



Characterization of biosorption process of As(III) on green algae *Ulothrix cylindricum*

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ABSTRACT

Arsenic (As) is generally found as As(III) and As(V) in environmental samples. Toxicity of As(III) is higher than As(V). This paper presents the characteristics of As(III) biosorption from aqueous solution using the green algae (*Ulothrix cylindricum*) biomass as a function of pH, biomass dosage, contact time, and temperature. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe the biosorption isotherm of As(III) by *U. cylindricum* biomass. The biosorption capacity of *U. cylindricum* biomass was found as 67.2 mg/g. The metal ions were desorbed from *U. cylindricum* using 1 M HCl. The high stability of *U. cylindricum* permitted 10 times of adsorption–elution process along the studies with a slightly decrease about 16% in recovery of As(III) ions. The mean free energy value evaluated from the D–R model indicated that the biosorption of As(III) onto *U. cylindricum* biomass was taken place by chemical ion-exchange. The calculated thermodynamic parameters, ΔG° , ΔH° and ΔS° showed that the biosorption of As(III) onto *U. cylindricum* biomass was feasible, spontaneous and exothermic under examined conditions. Experimental data were also tested in terms of biosorption kinetics using pseudo-first-order and pseudo-second-order kinetic models. The results showed that the biosorption processes of As(III) followed well pseudo-second-order kinetics.

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1. Introduction

Heavy metal pollution is increasing throughout the world with the growth of industrial activities. Unlike organic pollutants, heavy metals are non-biodegradable and therefore, the removal of them is extremely important in terms of healthy of living specimens [1,2]. Arsenic, a common element in nature, is a naturally occurring contaminant of drinking water and can be found in the earth's crust, ground and marine water and in the organic world as well. It is mobilized through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions [3,4] as well as through a range of 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 [5,6].

Contaminated groundwater by arsenic is a well known environmental problem that can have severe human health implications. Chronic exposure to arsenic concentrations above 100 ppb can

cause vascular disorders, such as dermal pigments (Blackfoot disease) and skin, liver and lung cancer [7,8]. An arsenic concentration of 10 $\mu\text{g/L}$ has been recommended by World Health Organization as a guideline value for drinking water [9].

Arsenic may exist in groundwater both in +3 and +5 oxidation states depending upon the prevalent redox conditions. As(III) is more toxic in biological systems than As(V) [10]. Several studies have demonstrated that arsenic removal can be achieved by various techniques, namely oxidation/precipitation [11,12], Fe-electrocoagulation/co-precipitation [13], alum coagulation/precipitation [14], lime softening, metal-oxide adsorption using packed beds of activated alumina [15,16], granular ferric hydroxide [17], iron-oxide coated sand [18], reverse osmosis and nanofiltration [19,20], ion-exchange resin [21,22], polymer ligand exchange [23], coagulation-microfiltration [24], 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. On the other hand, numerous biological materials have been tested for removal of toxic ions from aqueous solutions over the last two decades. However, only a limited number of studies have investigated the use of adsorbents obtained from biological sources, e.g., bio-char [25], methylated

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yeast biomass [26], fungal biomass [27], chicken feathers [28], alginate [29] and orange waste gel to remove arsenic from aqueous solution. It is noteworthy that the main advantages of biosorption technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic [30].

Marine algae otherwise known as seaweeds have been found to be potentially suitable biosorbents because of their cheap availability both in fresh and saltwater, relatively high surface area and high binding affinity [31]. Biosorption in algae has mainly been attributed the cell wall structure containing functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals via both electrostatic attraction, ion exchange and complexation [32,33]. Different species of algal biomasses (brown, green and red) have been used for the removal of heavy metals from aqueous solution [34–36].

Ulothrix is a genus of filamentous green algae, generally found in fresh and marine water. Its cells are normally as broad as they are long, and they thrive in the low temperatures of spring and winter. They become attached to surfaces by a modified holdfast cell. Reproduction is normally vegetative. They are Eukaryotic and unicellular. They are one of the five classes of microorganisms. There is abundantly available in some lakes and rivers of Turkey. According to authors' survey, there is no extensive study on the biosorption of As(III) using green algae (*Ulothrix cylindricum*) biomass as in literature. In addition, this new material was chosen as biosorbent in this study due to being of its natural, renewable and thus cost-effective biomass.

