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Biosorption of As(III) and As(V) from Aqueous Solution by Lichen (*Xanthoria parietina*) Biomass

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The biosorption of As(III) and As(V) from aqueous solution on lichen (*Xanthoria parietina*) biomass were investigated using different experimental parameters such as solution pH, biomass concentration, contact time, and temperature. The equilibrium data were evaluated by Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models. The biosorption capacity of *X. parietina* for As(III) and As(V) was found to be 63.8 mg/g and 60.3 mg/g. The mean sorption energy values calculated from D–R model indicated that the biosorption of As(III) and As(V) onto *X. parietina* biomass took place by chemical ion-exchange. The thermodynamic parameters showed that the biosorption of As(III) and As(V) ions onto *X. parietina* biomass was feasible, spontaneous, and exothermic in nature. Kinetic examination of the sorption data revealed that the biosorption processes of both As(III) and As(V) followed well the pseudo-second-order kinetics. The arsenic ions were desorbed from *X. parietina* using both 1 M HCl and 1 M HNO_3. The recovery yield of arsenic ions was found to be 80-90% and the biosorbent had good reusability after consecutive seven sorption-desorption cycles.

Keywords arsenic ions; biosorption; equilibrium; kinetics; thermodynamics; *Xanthoria parietina*

INTRODUCTION

Arsenic is one of the contaminants found in the environment which is notoriously toxic to man and other living organisms (1). Arsenic commonly present in water are pH dependant species of the arsenic (H_3AsO_4) and arsenous (H_3AsO_3) acid systems respectively. These anions have acidic characteristics, and the stability and dominance of a specific species depend on the pH of the solution.

The presence of arsenic in natural water is related to the process of leaching from the anthropogenic activities such as gold mining, non-ferrous smelting, petroleum-refining, combustion of fossil fuel in power plants, and the use of arsenical pesticides and herbicides (2–4). The presence of elevated concentrations of arsenic and other heavy metals in groundwater and surface waters is creating serious problems for humans as well as other living organisms (7). Usually arsenic is built up in the body through drinking water and food contaminated with arsenic and causes increased risks of cancer in the skin, lungs, liver, kidney, and bladder. Consumption of arsenic also leads to disturbance of the cardiovascular and nervous system functions and eventually leads to death (8).

The arsenic contamination has been acknowledged as a major public health issue (5). The WHO provisional guideline of 0.01 mg/L has been adopted as the drinking water standard. US EPA published a new 0.01 mg/L standard for arsenic in drinking water, requiring public water supplies to reduce arsenic from 0.05 mg/L (6). Effectively removing arsenic from waters is costly and requires expensive sorbents. Therefore, low-cost materials and methods are needed to remove arsenic from drinking water. Several studies have demonstrated that arsenic removal can be achieved by various techniques and sorbents, namely oxidation/precipitation (9), alum coagulation/precipitation (10), granular ferric hydroxide (11), reverse osmosis and nano filtration (12), ion-exchange resin (13), coagulation-microfiltration (14), etc. Most of these methods suffer from some drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries.

The main advantages of the biosorption technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, short operation time, and no production of secondary compounds which might be toxic (15).

Lichens are composite plants composed of fungi and algae (16) and they are considered as indicators of environmental quality due to their accumulating and retaining ability of a variety of contaminants, particularly heavy metals and radionuclides (17–22). This strong metal binding ability of lichens makes them potential biosorbents for the removal of heavy metals from aqueous solutions (23–29).

Xanthoria parietina (*X. parietina*) is foliose lichen, forming large, rounded patches up to 10 cm across, with wide, round-lipped marginal lobes. It can be found near the shore on rocks or walls. As far as the authors are

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aware, there is no study in the literature on the biosorption of As(III) and As(V) using the lichen biomass, *X. parietina*. In this regard, the objective of the present work is to investigate the biosorption potential of *X. parietina* biomass in the removal of As(III) and As(V) from aqueous solution. Optimum biosorption conditions were determined as a function of pH, biomass concentration, contact time, and temperature. The Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) models were used to describe equilibrium isotherms. The reusability of the biomass was tested for seven consecutive biosorption-desorption cycles. Some kinetic models were applied to clarify the biosorption mechanism of As(III) and As(V) onto *X. parietina* biomass. Thermodynamics parameters were also deduced from the equilibrium data.

EXPERIMENTAL

Biomass Preparation

The lichen biomass (*X. parietina*) sample was collected from the Black Sea coast of Turkey. Samples were washed with deionized water and inactivated by heating in an oven at 80°C for 48 h. The inactivated dried lichen biomass was ground and sieved through different sizes and 180–300 μm fraction was used in all experiments.

