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Adsorption isotherm for uranyl biosorption by *Saccharomyces cerevisiae* biomass

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Abstract Biosorption of uranyl ions from aqueous solution by *Saccharomyces cerevisiae* was studied in a batch system. The influence of contact time, initial pH, temperature and initial concentration was investigated. The optimal conditions were found to be 3.5 h of contact time and pH = 4.5. Temperature had no significant effect on adsorption. The uptake of uranyl ions was relatively fast and 85 % of the sorption was completed within 10 min. The experimental data were well fitted with Langmuir isotherm model and pseudo-second order kinetic model. According to this kinetic model, the sorption capacity and the rate constant were 0.455 mmol UO_2^{2+}/g dry biomass and 1.89 g $mmol^{-1}$ min^{-1}, respectively. The Langmuir isotherm indicated high affinity and capacity of the adsorbent for uranyl biosorption with the maximum loading of 0.477 mmol UO_2^{2+}/g dry weight.

Keywords Biosorption · *Saccharomyces cerevisiae* · Uranyl ions · Isotherms

Introduction

Pollution of the environment with toxic heavy metals is spreading throughout the world along with industrial progress. The commonly used treatment methods to remove heavy metals from wastewaters include chemical precipitation, ion exchange, reverse osmosis and membrane processes. However, these methods are not effective when the heavy metal concentrations in the wastewater are low [1]. The technologies are also expensive when a very low concentration of heavy metals in the treated water is required [2]. Biosorption, the uptake of heavy metals by non-living biomass, has gained increased credibility during recent years, as it offers a technically feasible and economical approach. Several biological materials have been investigated for heavy metal removal includes bacteria, yeasts, algae and fungi [3–7].

Uranium is one of the most seriously threatening heavy metals. It is naturally present in all environmental media at low concentrations [8]. Uranium species are both toxic and radiotoxic for humans and the contamination of this hazardous metal poses a threat in some surface and groundwater. So for this reason the removal of uranium from water and wastewater streams using natural and synthetic sorbents is a subject of continuously increasing importance [9–11].

In this work, the sorption of uranyl by *Saccharomyces cerevisiae* from aqueous solutions was investigated in a batch technique. The effect of pH, temperature, contact time and initial concentration on uranyl adsorption was studied. Two important isotherm models (Langmuir and Freundlich) and the pseudo-second-order kinetic model were applied to describe the uranyl adsorption.

Experimental

The strain of *S. cerevisiae* PTCC 5052 was obtained from the Persian Type Culture Collection, Tehran, Iran. The culture medium contained 120 g L^{-1} glucose (D(+)-glucose monohydrate, Carl Roth), 4 g L^{-1} yeast extract

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(Merck), 1 g L^{-1} NH_4Cl (Scharlau), 5 g L^{-1} $MgSO_4 \cdot 7H_2O$ (Carl Roth) and 1 g L^{-1} KH_2PO_4 (Scharlau) [9]. Yeast *S. cerevisiae* was grown in 200 mL sterile liquid media for 24 h on a rotary shaker at 30 °C. The growth temperature affects the adsorption capacity of the sorbent [12]. The biomass was harvested by centrifugation and washed twice with sterile distilled water and then dried in an oven at 60 °C for 24 h. The dry biomass was ground and stored for sorption studies.

Uranyl solutions were prepared by diluting 1 mM stock solution of UO_2^{2+} prepared by dissolving 0.251 g of $UO_2(NO_3)_2 \cdot 6H_2O$ (Merck) in 500 mL of distilled water. The initial pH of each solution was adjusted to the required value with 1 N HNO_3 or 1 N NaOH.

All biosorption experiments were carried out in a batch system, using 250 mL Erlenmeyer flasks. To each flask the same amount of biosorbent (0.02 g) was added and was mixed with 50 mL uranyl solution. The flasks were agitated on a rotary shaker at 200 rpm. After shaking, the biomass was separated by centrifugation and the uranyl concentration of the supernatant solution was determined using an Optima 7300 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). In each set of experiment, samples without biomass were used as controls.