The objective of the present work is to investigate the biosorption potential of *U. cylindricum* biomass in the removal of As(III) from aqueous solution. Optimum biosorption conditions were determined as a function of pH, biomass dosage, contact time, and temperature. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were used to describe equilibrium isotherms. Biosorption mechanisms of As(III) onto *U. cylindricum* biomass were also evaluated in terms of thermodynamics and kinetics.

2. Experimental procedures

2.1. Biomass preparation

The green alga (*U. cylindricum*) was used as biosorbent for the biosorption of As(III) ions. Samples of the biomass were collected from the Green River coast of Turkey. Samples were washed several times using deionized water to remove extraneous and salts. They were then dried in an oven at 333 K for 48 h. The dried algae biomass was chopped, sieved and the particles with an average of 0.5 mm were used for biosorption experiments.

2.2. Reagents and equipments

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Double deionised water (Aquamax 18.2 M Ω cm⁻¹ conductivity) was used for all dilutions. A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. 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. NaBH₄ (0.3%) (w/v) in NaOH (0.1%) (w/v) was used as reducing agent. The analytical measurement was based on peak height. Reading time and

argon flow rate was selected as 20 s and 70 mL min⁻¹. The metal determination was repeated as triplicate and the mean value was considered. Fourier Transform Infrared (FT-IR) spectra of dried unloaded biomass and As(III)-loaded biomass prepared as KBr discs were recorded at 400–4000 cm⁻¹ wavenumber range using a JASCO-430 model FT-IR spectrometer.

2.3. Batch biosorption procedure

Biosorption experiments were optimized out at the desired pH value, contact time and biomass dosage level using the necessary biomass in a 250 mL stoppered conical flask containing 25 mL of test solution. As(III) standard solution (1000 mg/L) was prepared from As₂O₃ (Merck). Sodium phosphate buffer (0.1 mol/L) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers (0.1 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 4–6. Ammonium chloride buffer solutions (0.1 mol/L) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8–9.

Necessary amount of the biomass was then added and contents in the flask were shaken for the desired contact time in an electrically thermostatic reciprocating shaker at 120 rpm. The experiments were repeated at 20, 30, 40, and 50 °C. The time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and the filtrate was analyzed for metal concentration by using HGAAS. Biosorption experiments for the effect of pH were conducted by using a solution having 10 mg/L of As(III) concentration with a biomass dosage of 4 g/L. Throughout the study, the contact time was varied from 5 to 90 min, the pH from 2 to 8, the initial metal concentration from 10 to 400 mg/L, and the biosorbent dosage from 0.1 to 20 g/L.

2.4. Desorption procedure

A sample volume of 25 mL, containing 10 mg/L of As(III), was transferred into a beaker; 10 mL of buffer solution was added. After a fast shaking, 4 g/L of *U. cylindricum* was added and the mixture was shaken again for 60 min at 100 rpm. The system was filtered with blue band filter paper. Then the filter and constituents were washed with distilled water. In order to elute the sorbed analytes by *U. cylindricum* 10 mL of 1 M HCl and 10 mL of 1 M HNO₃ was used separately. Analyte contents of the final solution were determined by HGAAS. The same procedure was applied to the blank solution. In order to use the biomass for the next experiment, the biomass was washed with excess of 1 M acid solution and distilled water, sequentially.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectroscopy method was used to obtain information on the nature of possible cell-metal ions interactions and presented in Fig. 1. The broad and strong bands at 3337–3674 cm⁻¹ were due to bounded hydroxyl (–OH) or amine (–NH) groups. The bands peaks at 1671 and 1425 cm⁻¹ may be attributed to asymmetric and symmetric stretching vibration of C=O groups. The bands observed at 1052 cm⁻¹ were assigned to C–O stretching of alcohols and carboxylic acids. The peaks observed at 2893 cm⁻¹ can be

