Effects of pH and biomass concentrations in the removal of selenite from acid mine drainage by Aspergillus niger as biosorbent in Sarcheshmeh porphyry copper mine

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ABSTRACT

The biosorption process of a lypophilised cell suspension of Aspergillus niger was studied for selenite (SeO_3^{2-}) removal from acid mine drainage in the Sarcheshmeh porphyry copper mine. The biomass was first characterised by the potentiometric titration, and the major ionic content was evaluated. The experimental data suggest that the biomass cell wall contains two main acidic groups with a total amount of 5 meq/g. Equilibrium biosorption trials of selenite were carried out to investigate the effects of two major experimental factors, the pH and the biomass concentrations. Biosorption trials were also performed for selenite concentrations between 0 and 2 mmol/l at different equilibrium pH between 3 and 6. Selenite biosorption extent was repressed by pH decrease. The effect of the biomass concentrations changes both with the equilibrium pH value and the kind of oxyanion adsorbed. In the case of selenite biosorption at pH above 5, the increase of biomass concentration causes a decrease of maximum specific oxyanion uptake most likely due to cell aggregation phenomenon. Experimental data obtained for selenite was fitted using adsorption models including Langmuir and Freundlich isotherms. Analysis of FTIR showed that selenite was adsorbed on extracellular of biomass.

INTRODUCTION

Acid mine drainage is one of the major environmental problems facing the mining industry and clearly poses a serious unfavourable impacts on receiving waters (Gray, 1998). Acid mine drainage is characterised by low pH, high concentrations of iron, sulphates and variable concentrations of toxic heavy metals. Selenite (SeO_3^{2-}) is considered to be the most important toxic oxyanions which is associated with acid mine drainage. It can also be found in agricultural effluents (Adams *et al.*, 1993).

Selenium even with low concentrations is a toxic metal with 0.001 ppm as an acceptable concentration of selenium for drinking water. Selenite is usually dissolved in water and different forms of selenium such as elemental selenium, selenite and selenate have potential for water pollution (Oremland *et al.*, 1990). It is however, necessary for many strains of microorganisms to consume selenium as a nutrient (Bennet *et al*., 1993). Using microorganisms as biological adsorbents, many oxyanions such as selenite oxyanion can be removed from industrial effluents in particular acid mine drainage, or its concentration reduced to an acceptable level (Schmite & Kavana, 1999). Equilibrium data based on the adsorption isotherms have been used to design adsorption scheme. The adsorption isotherms including the Langmuir and Freundlich models are normally used to describe the equilibrium system between adsorbed oxyanion on fungal cells (q_{eq}) and those oxyanions remained in the solution phase (C_{eq}) at a constant temperature (Aksu, 2001). Kinetics studies of the biosorption processes is also considered in the present study. Studies by Volesky and Holan (1994) revealed that the second order kinetics is appropriate to describe the rate of sorption.

The paper describes the results of an experimental study using the biosorption process of a lypophilised cell suspension of Aspergillus niger for the removal of selenite (SeO_3^{2-}) from acid mine drainage in the Sarcheshmeh porphyry copper mine in Iran.

EXPERIMENTAL SETTINGS

Microbiological growth media

Aspergillus niger stain was extracted from the surface and deeper sediment samples of Shour river in Sarcheshmeh porphyry copper mine. The samples were taken from the discharge of acid mine drainage into the Shour river. The media composition for growth of Aspergillus niger is as follows (all gl^{-1}): glucose, 2.0; yeast extract, 1.0; peptone, 0.5; $FeSO_4$. $7H_2O$, 0.01; $MgSO_4$. 7 H_2O, 0.05; $NaSeSO_4$, 0.1. The pH of the medium was

adjusted to 5.0. Inoculation of Aspergillus niger strain was made in the shake flasks containing growth media. These flasks were air dried and incubated at 25 ^{o}C and spinning at 150 rpm.