The biosorption equilibrium uptake (q, mmol cation/g biomass dry wt.) for each sample was calculated by the following equation:

$$q = \frac{V(C_0 - C_e)}{M} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of uranyl ion in solution (mM) respectively, V is the volume of the solution (L), and M is the weight of the dry biosorbent used (g) [13].

Kinetic study of biosorption

In order to determine a suitable contact time for the sorption equilibrium experiments, the sorption studies were carried out over a time interval (0–390 min). Uranyl sorption kinetics was studied at 25 °C and pH = 4.5. The initial concentration of UO_2^{2+} in the solution was 0.2 mM.

Effect of solution pH

The optimal pH for uranyl removal was determined by measuring of uranyl uptake from 0.02 mM solutions over a range of pH values from 3.5 to 5.5, at 25 °C with 3.5 h of contact time.

Effect of temperature

In order to examine the effect of temperature on the uranyl biosorptive uptake, the experimental sets were tested at four different temperatures of 20, 25, 30 and 40 °C.

Effect of initial uranyl concentration

Experiments were carried out at different initial UO_2^{2+} concentrations ranging from 0.02 to 1 mM at pH = 4.5, T = 25 °C with 3.5 h of contact time.

Results and discussion

The mechanism of biosorption is complex, mainly ion exchange, chelation, adsorption by physical forces, entrapment in inter and intrafibrillar capillaries and spaces of the structural polysaccharide network as a result of the concentration gradient and diffusion through cell walls and membranes [14].

The mechanism of biosorption was based on the interactions between metal ions and the functional groups on the cell wall surface of the biomass. It was known that *S. cerevisiae* contains reasonable amount of protein and amino acids like histidine, which serve as a matrix of –COOH and $–NH_2$ groups, which in turn take part in binding of metal ion. Carboxyl groups, associated with cell wall surface components, are considered to be among the main groups of cell membrane responsible for metal binding. Hence it can be concluded that non-living *S. cerevisiae* biomass can be used as an effective biosorbent for uranyl removal [12, 15].

Figure 1, shows the adsorption capacity of the adsorbent for UO_2^{2+} ions by *S. cerevisiae* versus contact time. The studied biomass exhibited a rapid cation uptake, 85 % of equilibrium was reached within 10 min and the process saturates after 3.5 h. The rapid cation uptake has been suggested as being essential for any good biosorbent as it allows short solution-sorbent contact time.

In order to modeling the sorption rate of uranyl ion, the pseudo-second order rate equation was applied. Assuming the sorption capacity of uranyl by the biomass is proportional to the number of active sites occupied on the sorbent, the pseudo-second order rate equation is given by:

$$\frac{dq_t}{dt} = k(q_{eq} - q_t)^2 \quad (2)$$

where q_{eq} and q_t are the amount of metal sorbed per unit weight of the sorbent at equilibrium and at any time t, respectively (mmol g^{-1}) and k is the rate constant of pseudo-second order sorption (g $mmol^{-1}$ min^{-1}).

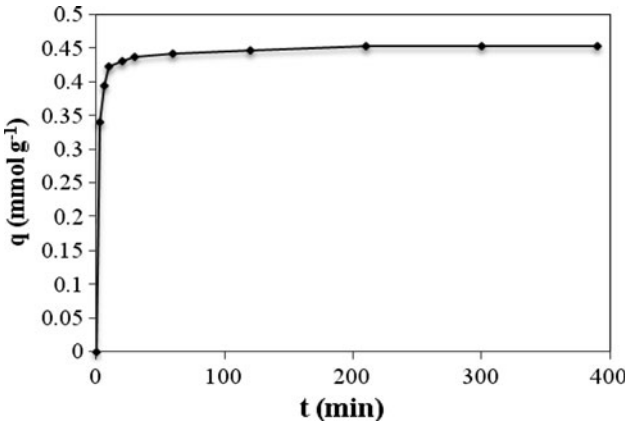

Fig. 1 Biosorption rate of UO_2^{2+} at 0.2 mM UO_2^{2+} solution (pH = 4.5, $T = 25$ °C, sorbent concentration = 0.4 g L^{-1} and agitation rate = 200 rpm)