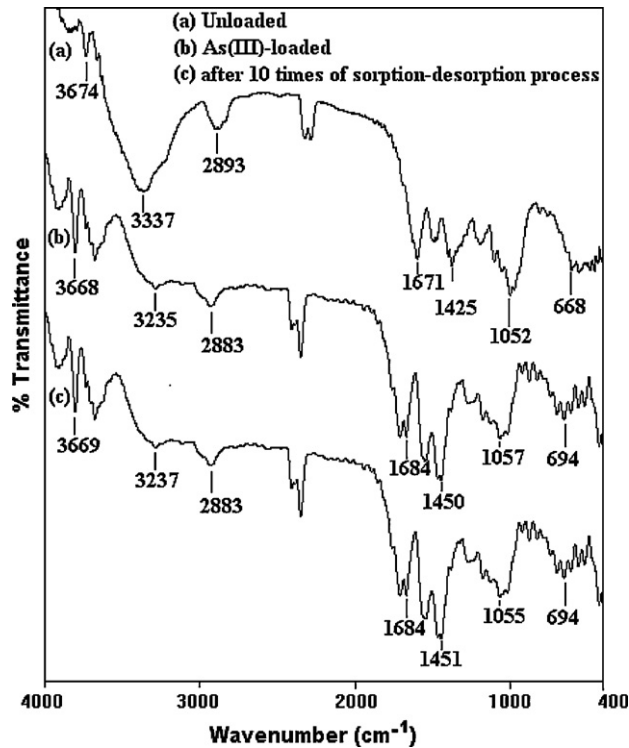


Fig. 1. FT-IR spectrum of unloaded and As(III)-loaded biomass.

assigned to the $-\text{CH}$ group. Some bands in the fingerprint region could be attributed to the phosphate groups. After As(III) biosorption, the asymmetrical stretching vibration at $3202\text{--}3623\text{ cm}^{-1}$ shifted was to $3235\text{--}3668$ for As(III)-loaded biomass. The bands observed at 1671 , 1425 , 1052 cm^{-1} were also shifted to 1684 , 1450 , and 1057 cm^{-1} . The results indicated that the chemical interactions as ion-exchange between the hydrogen atoms of carboxyl ($-\text{COOH}$), hydroxyl ($-\text{OH}$), and amine ($-\text{NH}$) groups of the biomass and the metal ions were mainly involved in the biosorption of As(III) by *U. cylindricum* biomass. The similar FT-IR results were reported for the biosorption of different heavy metals on various algae species [37,38]. In addition, it can be seen from the FT-IR spectrum, there is no considerable change in frequency bands after 10 times biosorption-desorption processes.

3.2. Effect of pH

One of the more important factors affecting biosorption of metal ions is acidity of solution. This parameter directly related with competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface. The effect of pH on the biosorption of As(III) onto *U. cylindricum* biomass was studied at pH 2–9 and the results were presented in Fig. 2. At pH 2–6, the biosorption efficiency was increased 80–96% when pH was increased from 6 to 9 it was decreased from 96 to 85%. The maximum biosorption was found to be 98% at pH 6. Therefore, all the biosorption experiments were carried at this pH value. Several researchers have investigated the effect of pH on sorption of As(III) using different kinds of sorbents and they reported almost same pH dependent and maximum biosorption was obtained in the pH range 6.0 [9,39,40].

The predominant monoanionic (H_2AsO_3^-) and neutral (H_3AsO_3) species are thus considered to be responsible for the sorption of As(III), substituting hydroxyl ions or water molecules [3]. Arsenite speciation in an aqueous medium in the pH range of 3–11 is controlled by $\text{H}_3\text{AsO}_3 \rightarrow \text{H}_2\text{AsO}_3^- + \text{H}^+$ [41]. At pH 6,

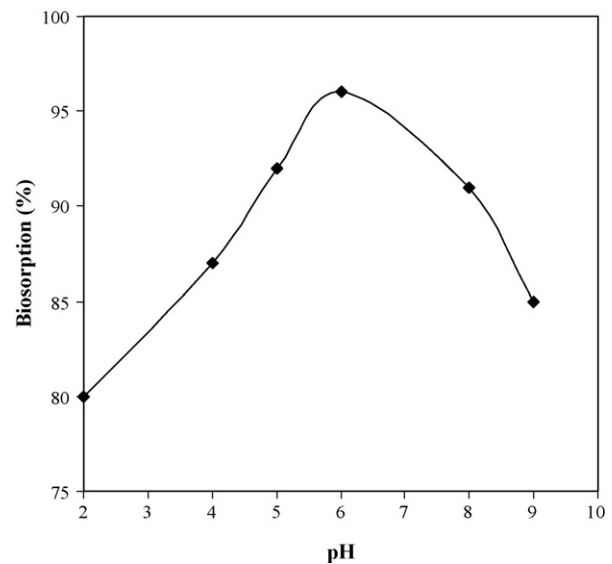


Fig. 2. Effect of pH on the biosorption of As(III) by *U. cylindricum* biomass (metal concentration: 10 mg/L; temperature: 20 °C).

the predominant arsenite species present in aqueous medium is uncharged H_3AsO_3 , which cannot undergo electrostatic interaction with the adsorbent. However, such species can interact with the unprotonated amino groups. Some hydroxyl groups in the sorbent may be involved in coordination with the sorbate [42,43]. A reduced removal of As(III) at a pH greater than pH 6 may be due to the reason that the density of OH^- ion becomes dominant at an alkaline pH and this ion competes with arsenic species, H_2AsO_3^- [39]. 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 H_2AsO_3^- anions, resulting in reduced sorption efficiency [40].