Solutions containing selenite and effect of Aspergillus niger strain on biosorption system
After 4 to 5 days of the Aspergillus niger growth, fungal cells were centrifuged at room temperature and agitated at 400 rpm for 5-6 min. The samples were washed twice and then were dried at 60 °C for 24 hr. In order to perform biosorption study, 7.5 g of fungal strain (dried biomass) was mixed in flask containing 100 ml water. The samples were finally homogenised at 8000 rpm for 30 minutes and were placed in the refrigerator. Solutions containing selenite were in the range of 25-200 mgl^{-1}. To perform biosorption experiment, the pH of each solution was first adjusted with HNO_3 solution before mixing with fungal suspension.
Biosorption study in a batch system
Biosorption tests were performed in 250 ml flask containing100 ml selenite solution. The solution system within the available flasks was agitated in a shaker equipment at 150 rpm for 240 min. Five ml samples were used to determined the residual concentrations of selenite in the solution phase at various time intervals (0, 5, 10, 15, 30, 60, 120 and 240 min) prior to mixing the samples the biosorbent and selenite solutions. Finally, an atomic adsorption was used to determine the selenite concentration.

RESULTS AND DISCUSSION
Effect of equilibrium pH on biosorption of selenite
Figure 1 shows the quantity of selenite adsorbed by Aspergillus niger as the solution pH changes at a constant temperature of 20 °C and selenite initial concentration of 100 mgl^{-1}. As Figure 1 shows, biosorption of selenite increased at a steady rate as pH increased up to 5. The biosorption of selenite decreases sharply as pH increases from 5 to 6 and then decreases steadily as the pH increases. The maximum equilibrium sorption of 62.3 mgg^{-1} was obtained at pH of 5.

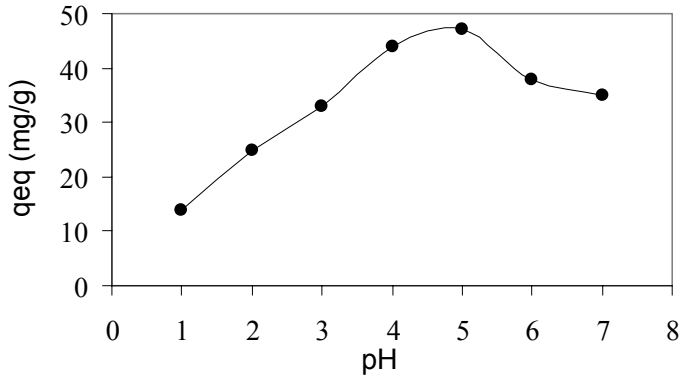

Figure 1. Effect of initial pH on the equilibrium adsorption capacity of Aspergillus niger (temperature, 20 °C; agitating speed, 150 rpm; selenite initial concentration, 100 mgl^{-1}).

Effect of temperature on biosorption of selenite
Figure 2 shows the effect of temperature on biosorption of selenite by Aspergillus niger strain. Selenite adsorption is normally an exothermic reaction and increases as temperature decreases. The optimum temperature for adsorption of oxyanion selenite by Aspergillus niger is 20 °C.

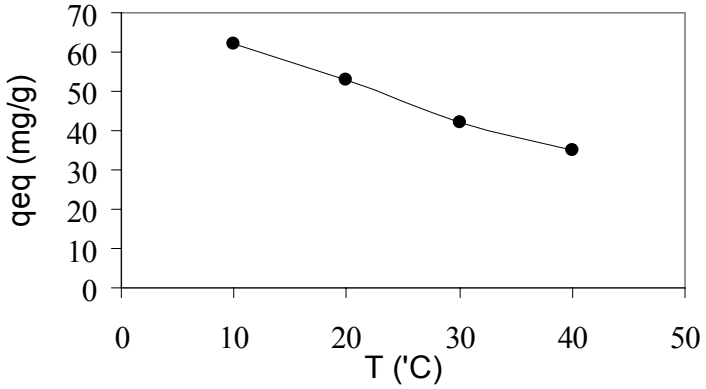

Figure 2. Effect of temperature on the equilibrium adsorption capacity of Aspergillus niger (pH, 4; agitating speed, 150 rpm; selenite initial concentration, 100 mgl^{-1}).

