Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2019.24445

165 (2019) 188–196
October

Biosorption of arsenic ions from the aqueous solutions using *Chlorella vulgaris* micro algae

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Received 17 September 2018; Accepted 20 May 2019

ABSTRACT

Heavy metals are considered as the hazardous pollutants of water sources around the world. The objective of this study is to investigate the kinetics, thermodynamics, and the isotherms of arsenic heavy metal ion removal process from the aqueous solution using *Chlorella vulgaris* micro algae. The effects of various parameters such as temperature, initial arsenic concentration, contact time, and the adsorbent dosage were studied on the overall adsorption efficiency. Based on the results of the experiments, the optimum values of temperature, arsenic ion initial concentration, contact time, and adsorbent dosage were 323.15 K, 25 ppm, 210 min, and 6 g/L, respectively. In order to study the adsorption kinetics behavior, pseudo-first order and pseudo-second order kinetic models were used. The results showed that the pseudo-second order model was better to describe arsenic ions adsorption kinetics. The maximum adsorption efficiency was estimated 13 mg/g. The R_L, n, and B_1 and values of Langmuir, Freundlich, and Temkin models were equal to 0.645, 1.296, and 4.68 respectively, which approve that as a physical process, arsenic ion adsorption was desirable. Based on evaluated thermodynamic parameters such as enthalpy, entropy, and Gibbs free energy, it can be said that the current adsorption process was spontaneous.

Keywords: Adsorption; Arsenic; Kinetics behavior; Isotherm; *Chlorella vulgaris* micro algae; Adsorbent

1. Introduction

Today, bioenvironmental problems are considered as major issues and the heavy metals emissions are one of the most prominent of such environmental challenges. The accumulation of these poisonous elements in the food chain has generated a worldwide bioenvironmental health crisis [1]. As the main source, industrial sewage containing heavy metals is harmful to the human health and the other living beings. Arsenic is a poisonous pseudo-metal and has been recognized as one of the heavy metal pollutants. It is found abundantly in the earth's crust and enters into the environment from the natural resources or by human activities [2].

The water resource contaminations caused by arsenic have been reported in many countries around the world. Based on recent studies the concentration range of this element in the surface water sources 200 µg/l–2000 µg/l [3,4]. Surface water contamination by arsenic has also been considered as a major environment challenge in Iran [5]. This element is usually found in the surface waters in the form of arsenite (H_2AsO_3, $H_2AsO_4^-$, $HAsO_3^{2-}$) and arsenate (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$) [6]. Arsenite is more poisonous than the other one because of its higher rate of transferability. Due to the remarkably high toxicity of arsenic and its related compounds and consequently their harmful effects on the human health, World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA),

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have limited a value of 10 µg/l as the permissible concentration for arsenic [7,8]. Additionally, the Food and Agriculture Organization (FAO) has recommended a concentration value of 0.1 mg/l as the allowed value of arsenic in irrigation water [3].

Generally speaking, physical and chemical methods like sedimentation, ion exchange, reverse osmosis, coagulation, and surface adsorption are considered as the most common processes for the treatment of heavy metal contaminated areas [9]. Among these techniques, adsorption on various novel adsorbents has received considerable attention to remove chemical pollutants from the waste waters because of its simplicity, low cost and high effectiveness [10]. As a natural adsorbent, micro algae adsorb metals from their exterior environment depending on their concentration [11]. Many studies have been undertaken on the less valuable and easily accessible natural adsorbents which most often are originated from agricultural and biological sources [12]. In a research on arsenic adsorption rate by water hyacinth (*Eichhornia Crassipes*), the results showed that arsenic can be efficiently removed from the environment by water hyacinth [2]. The use of modified rice hulls as natural adsorbents of heavy metals, included cadmium and lead, has also been studied [13]. The removal of arsenite (As(III)) and arsenate (As(V)) by *perilla* leaf-derived biochars was the subject of a study by Niazi et al.. Their findings showed that the removal efficiency was about 90% [14]. In another research the enhancement of arsenic removal from the arsenic-contaminated water by *Echinodoruscordifolius*–endophytic *Arthrobactercreatinolyticus* interactions has been investigated. The results approved the higher arsenic removal of the current adsorbent than the conventional methods [15]. Barquilha et al. carried out a set of experiments to remove nickel and copper ions from aqueous solutions using *sargassum* species [16]. *Aspergillus Flavus* is a fungus whose biomass has been applied for the removal of lead and copper ions from aqueous solutions in a research. It was showed that the tendency for adsorbing lead ions was higher than copper ions under the competitive conditions [17]. The removal of lead and copper heavy metals from water by means of home garbage has also been investigated in another research. Additionally, Eggshell, banana peel, and pumpkin have shown an acceptable removal efficiency. Among these, eggshell was introduced as the best adsorbent for the studied metalions [18]. The removal of divalent cadmium (Cd(II)) using raw coconut fiber residue (CFR) was investigated by Tang et al. Their results showed that the maximum adsorption capacity of CFR for Cd(II) was significantly higher than other lignocellulosic materials [19]. The experiments on the adsorption of heavy metal ions (Fe(III), Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II)) from aqueous solution by the chemically modified mangosteen pericarp showed that it was a promising adsorbent for the removal of these heavy metal ions [20]. The adsorption of Ni(II), Cd(II), and Cr(VI) ions by the dried biomass of *Trichoderma sp.* approved that it was a pH dependent adsorption process. Additionally, the maximum adsorption capacity was achieved for Cr(VI) [21]. Sarwar et al. investigated the As(III) and As(V) ions removal efficiency by *Melia azedarach* biomass. Based on the received data efficiencies higher than 90% were achieved during their experiments [22].