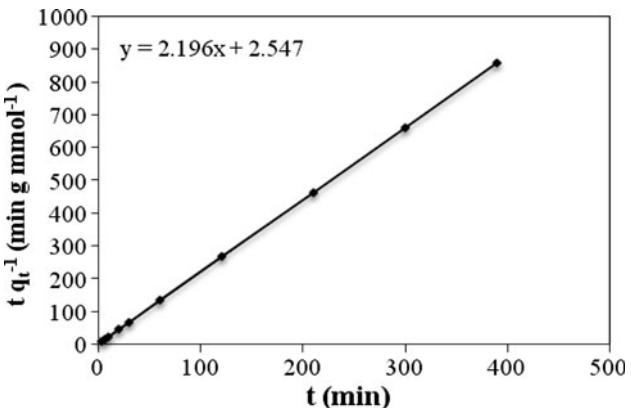

Fig. 2 Pseudo-second order sorption kinetics at 0.2 mM UO_2^{2+} solution (pH = 4.5, $T = 25$ °C, sorbent concentration = 0.4 g L^{-1} and agitation rate = 200 rpm)

Integrating the Eq. 2 for the boundary conditions for $t = 0$, $q_t = 0$ gives;

$$\frac{t}{q_t} = \frac{1}{q_{eq}} t + \frac{1}{q_{eq}^2 k} \quad (3)$$

The intercept of the linearized pseudo-second order rate equation gives the second order rate constant, k [16].

The linearized form of the pseudo-second order model for contact times of 390 min is given in Fig. 2. The correlation coefficient for the linear plot of $t/tq.q$ versus time was 1. The values of q_{eq} and k are tabulated in Table 1, the theoretical value of q_{eq} is in good agreement with the experimental data. Therefore, the pseudo-second order kinetic model provided a good correlation for the biosorption of uranyl ions.

pH is one of the most important physical parameters that influence the biosorption process [17]. In the present investigation, biosorption of uranyl ions was studied in

Table 1 The Pseudo-second order rate constants for the sorption of UO_2^{2+}

Sorbent	q_{eq} (mmol g^{-1})	K (g $mmol^{-1}$ min^{-1})	R^2	$q_{eq\text{-}exp}$ (mmol g^{-1})
Dry biomass	0.455	1.89	>0.999	0.454

solutions with pH ranging from 3.5 to 5.5 at 0.2 mM (UO_2^{2+}) at 25 °C. Figure 3, represents the effect of initial pH on the removal of uranyl ions by *S. cerevisiae* biomass. It is evident from the figure that the sorption rate increased with increase in pH value up to 4.5 and then declined with further increase in pH. This implies that uranyl removal is pH dependant and is maximal at pH 4.5. Studies on uranium sorption by different kinds of adsorbents, for example U(VI) sorption on ACSD,[1] U(VI) removal by CNAB[2] and olive cake showed the similar adsorption behavior in the defined pH range. The difference between optimal pH was related to the difference of adsorbents negative surface charges [18–20]. for example the optimum pH for the removal of uranium by olive cake was found about pH 7.5. This value is higher than corresponding values given in the literature for uranium adsorption on microorganisms and algae, indicating that, in the case of olive cake, surface groups of weaker acidity (e.g., phenolic groups) play an important role in uranium adsorption on the surface [20].

