a normal an L-type Langmuir isotherm, and the higher the n value the stronger the adsorption intensity. In particular, the value of n, which is significantly higher than unity, indicated that chromium(VI) ions are favorably adsorbed under all the experimental conditions examined. The values of n at different salt concentrations also indicated that the chromium(VI) biosorption intensity was contrarily affected by salt added into biosorption medium. The constant K_F, related to biosorption capacity, can be defined as a sorption coefficient which represents the quantity of adsorbed metal ions for a unit equilibrium concentration (i.e. $C_{eq} = 1$). From the table, the magnitude of K_F showed a relatively easy uptake of chromium(VI) ions from aqueous solution with high adsorptive capacity of biomass for chromium(VI) in both single and binary systems. The co-existence of salt at its any initial concentration reduced K_F constant significantly. The highest K_F value was 22.67 in the absence of salt and the value of K_F decreased to 8.59 with the addition of 50 g l^{-1} salt which was consistent with the experimental observation.

Table 5 also indicates the effect of salt added at different levels on the Langmuir constants (Q^o and b). While the Freundlich model does not describe the saturation behavior of the biosorbent, Q^o represents the monolayer saturation at equilibrium or the total capacity of the adsorbent for chromium(VI). As seen from Table 5, dried *R. arrhizus* exhibited the maximum biosorption capacity (Q^o) for single chromium(VI) biosorption. The addition of salt decreased the Q^o value of chromium(VI) biosorption insignificantly. The presence of 50 g l^{-1} salt reduced the maximum chromium(VI) uptake capacity of biomass from 114.9 to 107.5 mg g^{-1} compared to the monometal conditions. A high value of the other Langmuir parameter, b, indicates a steep desirable beginning of the isotherm which reflects the high affinity of the biosorbent for the sorbate. Its value is the reciprocal of the chromium(VI) concentration at which half of the saturation of the biosorbent is attained. The highest b value obtained for monometal conditions also decreased with the addition of salt indicating its negative effect on chromium(VI) biosorption.

Related biosorption parameters were also calculated according to the three-parameter isotherm of Redlich–Peterson using non-linear regression method for chromium(VI) biosorption at different salt levels and are tabulated in Table 5. Redlich–Peterson constant K_{RP} indicated that the adsorption capacity of biosorbent also diminished with increasing salt concentration. It is noted that β normally lies between 0 and 1, indicating favorable biosorption. The value of β is equal to 1.0 for 50 g l^{-1} salt containing medium and tends to unity for other salt concentrations studies, that is the isotherms approach the Langmuir form.

The corresponding Langmuir–Freundlich parameters of A, B and m for different salt concentrations along with percentage errors are also given in Table 5. Langmuir–Freundlich constant A indicated that the biosorption capacity and affinity of biosorbent to chromium(VI) ions also decreased with salt addition. The value of m, an indicator of heterogeneity index, calculated as about 1.0 for all levels of salt showed that the chromium(VI) sorption data obtained in this study is more of Langmuir form rather than that of Freundlich, which was also confirmed in Table 5, and thus, the fungus has a homogeneous surface.

The results showed that three parameter models represented the biosorption isotherm data much more better than two parameter models for all cases with low percentage error values. Although, the equilibrium model constants have different meanings, such as Q^o is the monolayer adsorption capacity while K_F is the relative adsorption capacity or adsorption power, etc., all of them led to the same conclusion about the correlation of the experimental data: as indicated in Table 5, the adsorption capacity of biomass for chromium(VI) decreased with increasing salt concentration.

Again all these parameters changed with respect to the level of salt could be used to predict the adsorption behavior of chromium(VI) in an aqueous solution at a definite salt concentration. When isotherm constants were plotted against the salt concentration, it was seen that the functional relationship between isotherm constants and salt concentration are not linear for the entire range of salt concentration (data not shown). Regressing the corresponding nonlinear plots, isotherm parameters of each model were expressed as a function of salt concentration and presented in Table 6. The Freundlich and Langmuir parameters decreased following a second-order polynomial function of salt concentration with high linear regression coefficients of determination, as expressed in the table. An exponential relationship between the Redlich–Peterson parameters of a_{RP} and K_{RP} of chromium(VI) and salt concentration was obtained (β is assumed as 1 for all cases) and also submitted in the table with the correlation coefficients of 0.935 and 0.981, respectively. The relationship between the Langmuir–Freundlich model constants of A and B of