Effect of the initial concentration of oxyanion selenite on biosorption process
The sorption efficiency of selenite by Aspergillus niger is controlled by its initial concentration. Higher values of selenite initial concentrations caused bigger sorption efficiency. Although not shown, the equilibrium sorption capacity of biomass increased when the initial concentration of oxyanion selenite increased up to 200 mgl^{-1}. For a constant selenite initial concentration of 200 mgl^{-1}, when temperature increased from 20 °C to 50 °C, the sorption capacity decreased from 85.3 to 51.2 mgg^{-1}.

Effect of temperature on biosorption kinetics of oxyanion selenite
Figure 3 shows the biosorption kinetics of oxyanion selenite at different temperatures. The initial concentration of oxyanion selenite was maintained at 100 mgl^{-1}. In total, about 62.3 mg selenite per g of dried fungus was adsorbed at temperature of 20 °C. The removal efficiency of selenite decreased from 61 to 34.9 percent when temperature increased from 20 °C to 50 °C.

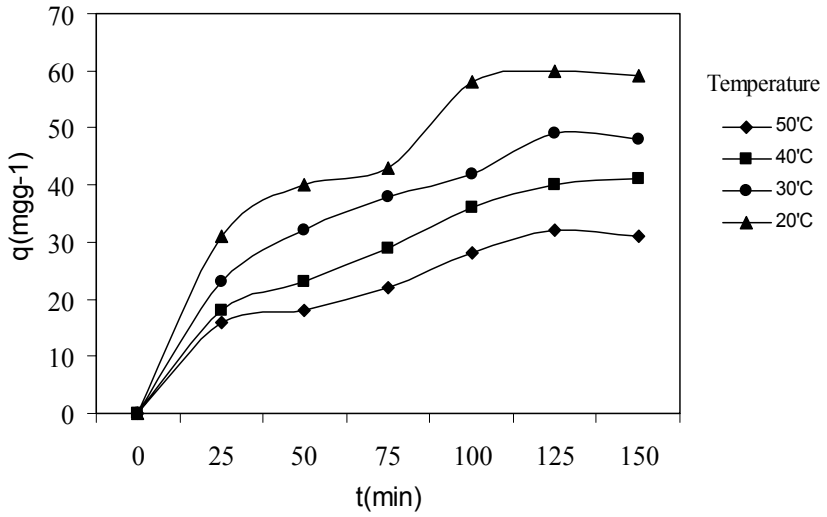

Figure 3. Change in kinetics for biosorption of selenite at different temperatures (pH, 4; agitating speed, 150 rpm; selenite initial concentration, 100 mgl^{-1}).

SORPTION ISOTHERMS
Sorption isotherms are often used to describe interactions between solutes and solid matrix (Nitzsche and Vereecken, 2002). The adsorption isotherms depict the relationships between equilibrium concentrations of adsorbate in the solid phase (S), and in the liquid phase (C) at constant temperature (Gokmen and Serpen, 2002). The distribution of solute between the adsorbent and the solution under equilibrium conditions is important in understanding the capacity of the adsorbent for the solute removal (Mohan *et al.*, 2002). Sorption isotherms are obtained in the laboratory using batch tests. Isotherm results are usually fitted into different isotherm models to find the appropriate model that can be used for design process. Two of the most common non-linear isotherm models are the Langmuir and the Freundlich isotherms (Domenico & Schwartz, 1990; Reddi & Inyang 2000; Nitzsche & Vereecken, 2002):

The Langmuir isotherm model is defined by Equation (1):

$$S = \frac{Q_0 K_L C}{1 + K_L C} \qquad (1)$$

The general form of the Freundlich isotherm model is:

$$S = K_F C^n \qquad (2)$$

where,

S = quantity of mass sorbed on the solid surface (mg/g);

C = equilibrium concentration of the solution (mg/l);

Q_0 = maximum adsorption capacity;

K_L = Langmuir constant;

K_F = partition coefficient indicating adsorption capacity;

n = Freundlich exponent, generally ranging between 0.7 and 1.2.

In this study, the experimental isotherm data set obtained for selenite was fitted using adsorption models including the Langmuir and Freundlich isotherms. The Langmuir and Freundlich isotherm constants were determined for oxyanion selenite at different temperatures of 20, 30, 40 and 50 °C (Table 1). As Table 1 shows, the high values of R-squared (> 95 %) for both isotherms represent that the biosorption process of selenite by Aspergillus niger could be well described by the Langmuir and Freundlich isotherms.