3.3. Biosorption isotherm models

The capacity of a biomass can be described by equilibrium sorption isotherm, which is characterized by certain constants whose values express 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 were analyzed.

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 non-linear form [44].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

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

The coefficients of determination (R^2) for the model were found to be 0.997. These results indicate that the biosorption of the metal ions onto *U. cylindricum* biomass fitted well the Langmuir model. In other words, the sorption of As(III) using *U. cylindricum* was taken place at the functional groups/binding sites on the surface of the biomass which is regarded as monolayer biosorption. From the non-linear Langmuir isotherm model, the maximum biosorption capacity (q_m) of *U. cylindricum* biomass was found to be 67.2 mg/g. Moreover, the K_L value was found as 0.01 L/mg. The

biosorption capacity of *U. cylindricum* biomass for As(III) is higher than that of the majority of other biomasses mentioned in literature [3,9,18,39,42,45–52]. Therefore, it can be worthy noted that the *U. cylindricum* biomass has important potential for the removal of As(III) from aqueous solution.

The Freundlich model assumes a heterogeneous adsorption surface and active sites with different energy. The Freundlich model [53] is

$$q_e = K_f C_e^{1/n} \quad (2)$$

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

From the non-linear Freundlich isotherm that obtained by plotting q_e vs. C_e values, K_f and $1/n$ value was found to be 2.85 and 0.53, respectively. The $1/n$ value were between 0 and 1 indicating that the biosorption of As(III) using *U. cylindricum* biomass was favourable at studied conditions. However, the R^2 values were found to be 0.980, indicating that the Freundlich model was not able to adequately to describe the relationship between the amounts of sorbed metal ions and their equilibrium concentration in the solution.

The equilibrium data were also subjected to the D–R isotherm model to determine the nature of biosorption processes as physical or chemical. The linear presentation of the D–R isotherm equation [54] is expressed by

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (3)$$

where q_e is the amount of metal ions adsorbed on per unit weight of biomass (mol/L), q_m is the maximum biosorption capacity (mol/g), β is the activity coefficient related to biosorption mean free energy (mol²/J²) 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 0.991 (Fig. 3). The q_m value was found using the intercept of the plots to be 5.2×10^{-4} mol/g. The biosorption mean free energy (E ; kJ/mol) is as follow:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (4)$$

The E (kJ/mol) value gives information about adsorption mechanism, physical or chemical. If it lies between 8 and 16 kJ/mol, the

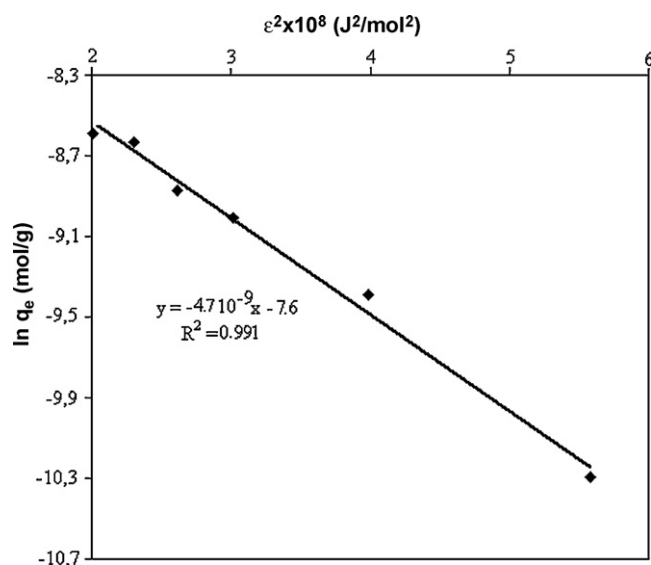


Fig. 3. D–R isotherm plots for the biosorption of As(III) by *U. cylindricum* biomass (pH: 6; biomass dosage: 4 g/L; contact time: 60 min; temperature: 20 °C).

Table 1

Influence of various eluents on the desorption of As(III) from *U. cylindricum*.