The pH dependence of metal biosorption can largely be related to type and ionic state of the functional groups present on the biosorbent and the type of metal species present in the solution [17]. Metal sequestering by different parts of the cell can occur via various processes; complexation, chelation, coordination, ion exchange, micro precipitation and reduction. It has been suggested by many researchers that ion exchange is neither the sole nor the main mechanism for metal biosorption [21]. The ion exchange mechanism for uranyl ions binding to the biomass is complicated by the fact that the uranyl cation UO_2^{2+} is hydrolyzed in aqueous solutions within the range of the sorption system pH. Portioning of the hydrolyzed uranyl species depends on the solution pH and on the total uranyl concentration in the solution. In the range of acidic to near neutral pH values, four major hydrolyzed complex ions, UO_2^{2+}, $(UO_2)_2(OH)_2^{2+}$, UO_2OH^+, $(UO_2)_3(OH)_5^+$ and a dissolved solid Schoepite ($4UO_3{\cdot}H_2O$), uranyl hydroxide, exist in the solution. The hydrolysis equilibrium constants are pK = 5.8 for UO_2OH^+, pK = 5.62 for $(UO_2)_2(OH)_2^{2+}$ and pK = 15.63 for $(UO_2)_3(OH)_5^+$ [22]. According to the results obtained by experiment, pH 4.5 seems to be optimal

[1] Alginate coated $CaSO_4.2H_2O$ sepiolite and calcined diatomite earth.

[2] Chitosan coated natural attapulgite beads.

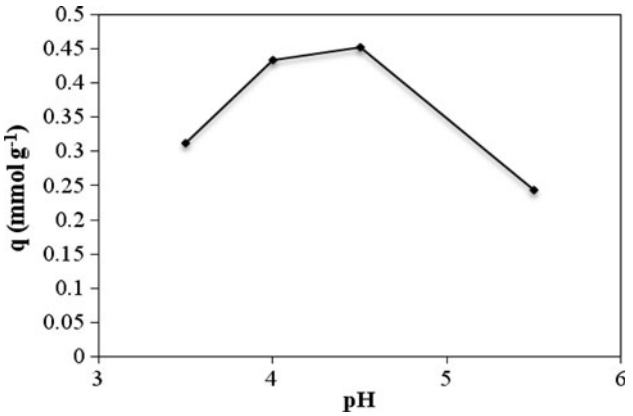

Fig. 3 Effect of pH on UO_2^{2+} biosorption at 0.2 mM UO_2^{2+} (T = 25 °C, sorbent concentration = 0.4 g L^{-1}, 3.5 h of contact, agitation rate = 200 rpm)

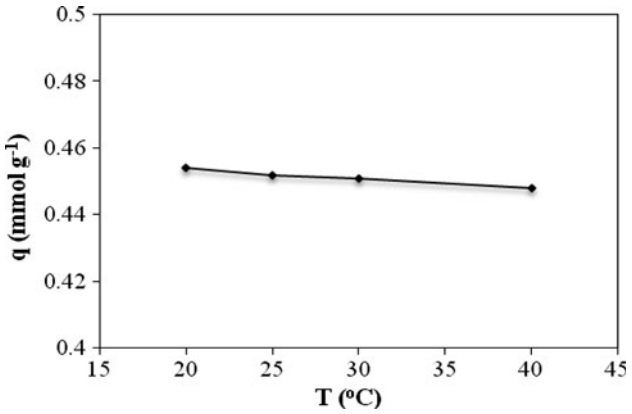

Fig. 4 Effect of temperature on UO_2^{2+} biosorption at 0.2 mM UO_2^{2+} (pH = 4.5, sorbent concentration = 0.4 g L^{-1}, 3.5 h of contact, agitation rate = 200 rpm)

for uranyl biosorption. The dominant species of uranium at the pH 4.5 are UO_2^{2+} and $(UO_2)_2(OH)_2^{2+}$ [9].

The hydrolyzed species can obviously be adsorbed better than the free hydrated ions. They could replace protons on separate binding sites in the biomass through ion exchange process [23].