Table 1. Langmuir and Freundlich isotherm constants for oxyanion selenite at different temperature.

Freundlich isotherm constants				Langmuir isotherm constants		
T(°C)	K_F	n	R^2	Q^0(mgg^{-1})	b(1 mg^{-1})	R^2
20	8.23	2.05	0.983	111.1	0.025	0.993
30	5.62	1.92	0.954	90.9	0.022	0.996
40	3.42	1.73	0.989	83.3	0.015	0.994
50	1.87	1.53	0.988	76.9	0.009	0.993

KINETICS MODEL

The study of the adsorption kinetics is the main factor for designing an appropriate adsorption system. In order to consider the kinetics effects, the following Lagergren pseudo-first order equation can be used to determine the rate constants (Mohan *et al.*, 2002).

$$\ell og\,(q_e - q_t) = \ell og\, q_e - \frac{K_{1,\,ad}}{2.303}(t) \qquad (3)$$

where,

q_e = quantity of dye adsorbed at equilibrium (mg/g);

q_t = quantity of dye adsorbed at time *t* (mg/g);

$K_{1,\,ad}$ = pseudo-first order rate constant ($\min^{-1}$);

t = time (min).

In many cases the Equation 3 cannot be used to describe the kinetics of the adsorption process. In such cases, a pseudo-second order expression may be used. This model reduces to:

$$\frac{t}{q_t} = \frac{1}{K_{2,\,ad}\, q_e^2} + \frac{1}{q_e}(t) \qquad (4)$$

where,

$K_{2,\,ad}$ = pseudo-second order rate constant ($g\,mg^{-1}\,\min^{-1}$).

In this study, both first and second order kinetics model were considered for the biosorption process of selenite. Table 2 shows the kinetics constants obtained at different temperatures, selenite initial concentration of 100 mgl^{-1}, an agitating speed of 150 rpm and a pH value of 4. As Table 2 shows, the biosorption kinetics of selenite follows the pseudo-second order rate expression with R-squared value greater than 0.998 at various temperatures.

Table 2. Kinetics parameters for the first and second order models at different temperature.

First order kinetic model				Second order kinetic model			
T (°C)	$k_{1,ad}$ (min^{-1})	q_{eq} (mgg^{-1})	R^2	$k_{2,ad}$*10^3 (g mg^{-1} min^{-1})	q_{eq} (mgg^{-1})	R^2	$q_{eq,exp}$ (mgg^{-1})
20	0.096	56.0	0.985	3.41	62.5	0.999	62.3
30	0.062	42.0	0.948	2.99	54.6	0.999	52.4
40	0.058	36.7	0.995	2.67	44.5	0.999	42.0
50	0.053	30.5	0.964	2.54	37.5	0.998	35.2

ACTIVATION ENERGY FOR BIOSORPTION

The second order kinetics rate constant as a function of temperature using Arinous equation is noted. However, activation energy of -8.0 kJ mol^{-1} was obtained for biosorption system of selenite by Aspergillus niger representing that the biosorption process of selenite by Aspergillus niger is exothermic.

CONCLUSIONS

In this paper, the biosorption process of a lypophilised cell suspension of Aspergillus niger was used to remove selenite (SeO_3^{2-}) from acid mine drainage in the Sarcheshmeh porphyry copper mine in Iran. Equilibrium biosorption trials of selenite were performed to investigate the effects of pH and the biomass concentrations. The results indicate that selenite biosorption capacity was controlled by pH of the solution. Furthermore, at pH above 5, an increase in the biomass concentration decreased the maximum specific oxyanion uptake most likely due to cell aggregation phenomena. The equilibrium and kinetics studies show that the biosorption process could be well described by the Langmuir and Freundlich isotherms. In addition, a pseudo-second order kinetics appear to model the rate of sorption. It was found that lypophilised cell of Aspergillus niger had a biosorption capacity of 111.1 mgg^{-1} for selenite. Moreover, FTIR analysis showed that selenite was adsorbed on extracellular of biomass.

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