The present study intends to utilize a biosorbent that has been prepared from the biomass of an algae type called *chlorella vulgaris*. In order to investigate its efficiency, the effects of parameters such as initial concentration, temperature, contact time, and adsorbent dosage were studied. Additionally, the kinetics, equilibrium, and thermo dynamics of the adsorption process were evaluated and analyzed the proposed biosorbents behavior.

2. Materials and methods

2.1. Materials

In order to perform the laboratory experiments, some chemical compounds having high purity were used. To prepare the stock solution, sodium arsenite ($AsNaO_2$)was purchased from Sigma-Aldrich Company (USA), Glucose ($C_6H_{12}O_2$) and dihydrogen phosphate (KH_2PO_4) were purchased from SAMCHUN Company (South Korea). Other chemicals like glycol ($C_3H_8O_2$), ammonium chloride (NH_4CL), and sodium bicarbonate (Na_2CO_3) were purchased from Merck Company (Germany) and were used to synthetize the artificial sewage. Agar which was also used as the cultivation environment, was purchased from QUELAB Company (Canada).

The arsenic ion stock solution is prepared by dissolving 1 g of sodium arsenite salt in 10 ml of deionized distilled water to have the required concentration of arsenic stock solution. Additionally, 3 L of the synthesized artificial sewage and 3 L of urban sewage from Bushehr Port were autoclaved and sterilized for 20 min in 180°C. In order to synthesize the artificial sewage, a mixture of glucose and propylene glycol were utilized as the carbon source. Chloro-ammonium and dihydrogen phosphate were also used as the nitrogen and phosphorus sources, respectively. The chemical compositions of the artificial sewage and their specifications are presented in Tables 1 and 2, respectively. It is worth noting that in the present study, the urban sewage was sampled from anaerobic lagoon of Bushehr Water Treatment Plant. The sewage samples were filtered to remove all of the extraneous materials. The specifications of the urban sewage are also given in Table 2.

2.2. Collection of the adsorbent

In order to prepare the adsorbent, *Chlorella Vulgaris*, a type of the algae, was collected from the Persian Gulf. The algae was both utilized in its living and powder forms.

Table 1
Composition of the artificial sewage

Type of composition	The amount required in one liter of urban water
$C_3H_8O_2$	0.6 ml
$C_6H_{12}O_2$	476 mg
NH_3CL	28 mg
KH_2PO_4	6.5 mg
Na_2CO_3	0.8 mg

Table 2
Specifications of artificial raw sewage and urban sewage

Parameter	Artificial raw sewage (concentration in mg/l)	Urban sewage (concentration in mg/l)
COD	500	450
Nitrate	25	60
Phosphate	5	6
pH	7 ± 5	7 ± 5
TSS	65	55

2.2.1. Preparation of alive adsorbent

At the beginning, the cultivation environment of the f/2 micro algae was prepared according to Gillard and Reider's guidelines [23]. It was comprised of 250 ml double-distilled water, 250 µl micro element from the stock solution, 250 µl of nitrate, 250 µl of mixture of biotin, B_{12}, and B_1 vitamins in addition to 25% of seawater for preserving the salinity and the minerals required for the algae to grow. Then, 1 ml of *Chlorella Vulgaris* algae was added which was sampled from the sewage that was discharged to the Persian Gulf. The algae was allowed to grow for a period of ten days under a light intensity of 5000 lux and 12/12 light cycle. Then it was placed on a shaker to be stirred every day to avoid the sedimentation and sticking to the vessel wall.