At low pH values, the cell wall ligands will be closely associated with hydronium ions (H_3O^+), which will restrict uranyl ions access to ligands as a result of repulsive forces; this repulsion becomes stronger with a decrease in pH [24]. In other words, at low pH some binding sites are not available to the divalent UO_2^{2+}. As the pH increases, more ligands will be exposed, i.e. carrying negative charges, with the subsequent attraction of metallic ions with positive charges and adsorption to the cell surface. On the other hand, the non-ion dissolved solid Schoepite starts appearing in the solution when the pH level is high. At too high pH values, the uranium sorption is hindered by the decrease in ion concentration [25].

Figure 4, illustrates the effect of temperature on sorption capacity. This profile indicates that temperature has no significant effect on uranyl sorption capacity. Similar result was also reported for the biosorption of U(VI) onto fungus Aspergillus fumigates [26].

However, temperature increase resulted in a very small q decrease. It is suggested that high temperatures might affect the integrity of the cell membranes and hinder compartmentalization of metal ions, leading to reduced uptake levels [27].

Uranyl ions sorption was studied at initial concentrations ranging from 0.02 to 1.0 mM and equilibrium sorption capacity of the sorbent was calculated. Figure 5, shows the biosorption isotherm at 25 °C. The experimental results showed that the uranyl uptake (q) increases rapidly with the increased equilibrium ion concentration. At low concentrations biosorbent sites take up the available metal

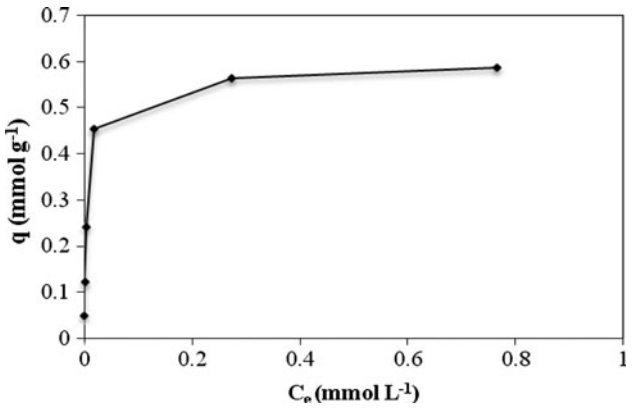

Fig. 5 Isotherm for sorption of UO_2^{2+} at 25 °C (pH = 4.5, sorbent concentration = 0.4 g L^{-1}, 3.5 h of contact, agitation rate = 200 rpm)

ions more quickly. However, when the uranyl ion concentration reaches a certain level, the upward trend of sorption capacity becomes slower. The analysis of the isotherm data is important to develop an equation, which accurately represents the results and could be used for design purposes. In order to investigate the sorption isotherm, two important models were analyzed, the Langmuir, and the Freundlich. The Langmuir sorption isotherm is perhaps the best known of all isotherms describing sorption [28]. This is based on an assumption that the sorption occurs at specific homogeneous sites within the adsorbent. The equation is:

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

where q_e is the amount of uranyl adsorbed (mmol g^{-1}), C_e is the equilibrium concentration of uranyl in solution (mM), $q_{\max}$ is the monolayer sorption capacity (mmol g^{-1}) and b is the constant related to the free energy of sorption (mM^{-1}).

The constants q_{max} and b are the characteristics of the Langmuir equation and can be determined from a linearized form of Eq. 4, represented by:

$$\frac{1}{q_e} = \frac{1}{bq_{max}C_e} + \frac{1}{q_{max}} \quad (5)$$

The Freundlich isotherm [29] is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed by Eq. 6:

$$q_e = KC_e^{1/n} \quad (6)$$

and the Eq. 6 may be linearized by taking logarithms:

$$\log q_e = \frac{1}{n}\log C_e + \log K \quad (7)$$

where K and n are Freundlich sorption isotherm constants, indicative of the extent of the sorption and the degree of nonlinearity between solution concentration and sorption, respectively.