Reagents and Equipments

Analytical reagent grade chemicals were used unless otherwise stated in this study. Double deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity) was used for all dilutions. A pH meter (Sartorius pp-15, Germany) was employed for measuring the pH values. Perkin Elmer Analyst 700 model AAS equipped with MHS 15 HGAAS system was used for arsenic determination. A hollow cathode lamp operating at 18 mA was used and a spectral bandwidth of 0.7 nm was selected to isolate the 193.7 nm arsenic line. Arsenic contents of the solutions were determined by hydride generation atomic absorption spectrometry. For this, the samples were pre-reduced from As(V) to As(III) by adding 0.75% KI and 1.25% ascorbic acid (30,31). Then for arsenic quantification, a 1 mL sample was pipetted into a 50 mL volumetric flask where 10 mL of 1.5% HCl was added as diluent. $NaBH_4$ (0.3%) (w/v) in NaOH (0.1%) (w/v) was used as reducing agent. The analytical measurement was based on the peak height. The reading time and the argon flow rate was selected as 20 s and 70 mL/min.

Batch Biosorption Procedure

As(III) standard solution (1000 mg/L) was prepared from As_2O_3 (Merck). As(V) standard solution (1000 mg/L) was prepared from KH_2AsO_4 (Sigma). Biosorption experiments were conducted using the solutions having 25 mg/L of As(III) and 25 mg/L of As(V) with a optimum biomass concentration of 10 g/L.

The solutions (25 mL) including the biomass were shaken for the desired contact time in an electrically thermostatic reciprocating shaker (Selecta multimatic-55, Spain) at 120 rpm. The batch studies were performed at different experimental conditions such as initial metal concentration (25–400 mg/L), contact time (5–90 min), pH 2–10, biomass concentration (0.4–20 g/L), and temperature (20–50°C). The equilibrium time was estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through 0.25 μm filters (Double rings, China). The metal concentration of filtrate was analyzed using HGAAS. Each determination was repeated three times and the results are given as average values. The error bars are indicated wherever necessary. The biosorption percent was calculated as follows:

$$Biosorption\ (\%) = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (1)$$

where C_i and C_f are the initial and final metal ion concentrations, respectively.

Desorption Procedure

The desorption studies of As(III) and As(V) from *X. parietina* was carried out using 1 M HNO_3 and 1 M HCl. After determination of metal contents of the final solutions, the biosorbent was washed with excess of the acid solution and distilled water in order to reuse for the next experiment. Consecutive sorption-desorption cycles were repeated seven times to establish the usability of the biosorbent.

RESULTS AND DISCUSSION

Effect of pH

The pH parameter has been identified as one of the most important variable governing metal sorption. The dependence of metal uptake on pH is related to both the surface functional groups on the biomass cell walls and to the metal chemistry in solution. The pH value can change the state of the active-binding sites, which are usually acidic. Their protonation and consequently their availability can change dramatically if the pH varied by 1 or 2 units (32).

The effect of pH on the biosorption of As(III) and As(V) onto *X. parietina* biomass was studied at pH 2–10 (metal concentration: 25 mg/L; volume of solution: 25 mL; temperature: 20°C) and the results were presented in Fig. 1. The biosorption of As(V) reaches a maximum value (91%) under acidic conditions at pH 2–4. Therefore, pH 2 was selected for further batch studies in the biosorption of As(V). As(V) and As(III) can exist as different ionic species depending on the pH of the solution (33). The dominant species in the above-mentioned pH range are $H_2AsO_4^-$ and $HAsO_4^{2-}$ ions which can be sorbed on the

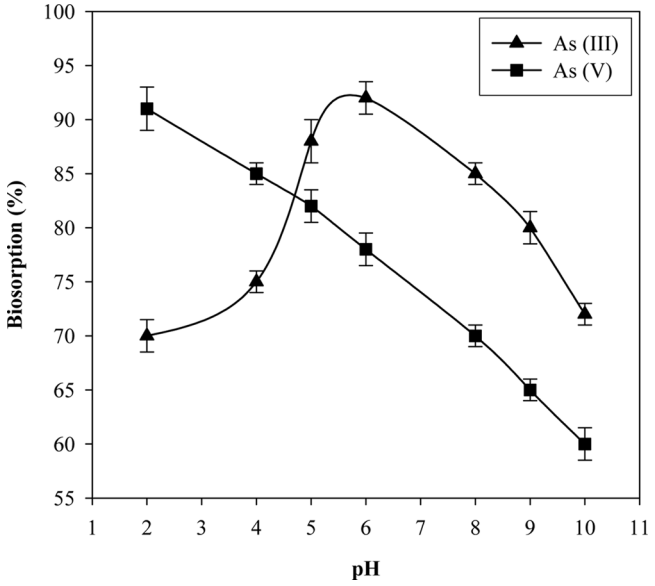

FIG. 1. Effect of pH on the biosorption of As(III) and As(V) onto *X. parietina* biomass (metal concentration: 25 mg/L; volume of solution: 25 mL; temperature: 20°C).