2.2.2. Preparation of adsorbent powder

In order to achieve the powder adsorbent, the f/2 *Chlorella vulgaris* micro algae was cultivated in 1 L of cultivation medium. At the end of the algae growth period, the algae biomass was separated from the liquid environment via centrifuge. Then, it was poured on a plate and dried in oven at 37°C for a period of 48 h.

2.3. The adsorption procedure

The adsorption tests were carried out in batch manner and within different time intervals and under various environmental conditions by varying the concentration of the arsenic ions in a range of 0–90 ppm on 1 ml of *Chlorella vulgaris* during the algae growth period. Parameters including adsorbent dosage (1–6 g/l) and contact time (10–210 min) were also evaluated. The experiments were conducted in temperatures range of 30–50°C and a stirring speed of 200 rpm. The stock solution of arsenic ion was prepared by dissolving an appropriate amount of sodium arsenite in double distilled water in a 250 mL Erlenmeyer to reach a 100 mL working volume, and then it was diluted by double distilled water to have the considered concentration of arsenic ion solutions. The effects of initial concentration of the pseudo-metal arsenic, temperature, contact time, and the adsorbent dosage as well as the adsorption kinetics, isotherms, thermodynamics of the reaction were investigated and specified. In order to determine the adsorbed arsenic ion concentration, furnace atomic adsorption device (Perkin Elmer FFS-240, Varian) was applied.

In the analyses, the amount of metal ion adsorbed by the biosorbent per every gram of the adsorbent is obtained via the following equation [24]:

$$q_e = \frac{\left(C_i - C_e\right)V}{W} \tag{1}$$

In this equation, q_e is the equilibrium value of the adsorbed material per each gram of the biosorbent (mg/g), C_i and C_e are the initial and equilibrium arsenic concentration (mg/l), respectively. V is the solution volume (L) and W is the mass of the nano-sorbent material. In the current research, the value of the arsenic metal ion adsorption under various reaction conditions can be determined via Eq. (2):

$$\text{Adsorption}\,\% = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

3. Results and discussions

The rate of the heavy metal ion adsorption is an important feature of the adsorption process. In batch adsorption processes, the initial concentration of the metal ions in the solution plays a key role in generating the driving force for the dynamic mass transfer between the solid and the liquid phases [25]. The percentages of arsenic pseudo-metal ion adsorption from the artificial and urban sewage samples based on using the *Chlorella vulgaris* algae have been shown in Figs. 1 and 2, respectively. Based on these data, there is a positive correlation between the adsorption percentage and the arsenic ion initial concentration and the contact time. The results of the artificial sewage treatment indicated that by varying the initial concentration of arsenic ion within the range of 15–90 ppm during 14 d of the algae growth period in the 3rd, 7th, and 14th day, the adsorption percentages were 9.8%, 72%, and 85%, respectively. While, the corresponding adsorption percentages for the urban sewage were 20%, 81.4%, and 93.5% for the 3rd, 7th, and 14th day of algae growth period in the initial concentration range of 25–75 ppm. According to the results, the maximum value of arsenic adsorption was found in the urban sewage of Bushehr Port. The possible reason of this result is that the micro algae was collected from the location of urban sewage discharge. Fur-

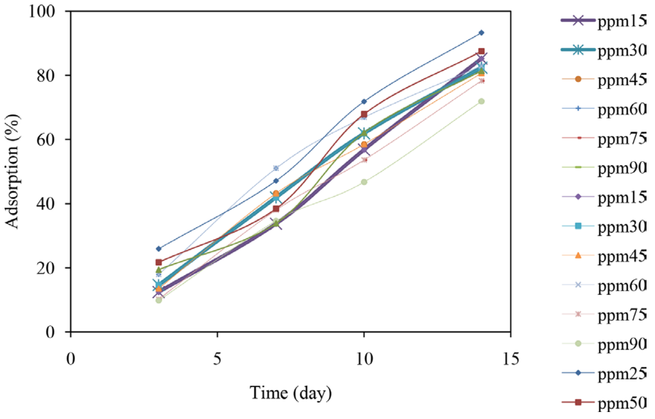

Fig. 1. The effect of the metal ion initial concentration on the adsorption percentage in artificial sewage.