Eluent	Recovery, (%)
0.1 mol L ⁻¹ HCl	60 ± 2
0.5 mol L ⁻¹ HCl	80 ± 3
1 mol L ⁻¹ HCl	95 ± 3
0.1 mol L ⁻¹ HNO ₃	55 ± 2
0.5 mol L ⁻¹ HNO ₃	70 ± 3
1 mol L ⁻¹ HNO ₃	85 ± 3

adsorption process takes place chemically and while $E < 8$ kJ/mol, the adsorption process proceeds physically [9]. The mean biosorption energy was calculated as 10.2 kJ/mol. These results suggest that the biosorption processes of As(III) by *U. cylindricum* biomass could be taken place by chemical ion-exchange mechanism because the sorption energies lie within 8–16 kJ/mol.

3.4. Desorption efficiency

Desorption of As(III) from *U. cylindricum* was also studied by using HCl and HNO₃ at various concentrations in Table 1. For these studies, 10 mL of each eluent was used. Analyte ions were desorbed from *U. cylindricum* with both 1 M HCl and 1 M HNO₃. The highest recovery was found to be 95% and 85% using 10 mL of 1 M HCl and 10 mL of 1 M HNO₃, respectively. In addition, as it can be seen from Fig. 4, the high stability of *U. cylindricum* permitted 10 times of biosorption-desorption process along the studies with a decrease about 16% in recovery of As(III).

3.5. Biosorption kinetics

The prediction of biosorption rate gives important information for designing batch biosorption systems. Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full-scale batch process. In order to clarify the biosorption kinetics of As(III) by *U. cylindricum* biomass two kinetic models, which are 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 [55] is given as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

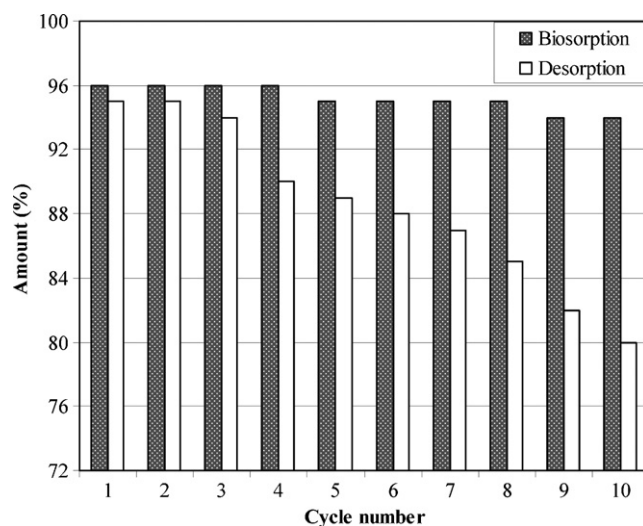


Fig. 4. Biosorption-desorption efficiency with cycle number (biomass dosage: 4 g/L; contact time: 60 min; temperature: 20 °C).

Table 2
Kinetic parameters obtained from pseudo-first-order and pseudo-second-order at different temperatures (metal concentration: 10 mg/L; pH: 6; biomass dosage: 4 g/L).

Temperature (°C)	$q_{e, \text{exp}}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (1/min)	$q_{e1, \text{cal}}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e2, \text{cal}}$ (mg/g)	R^2
20	4.5	4.3×10^{-2}	1.7	0.854	17.9×10^{-2}	4.4	0.997
30	4.2	3.9×10^{-2}	1.4	0.862	15.1×10^{-2}	4.2	0.999
40	4.0	3.7×10^{-2}	1.3	0.910	12.7×10^{-2}	3.7	0.997
50	3.6	3.5×10^{-2}	1.2	0.946	11.8×10^{-2}	3.5	0.998

where q_t and q_e (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the equation (min^{-1}). The biosorption rate constants (k_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 figure because the coefficients of determination for this model at studied temperatures is low. It can be concluded from the R^2 values in Table 2 that the biosorption mechanism of As(III) does not follow the pseudo-first-order kinetic model. Moreover, the experimental values of $q_{e, \text{exp}}$ are not in good agreement with the theoretical values calculated ($q_{e1, \text{cal}}$) from Eq. (5). Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of As(III) by *U. cylindricum*.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [56]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (6)$$

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 [57]. The linear plots of t/q_t vs. t for the pseudo-second-order model for the biosorption of As(III) by *U. cylindricum* at 20–50 °C were shown in Fig. 5. The rate constants (k_2), the R^2 and q_e values are given in Table 2. The R^2 value is in range of 0.997–0.999 and the theoretical $q_{e2, \text{cal}}$ values were closer to the experimental $q_{e, \text{exp}}$ values. Based on these results, it can be concluded that the pseudo-second-order kinetic model provided a good correlation for the biosorption of As(III) by *U. cylindricum* in contrast to the pseudo-first-order model.