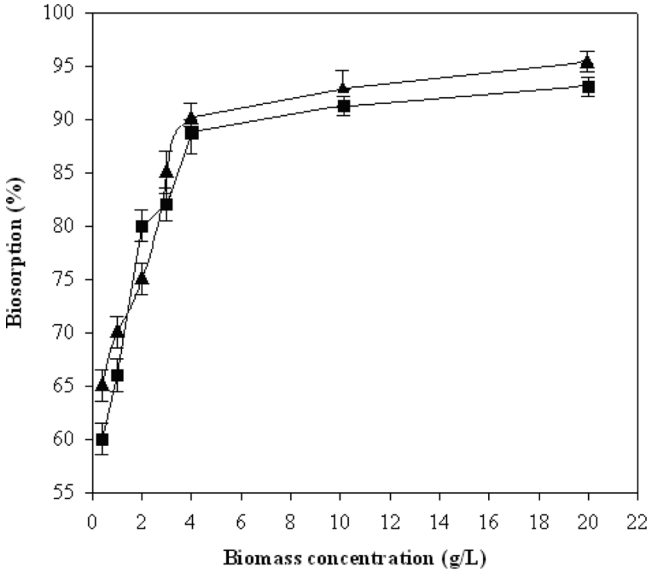

FIG. 2. Effect of biomass dosage on the biosorption of As(III) and As(V) onto *X. parietina* biomass (metal concentration: 25 mg/L; volume of solution: 25 mL; pH 6 for As(III); pH 2 for As(V); temperature: 20°C).

sorbent by substituting hydroxyl ions (4) or coordination of hydroxyl groups with the sorbate (8).

On the other hand, although the maximum biosorption of As(III) occurred at pH 5–6, therefore, pH 6 was selected for further batch-mode sorption tests for As(III). The predominant mono anionic ($H_2AsO_3^-$) and neutral (H_3AsO_3) species are thus considered to be responsible for the biosorption of As(III), substituting hydroxyl ions or water molecules (4). The neutral species (H_3AsO_3) cannot undergo electrostatic interaction with the adsorbent. However, such species can interact with the unprotonated amino groups (8). The biosorption yield of As(III) decreases with a further increase in pH. It can be attributed to the competition between the hydroxyl ions, present at higher pH, and arsenic species for biosorption sites. In addition, the carboxyl, hydroxyl, and amide groups of the biomass will be negatively charged at alkaline conditions. Therefore, there exists a repulsive force between the negatively charged sorbent and anionic species of arsenic, resulting in reduced sorption efficiency (34,35). Moreover, extreme pH values can damage the structure of the (bio)sorbent and therefore decrease metal uptake (36).

Effect of Biomass Concentration

The biosorption efficiency for As(III) and As(V) ions as a function of biomass concentration was investigated at other experimental conditions, metal concentration, 25 mg/L, volume of solution, 25 mL; biomass concentration, 10 g/L; pH 6 for As(III); pH 2 for As(V). The metal biosorption steeply increases with the biomass concentration up to 20 g/L (Fig. 2). This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction whereas the number of sites available for the biosorption site increases by increasing the biosorbent concentration (37). The maximum biosorption was attained as 92% for As(III) and 90% for As(V) at biomass concentration, 10 g/L. When the biomass concentration was 20 g/L, the biosorption was found to be 95% and 94% for As(III) and As(V), respectively. This result means that further increase in biomass concentration over 10 g/L did not lead to a significant improvement in biosorption yield due to the saturation of the biosorbent surface with the metal ions. Therefore, the optimum biomass concentration was taken as 10 g/L for further batch experiments.

Effects of Contact Time and Temperature

The rate of biosorption is important when designing batch biosorption experiments. The effect of contact time on the biosorption of As(III) and As(V) was investigated at other conditions, metal concentration: 25 mg/L; volume of solution: 25 mL; biomass concentration: 10 g/L; pH 6 for As(III); pH 2 for As(V) and the results were shown in Fig. 3. The biosorption yield of As(III) and As(V) increased considerably with increasing contact time up to 60 min and then it continued with a constant rate. Therefore, the optimum contact time was selected as 60 min for further experiments.