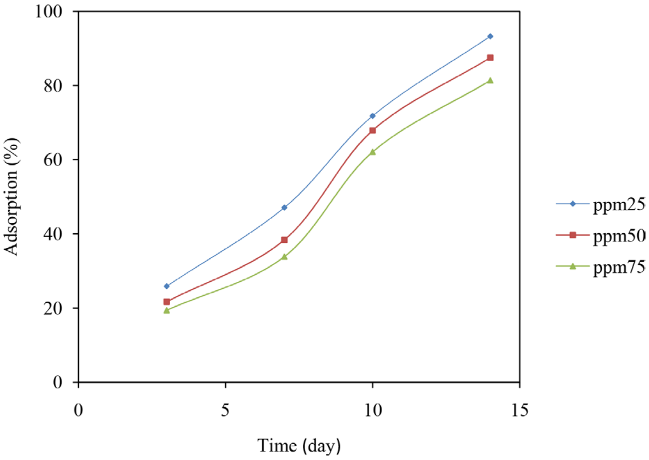

Fig. 2. The effect of the metal ion initial concentration on the adsorption percentage in urban sewage.

thermore, the highest adsorption percentage was achieved in the concentration of 25 pm in the artificial sewage tests, because the micro algae exhibited the maximum growth in the artificial sewage. As mentioned before, the adsorption output increased with contact time. Moreover, it was found that the rate of arsenic adsorption by the micro algae was higher during the growth termination times of the alive algae and this can be attributed to the augmentation of the micro algae present in the sewage which results in a raise in the number of adsorbent active sites. According to Fig. 2, a period of 14 d was selected as the equilibrium time for the arsenic ion adsorption in the sewage by the *Chlorella vulgaris* micro algae.

3.1. The effect of temperature on the adsorption percentage

Temperature is the other important factor influencing the heavy metal ion adsorption process efficiency. The adsorbent capacity depends on the endothermic/exothermic nature of the process. Fig. 3 shows the effect of temperature on the adsorbent efficiency. As it can be seen there is an increase of the arsenic ion adsorption percentage with the temperature from 72% to 96% within 210 min when the temperature increased from 303.15 K to 323.15 K. As it can be seen, there is a positive correlation between the temperature and the kinetic energy of the rest of the ions inside the aqueous solution. By increasing the temperature, the likelihood of affinity of the metal ions to the adsorbent active sites and also their penetration into the adsorbent layers increased which result in the higher adsorption process rates. The most striking result to emerge from these data is that the current adsorption process is endothermic. Therefore, the temperature of 323.15 K was set as the optimum temperature for recovering and removing the arsenic ion from the aqueous solutions by means of *Chlorella vulgaris* micro algae.

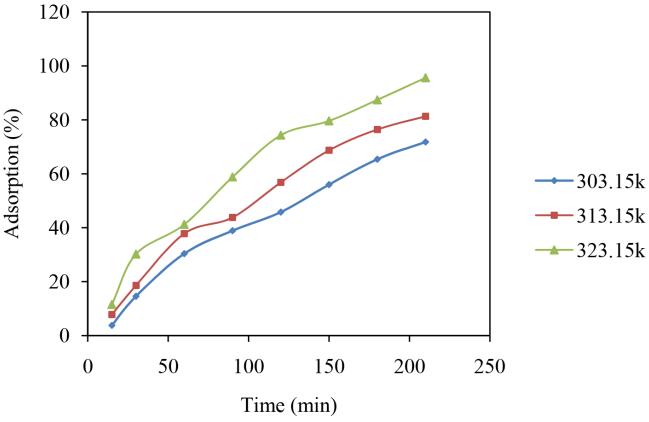

Fig. 3. The effect of temperature on the adsorption percentage.

3.2. The effect of adsorbent dosage on the adsorption output

In this section the adsorbent dosage effect on the adsorption process efficiency is evaluated. The operating conditions for these set of experiments were as the following: the adsorbent dosage range of 1–6 g/l, pH = 6, contact time = 210 min, stirring speed = 200 rpm, temperature of 323.15K, and the arsenic ion initial concentration = 25 ppm. Fig. 4 shows that there was a significant positive correlation between the adsorbent dosage and the adsorption efficiency which was increased from 68.5% to 95%. This can be related to the unsaturated active sites present on the adsorbent surface. Another reason is the rise of the adsorbent active sites as a result of the increase in the adsorbent dosage. Overall, these results indicate that a dosage of 6 g/l was specified as the appropriate and optimum value for recovering and removal of pseudo-metal arsenic ions from the aqueous solution by *Chlorella vulgaris*.