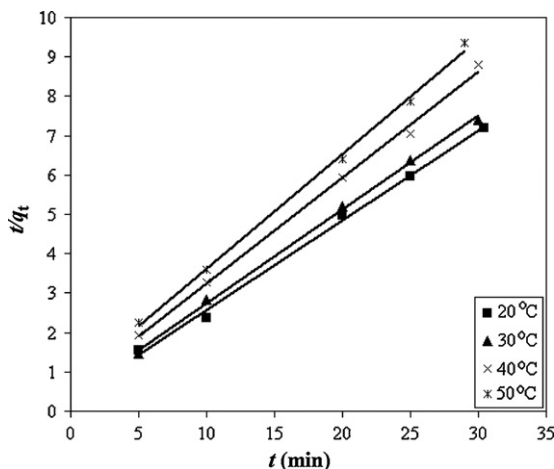


Fig. 5. Pseudo-second-order kinetic plots at different temperatures (metal concentration: 10 mg/L; pH: 6; biomass dosage: 4 g/L).

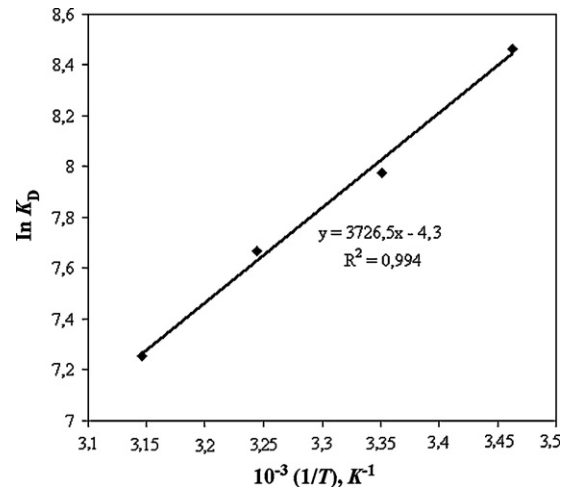


Fig. 6. Plot of $\ln K_D$ vs. $1/T$ for the estimation of thermodynamic parameters for biosorption of As(III) by *U. cylindricum* biomass (pH: 6; biomass dosage: 4 g/L; contact time: 60 min).

3.6. Biosorption thermodynamics

In order to describe thermodynamic behaviour of the biosorption of As(III) onto *U. cylindricum* biomass, thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from following equation:

$$\Delta G^\circ = -RT \ln K_D \quad (7)$$

where, R is the universal gas constant (8.314 J/mol K), T is temperature (K) and K_D (q_e/C_e) is the distribution coefficient [9,58].

The enthalpy (ΔH°) and entropy (ΔS°) parameters were estimated from the following equation:

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

According to Eq. (8), the ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of $\ln K_D$ vs. $1/T$ yields, respectively (Fig. 6). Gibbs free energy change (ΔG°) was calculated to be -20.6 , -20.1 , -19.9 , and -19.5 kJ/mol at 20, 30, 40, and 50 °C, respectively. The negative ΔG° values indicated 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 -30.9 kJ/mol, respectively. The negative ΔH° indicates the exothermic nature of the biosorption processes at 20–50 °C. Furthermore, the negative ΔS° (-35.8 J/mol K) value suggests a decrease in the randomness at the solid/solution interface during the biosorption process.

4. Conclusions

This study focused on the biosorption of As(III) onto *U. cylindricum* biomass from aqueous solution. The operating parameters,

pH of solution, biomass dosage, contact time, and temperature, were effective on the biosorption of As(III) using *U. cylindricum* biomass. The maximum biosorption capacity of *U. cylindricum* biomass was found as 67.2 mg/g at pH 6, 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) using *U. cylindricum* biomass was taken place by chemical ion-exchange. The kinetic data signified that the biosorption of As(III) using *U. cylindricum* followed well the pseudo-second-order kinetic model. The thermodynamic calculations showed the feasibility, exothermic and spontaneous nature of the biosorption at 20–50 °C. Furthermore, taking into consideration all results, *U. cylindricum* biomass can be evaluated as an alternative biosorbent to treatment wastewater containing As(III) ions, due to its being low-cost biomass and having a considerable high sorption capacity.

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