The temperature of the medium affects on the removal efficiency of the pollutant from aqueous solution. Figure 3 also shows the biosorption of As(III) and As(V) ions as a function of the temperature. When the temperature was increased from 20 to 50°C during the equilibrium time at

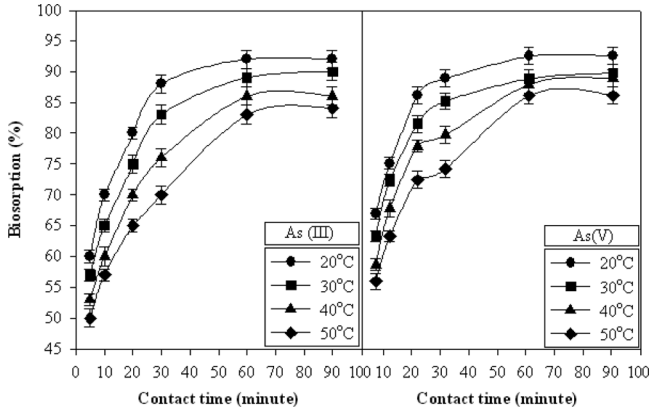

FIG. 3. Effect of contact time and temperature on the biosorption of As(III) and As(V) onto *X. parietina* biomass (metal concentration: 25 mg/L; volume of solution: 25 mL; biomass concentration: 10 g L^{-1}; pH 6 for As(III); pH 2 for As(V)).

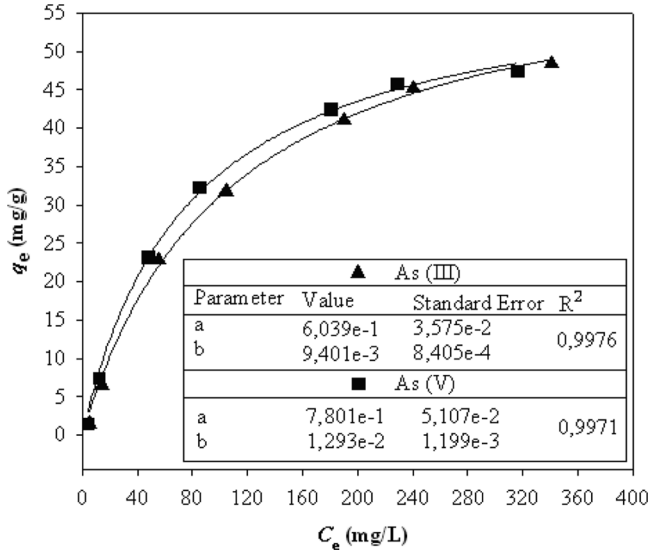

FIG. 4. Langmuir isotherm plots for the biosorption of As(III) and As(V) onto *X. parietina* biomass (volume of solution: 25 mL; contact time: 60 min; pH 6 for As(III); pH 2 for As(V); temperature: 20°C).

60 min, the biosorption decreased from 92% to 83% for As(III) and from 92% to 85% for As(V). These results indicated the exothermic nature of As(III) and As(V) biosorption onto *X. parietina*. The optimum temperature was selected as 20°C for further biosorption experiments.

Biosorption Isotherm Models

The capacity of a biomass can be described by equilibrium sorption isotherm which expresses the surface properties and affinity of the biomass. The biosorption isotherms were investigated using three equilibrium models, which are namely the Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models.

The Langmuir sorption isotherm has been successfully applied to many pollutant biosorption processes. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. This model can be written in a nonlinear form (38).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_e is the equilibrium metal ion concentration on the adsorbent (mg/L), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer biosorption capacity of the adsorbent (mg/g), and K_L is the Langmuir biosorption constant (L/mg) related with the free energy of biosorption.

Figure 4 indicates the nonlinear relationship between the amount (mg) of As(III) and As(V) ions sorbed per unit mass (g) of *X. parietina* biomass against the concentration of As(III) and As(V) ions remaining in solution (mg/L). The coefficients of determination (R^2) were found to be 0.9976 for As(III) and 0.9971 for As(V) biosorption. These results indicate that the biosorption of the metal ions onto *X. parietina* biomass fitted well the Langmuir model. In other words, the biosorption of arsenic ions onto *X. parietina* took place at the functional groups/binding sites on the surface of the biomass which is regarded as monolayer biosorption. As seen from Table 1, the maximum biosorption capacity (q_m) of *X. parietina* biomass was found to be 63.8 mg/L and 60.3 mg/L for As(III) and As(V), respectively. The K_L value was found as 9.4×10^{-3} L/mg for As(III) and 1.2×10^{-2} L/mg for As(V) biosorption.

On the other hand, when compared with the biosorption capacity (q_m) of *X. parietina* biomass for arsenic ions with that of various biomasses reported in literature, it can be noted that it has a higher sorption capacity for As(III) than chitosan-coated biosorbent (8) and a higher sorption capacity for As(V) than coconut shell carbon (39), peat-based carbon (39), and chitosan (40). The biosorption capacity of *X. parietina* biomass for As(III) and As(V) is higher than other biosorbents. Therefore, it can be noteworthy that the *X. parietina* biomass has an important potential for the removal of As(III) and As(V) ions from the aqueous solution.