Table 6
Functional relationships between the Freundlich, Langmuir, Redlich–Peterson and Langmuir–Freundlich model constants and salt concentration

$K_F = 0.005C_{0NaCl}^2 - 0.53C_{0NaCl} + 23.107$	$R^2 = 0.983$
$n = 0.0003C_{0NaCl}^2 - 0.0326C_{0NaCl} + 2.94$	$R^2 = 0.980$
$Q^O = 0.003C_{0NaCl}^2 - 0.31C_{0NaCl} + 115.0$	$R^2 = 0.998$
$b = 0.00004C_{0NaCl}^2 - 0.0038C_{0NaCl} + 0.12$	$R^2 = 0.996$
$a_{RP} = 0.102C_{0NaCl}^{0.247}$	$R^2 = 0.935$
$K_{RP} = 13.63C_{0NaCl}^{0.303}$	$R^2 = 0.981$
$A = 9.33C_{0NaCl}^{0.193}$	$R^2 = 0.933$
$B = 0.093C_{0NaCl}^{0.218}$	$R^2 = 0.983$
$m = 0.002C_{0NaCl} + 1.01$	$R^2 = 0.997$

chromium(VI) and salt concentration also followed an exponential equation with a high linear regression coefficient, while other Langmuir–Freundlich parameter *m* was varied linearly with salt concentration.

5. Conclusion

Biosorption characteristics of dried *R. arrhizus* for the removal of chromium(VI) ions from saline waters were examined as a function of pH, initial metal ion and salt concentrations. Biosorption at lower pH increased the efficiency of biosorption process, initial chromium(VI) concentration also had an increasing effect on biosorption capacity up to 250 mg l^{-1} and increasing the salinity up to 50 g l^{-1} led to a significant decrease in biosorption yield.

The Freundlich, Langmuir, Redlich–Peterson and Langmuir–Freundlich (Sips), the two and three parameter adsorption models were used for the mathematical description of the biosorption equilibrium of chromium(VI) ions to dried *R. arrhizus* both singly and in salt containing media and all the isotherm constants were evaluated to compare the biosorption properties of fungus. It was seen that the adsorption equilibrium data fitted very well to Langmuir–Freundlich (Sips) model at all salt concentrations studied. The suitability of the pseudo-first-order, pseudo-second-order and saturation type kinetic models for the sorption of chromium(VI) ions onto dried *R. arrhizus* for all situations was also discussed assuming no effect of mass transfer on the biosorption rate. The results calculated due to all kinetic models were also found to be in good agreement with the experimental results. Finally, all equilibrium and saturation type kinetic parameters were expressed as a function of salt concentration in that the equilibrium and kinetics of chromium(VI) biosorption should be defined in a aqueous solution containing any salt concentration.

The results obtained showed that dried *R. arrhizus* is a good adsorbing medium for single chromium(VI) biosorption and have high adsorption yield for the treatment of wastewaters containing chromium(VI) ions only. The comparison of sorption capacity of dried *R. arrhizus* used in this study ($Q^o = 114.9$ mg g^{-1}) with some of those obtained in the literature ($Q^o = 96.3$ mg g^{-1} for low cost activated carbon [30]; $Q^o = 5.9$ mg g^{-1} for *Tamarindus indica* seeds [26]; $Q^o = 15.9$ mg g^{-1} for pretreated *N. carassa* fungal biomass [23]; $Q^o = 285.7$ mg g^{-1} for rice bran [29]; $Q^o = 124.5$ mg g^{-1} for *A. caviae* [18]; $Q^o = 45.5$ and 58.3 mg g^{-1} for *Dunaliella* species [37]; $Q^o = 53.8$ mg g^{-1} for Pantoea sp. TEM18 [17]; $Q^o = 8.4$ mg g^{-1} for *R. arrhizus* [6]; $Q^o = 32.6$ mg g^{-1} for *S. cerevisiae* [16]; $Q^o = 79.3$ mg g^{-1} for *C. vulgaris* [6]; $Q^o = 33.1.0$ mg g^{-1} for *L. sajor-caju* mycelia [19]) showed that this microorganism is more effective for this purpose. Although, the salt addition (increasing ionic strength) affected the adsorption yield and equilibrium uptake adversely, the fungus still have a considerable potential for the uptake of chromium(VI) from saline waters due to salt level. This work can provide a useful data for bioremoval of chromium(VI) ions from salt-bearing wastewaters by fungus.

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