Figures 6 and 7 represent the fitted linear curves for Langmuir and Freundlich models using Eqs. 5 and 7, respectively. The parameters obtained from the two isotherms are given in Table 2. The average percentage errors (Ω %) between the experimental values and the predicted values using the Langmuir and Freundlich models for the entire data set were 14.9 and 19.9 %, respectively. The correlation coefficients (R^2) of Langmuir and Freundlich models were 0.992 and 0.836, respectively. The fitness of the experimental data to the linear form of Langmuir model can be seen in Fig. 6 as it is also evident from $R^2 = 0.992$. The adsorption process was not well fitted to the linear form of Freundlich isotherm (Fig. 7). Moreover, Based on the low correlation coefficient ($R^2 = 0.836$), it could be concluded that the Freundlich model cannot be used to describe UO_2^{2+} adsorption by the biosorbent. The high correlation coefficient obtained from Langmuir model indicates that high affinity between biosorbent surface and uranyl ions plays the major role in the adsorption mechanism and monolayer binding of UO_2^{2+} happens on to the adsorbent homogenous surface.

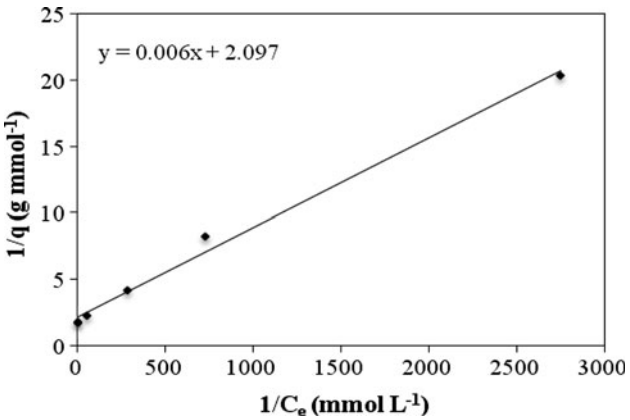

Fig. 6 Langmuir plot for sorption of uranyl ions

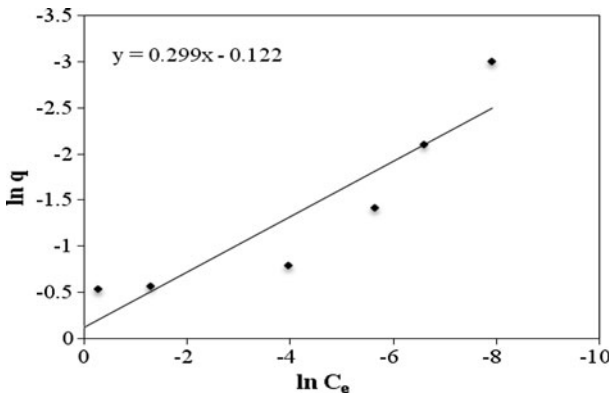

Fig. 7 Freundlich plot for sorption of uranyl ions

Table 2 Freundlich and Langmuir constants for biosorption of UO_2^{2+} at 25 °C (pH = 4.5, sorbent concentration = 0.4 g L^{-1}, 3.5 h of contact, agitation rate = 200 rpm)

Langmuir isotherm			Freundlich isotherm		
q_{max} (mmol g^{-1})	b (mM^{-1})	R^2	K	n	R^2
0.477	350	0.992	0.885	3.34	0.836

Conclusions

Dry biomass of *S. cerevisiae* is capable of removing uranyl ions from aqueous solution especially in very dilute solutions. The batch sorption process is found to be depended on pH, contact time and initial uranyl concentration. The optimum biosorption was seen at pH = 4.5 and 3.5 h of contact time. The temperature had no significant effect on the uranyl sorption. The equilibrium data fitted well to the Langmuir isotherm model with an appropriate R^2 value. This is suggesting monolayer adsorption on a homogeneous surface. Also, the time-dependent UO_2^{2+} sorption data were exceptionally well-described by pseudo-second-order model ($R^2 > 0.999$).

Thus, it can be concluded that the *S. cerevisiae* dry biomass can be used as an excellent sorbent for the removal of uranyl ions.

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