The Freundlich sorption isotherm has been successfully applied to many pollutant biosorption processes. A basic assumption of the Freundlich theory is that sorption takes place at specific heterogeneous sites within the sorbent. This model can be written in nonlinear form (41)

$$q_e = K_f C_e^{1/n} \tag{3}$$

where K_f is a constant relating to the biosorption capacity and $1/n$ is an empirical parameter relating to the biosorption intensity, which varies with the heterogeneity of the material.

TABLE 1
Kinetic parameters obtained from pseudo-first-order and pseudo-second-order for As(III) and As(V) bisorption onto *X. parietina* biomass at different temperatures (biomass concentration: 10 g L^{-1}; contact time: 60 min; pH 6 for As(III); pH 2 for As(V))

		Pseudo-first-order			Pseudo-second-order		
Temperature (°C)	$q_{e,\exp}$ (mgg^{-1})	k_1 (1/min)	$q_{e1,cal}$ (mgg^{-1})	R^2	k_2 (gmg^{-1} min^{-1})	$q_{e2,cal}$ (mgg^{-1})	R^2
As(III)							
20	1.50	5.3×10^{-2}	0.56	0.825	0.31	1.57	0.992
30	1.49	4.6×10^{-2}	0.55	0.901	0.25	1.55	0.995
40	1.40	4.4×10^{-2}	0.49	0.963	0.23	1.37	0.998
50	1.35	4.3×10^{-2}	0.43	0.955	0.19	1.28	0.993
As(V)							
20	1.48	5.5×10^{-2}	0.60	0.846	0.35	1.59	0.992
30	1.45	4.9×10^{-2}	0.58	0.901	0.33	1.54	0.995
40	1.41	4.7×10^{-2}	0.54	0.922	0.29	1.35	0.996
50	1.38	3.1×10^{-2}	0.53	0.937	0.24	1.28	0.994

Figure 5 indicates the nonlinear Freundlich isotherm plots. As seen from Table 1, the K_f were found to be 2.69 and 3.47 and the 1/n values were found as 0.51 and 0.47 As(III) and As(V), respectively. The $1/n$ values between 0 and 1 indicated that the biosorption of As(III) and As(V) onto *X. parietina* biomass was favorable at studied conditions. In addition, the R^2 values were found to be 0.9674 and 0.9542 for As(III) and As(V), respectively. These results indicate that the Freundlich model was not able to adequately describe the relationship between the amounts of the sorbed metal ions and their equilibrium concentrations in the solution.

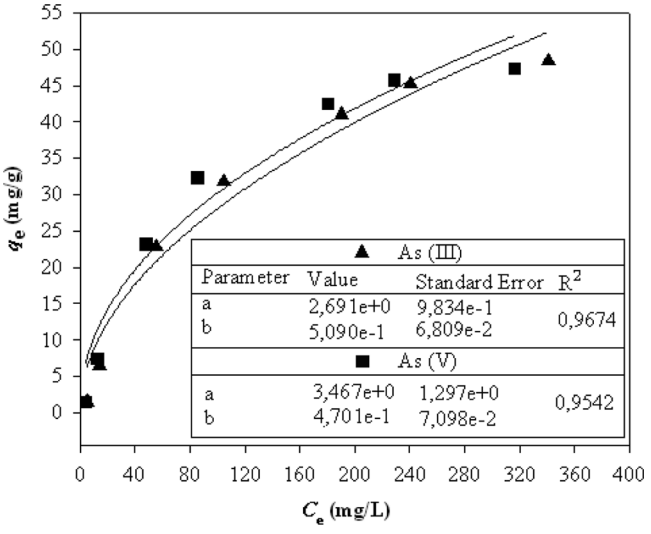

FIG. 5. Freundlich isotherm plots for the biosorption of As(III) and As(V) onto *X. parietina* biomass (volume of solution: 25 mL; contact time: 60 min; pH 6 for As(III); pH 2 for As(V); temperature: 20°C).

The equilibrium data were also subjected to the D–R isotherm model to determine the nature of the biosorption processes as physical or chemical. The linear presentation of the D–R isotherm equation (42) is expressed by

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{4}$$

where q_e is the amount of metal ions adsorbed on per unit weight of biomass (mol/g), q_m is the maximum biosorption capacity (mol/g), β is the activity coefficient related to the biosorption mean free energy (mol^2/J^2), and ε is the Polanyi potential ($\varepsilon = RT\ln(1 + 1/C_e)$).

The D–R isotherm model well fitted the equilibrium data since the R^2 value was found to be 0.9914 and 0.9932 for As(III) and As(V), respectively (Table 1 and Fig. 6). The q_m value was found using the intercept of the plots to be 4.6×0^{-4} mol/g for As(III) biosorption and 5.6×10^{-4} mol/g for As(III) biosorption. The biosorption mean free energy (E; kJ/mol) is as follows:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

The E (kJ/mol) value gives information about the sorption mechanism, physical or chemical. If it lies between 8 and 16 kJ/mol, the adsorption process takes place chemically and while $E < 8$ kJ/mol, the adsorption process proceeds physically (43). The mean biosorption energy was calculated as 9.3 and 10.4 kJ/mol for the biosorption of As(III) and As(V) ions, respectively. These results suggest that the biosorption processes of both metal ions onto *X. parietina* biomass could be taking place by chemical ion-exchange mechanism because the sorption energies lie within 8–16 kJ/mol.

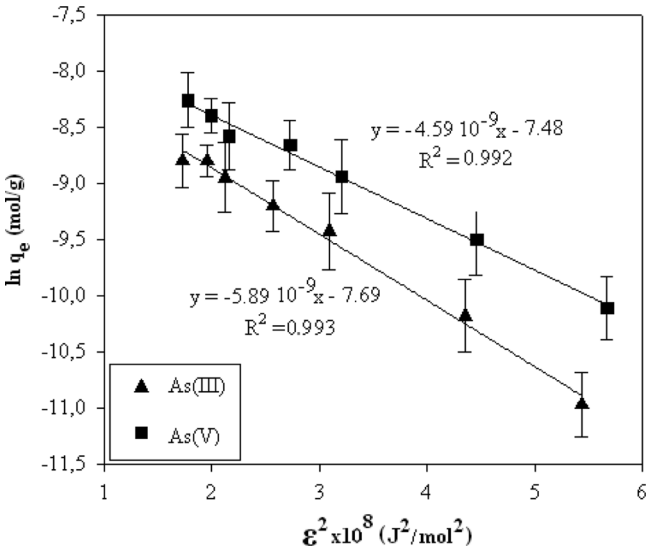

FIG. 6. D–R isotherm plots for the biosorption of As(III) and As(V) onto *X. parietina* biomass (pH 6 for As(III); pH 2 for As(V); volume of solution: 25 mL; biomass concentration: 10 g/L; contact time: 60 min; temperature: 20°C).

TABLE 2
The calculated values of isotherm parameters

	As(III)	As(V)
Langmuir isotherm		
q_m (mg/g)	63.8	60.3
K_L (L/mg)	9.4×10^{-3}	1.2×10^{-2}
R^2	0,9976	0,9971
Freundlich isotherm		
K_f	2,69	3,47
$1/n$	0,51	0,47
R^2	0,9674	0,9542
D–R isotherm		
q_m (mol/g)	4.6×0^{-4}	5.6×10^{-4}
E (kJ/mol)	9.3	10.4
R^2	0.9914	0.9932

Biosorption Kinetics

The prediction of the biosorption rate gives important information for designing batch biosorption systems. In order to clarify the biosorption kinetics of As(III) and As(V) ions onto *X. parietina* biomass, two kinetic models, namely Lagergren's pseudo-first-order and pseudo-second-order model, were applied to the experimental data. The linear form of the pseudo-first-order rate equation by Lagergren (44) is given as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

where q_t (mg/g) is the amount of the metal ion biosorbed at equilibrium and q_e (mg/g) is the amount of the metal ion biosorbed at any t time (min). The biosorption rate constants k_1 (min^{-1}) can be determined experimentally by plotting of $\ln(q_e - q_t)$ vs t.

The plots of $\ln(q_e - q_t)$ vs t for the pseudo-first-order model were not shown as the figure because the coefficients of determination for this model at studied temperatures have low values. It can be concluded from the R^2 values in Table 2 that the biosorption mechanisms of As(III) and As(V) ions onto *X. parietina* biomass does not follow the pseudo-first-order kinetic model. Moreover, from Table 2, it can be seen that the experimental values of $q_{e,exp}$ are not in good agreement with the theoretical values calculated ($q_{e1,cal}$) from Eq (6). Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of As(III) and As(V) onto *X. parietina*.

Experimental data were also tested by using Ho's pseudo-second-order kinetic model which is given in the following form (45):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \tag{7}$$

where k_2 (g/mg min) is the rate constant of the second-order equation, q_t (mg/g) is the amount of biosorption time t (min), and q_e is the amount of biosorption equilibrium (mg/g).

This model is more likely to predict kinetic behavior of biosorption with chemical sorption being the rate-controlling step (45). The linear plots of t/qt vs t for the pseudo-second-order model for the biosorption of As(III) and As(V) ions onto *X. parietina* at 20–50°C were shown in Fig. 7a and Fig. 7b, respectively. The rate constants (k_2), the R^2 and q_e values are given in Table 2. It is clear from these results that the R^2 values are very high (in range of 0.992–0.998 for As(III) biosorption and 0.992–0.996 for As(V) biosorption. In addition, the theoretical $q_{e2,cal}$ values were closer to the experimental $q_{e,exp}$ values (Table 2). Based on these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of As(III) and As(V) onto *X. parietina* in contrast to the pseudo-first-order model.

Biosorption Thermodynamics

The equilibrium constant (K_D) between the metal concentration in solution metal concentration sorbed onto the biosorbent can be written as follow:

$$K_D = \frac{q_e}{C_e} \tag{8}$$

This parameter can be used to estimate the thermodynamic parameters due to its dependence on temperature. The changes in energy (ΔG°), enthalpy (ΔH°), and

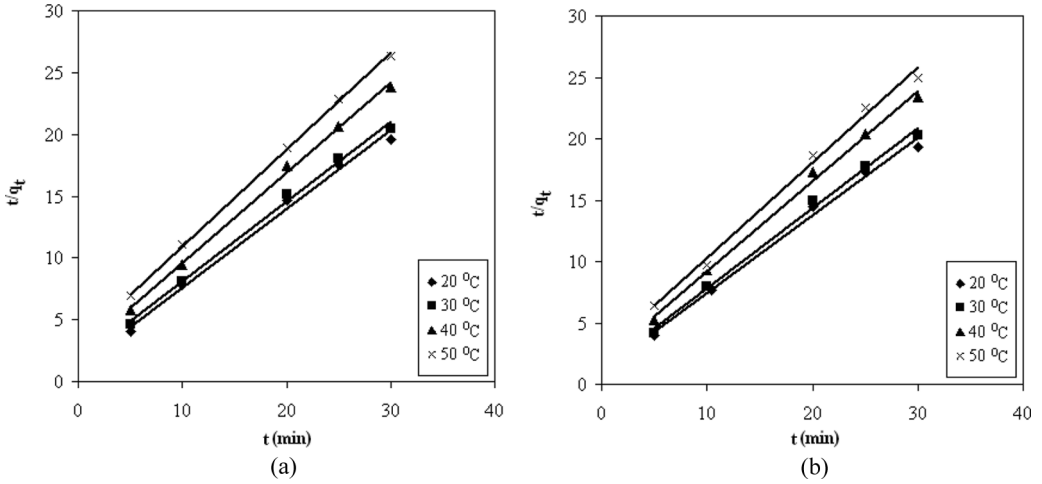

FIG. 7. Pseudo-second-order kinetic plots at different temperatures; (a) for As(III) biosorption (b) for As(V) biosorption (metal concentration: 25 mg/L; volume of solution: 25 mL; biomass concentration: 10 g/L; pH 6 for As(III); pH 2 for As(V)).

entropy (ΔS°) of the biosorption process were determined by using the following equations:

$$\Delta G^\circ = -RT \ln K_D \tag{9}$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

A Van't Hoff plot of ln K_D as a function of $1/T$ (Fig. 8) yields a straight line. The ΔH° and ΔS° parameters were calculated from the slope and intercept of the plot, respectively. The Gibbs free energy change (ΔG°) was calculated to be −18.9, −18.8, −18.7, and −18.5 kJ/mol for As(III) biosorption and −18.8, −18.3, −18.0, and −17.8 kJ/mol for the biosorption of As(V) at 20, 30, 40, and 50°C, respectively. The negative ΔG° values indicated a thermodynamically feasible and spontaneous nature of the biosorption. The decrease in ΔG° values with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures. The ΔH° parameter was found to be −21.1 and −28.8 kJ/mol for As(III) and As(V) biosorption, respectively. The negative ΔH° indicates the exothermic nature of the biosorption processes at 20–50°C. The ΔS° parameter was found to be −7.6 J/mol K for As(III) biosorption and −34.3 J/mol K for As(V) biosorption. The negative ΔS° value suggests a decrease in the randomness at the solid/solution interface during the biosorption process.

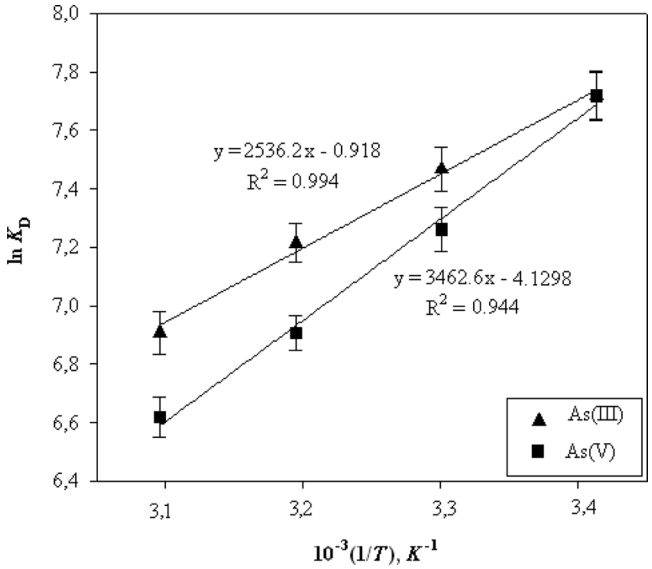

FIG. 8. Plot of ln K_D vs 1/T for the estimation of thermodynamic parameters for biosorption of As(III) and As(V) onto *X. parietina* biomass (volume of solution: 25 mL; biomass concentration: 10 g/L; pH 6 for As(III); pH 2 for As(V)).

Desorption Efficiency and Reusability

The regeneration of the biosorbent is one of the key factors in assessing its potential for commercial applications. Two different desorption agents were used for the recovery of As(III) and As(V) ions from the biosorbent (Table 3).

TABLE 3
Influence of various eluents on the desorption of As(III) and As(V) ions from *X. parietina*

Eluent	Recovery percent of As(III)	Recovery percent of As(V)
0.5 M HCl	60 ± 2	65 ± 2
1 M HCl	90 ± 2	92 ± 2
0.5 M HNO_3	50 ± 2	55 ± 3
1 M HNO_3	80 ± 3	85 ± 2

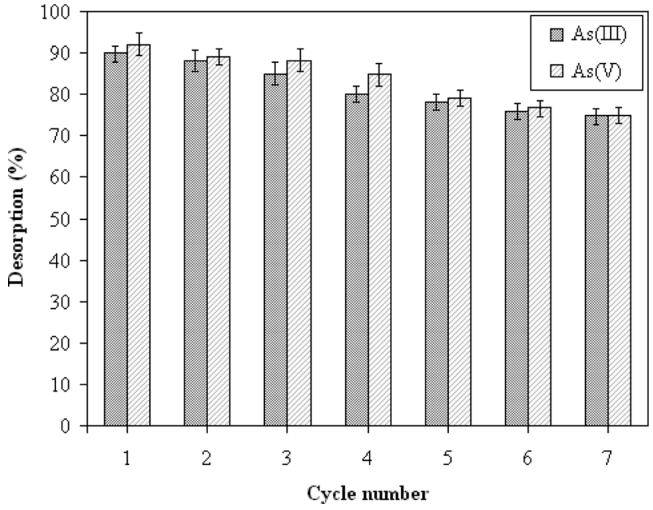

FIG. 9. Desorption efficiency of *X. parietina* biomass with cycle number.

The best regeneration was achieved with 1 M HCl solution and thus it was selected as a desorption agent for As(III) and As(V) ions. The recovery yield was found to be 80–90% for As(III) and 85–92% for As(V). The reusability of the biosorbent was tested during seven consecutive biosorption-desorption cycles (Fig. 9). These results revealed that the natural biosorbent *X. parietina* offers potential to be used repeatedly in As(III) and As(V) biosorption studies without any significant loss in the total biosorption capacity.

CONCLUSIONS

This study focused on the biosorption of As(III) and As(V) ions onto *X. parietina* biomass from aqueous solution. The operating parameters, the pH of the solution, biomass concentration, contact time, and temperature, were effective on the biosorption efficiency of As(III) and As(V). The biosorption capacity of *X. parietina* biomass was found to be 63.8 mg/g and 60.3 mg/g for As(III) and As(V) respectively, at optimum conditions of pH 6 for As(III) and pH 2 for As(V), a contact time of 60 min, and temperature of 20°C. The mean free energy values evaluated from the D–R model indicated that the biosorption of As(III) and As(V) onto *X. parietina* biomass took place by chemical ion-exchange. The kinetic data signified that the biosorption of As(III) and As(V) ions onto *X. parietina* followed well the pseudo-second-order kinetic model. The thermodynamic calculations showed the feasibility, the exothermic and the spontaneous nature of the biosorption of As(III) and As(V) ion onto *X. parietina* biomass at 20–50°C. The metal ions were desorbed from *X. parietina* using both 1 M HCl and 1 M HNO_3. The recovery yield was found to be 80–90% As(III) and 85–90% for As(V). After seven consecutive sorption-desorption cycles it was observed that the biosorbent had good reusability. By considering the present findings, it can be concluded that *X. parietina* is a good biosorbent for As(III) and As(V) removal from aqueous solution. Furthermore, *X. parietina* biomass can be evaluated as an alternative biosorbent to treatment wastewater containing As(III) and As(V) ions due to the advantages of being low-cost biomass and having considerable high sorption capacity.

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