3.3. Bio-adsorption kinetics

Adsorption kinetics is applied to determine the mechanism of control of surficial adsorption processes. This mechanism depends on the physical and chemical characteristics of the adsorbent. In the current research, certain kinetic models such as pseudo-first order and pseudo-second order

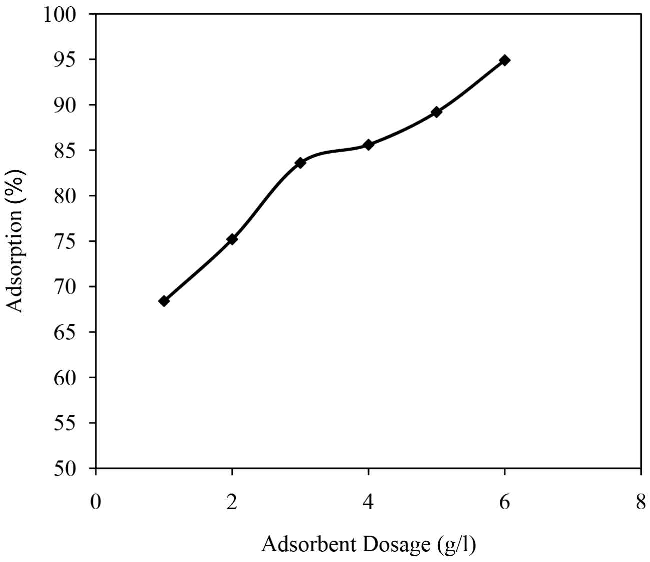

Fig. 4. The effect of adsorbent dosage on the adsorption percentage.

as well as the liquid film penetration were utilized to investigate the kinetics and mechanism of arsenic adsorption by the *Chlorella Vulgaris* micro algae. In order to determine the adsorption kinetics, batch adsorption tests were carried out in temperatures 303.15K, 313.15K, and 323.15K within the time interval 15–210 min.

3.3.1. Pseudo-first order kinetic model

The pseudo-first order kinetic model equation is as the following:

$$\ln\left(q_e - q_t\right) = \ln q_t - k_1 t \tag{3}$$

where q_t is the value of the metal ion adsorbed within a given period of time (mg/g), k_1 is the adsorption rate constant (min^{-1}), and t is time, min.

According to Fig. 5, it can be concluded that the pseudo-first order kinetic model is not capable of describing the kinetic behavior of the current adsorption process, because $q_{e.cal}$ which is calculated by this model is higher than the value obtained from experiments ($q_{e.exp}$). The values of the parameters and constants related to pseudo-first order kinetic model are summarized in Table 3.

3.3.2. Pseudo-second order kinetic model

Pseudo-second order kinetic model is widely applied for the description of adsorption processes. The linear form of the pseudo-second order kinetic model is given by Eq. (4):

$$\frac{t}{q_t} = \frac{1}{\left(k_2 \times q_e\right)^2} + \frac{t}{q_e} \tag{4}$$

where k_2 is the pseudo-second order kinetic model rate constant (g/mg·min). Fig. 6 presents the pseudo-second order linear form for the arsenic ion adsorption by *Chlorella vulgaris*. According to this figure, this kinetic model can describe the current process kinetics appropriately.

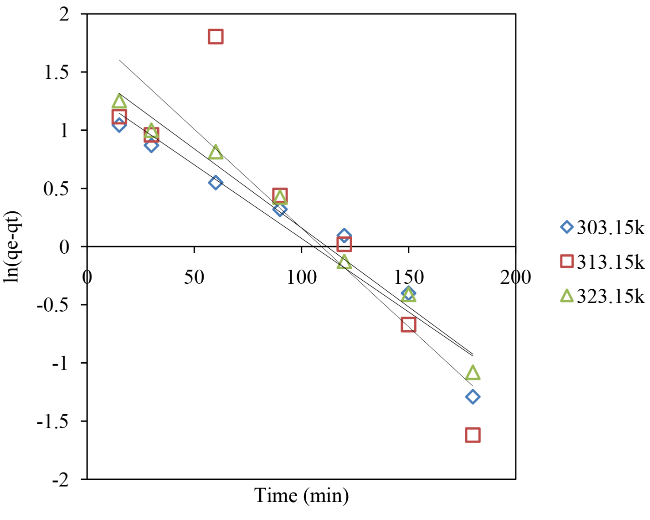

Fig. 5. $\ln(q_e - q_t)$ vs. t in the pseudo-first order kinetic model for the adsorption of arsenic ions by *Chlorella vulgaris* algae.

Table 3
Pseudo-first order, pseudo-second order, and liquid film penetration kinetic model parameters for the adsorption of arsenic ions by *Chlorella Vulgaris* algae

Temperature			Parameters
323.15 K	313.15k	303.15k	
Pseudo-first order kinetic model			
4.6081	5.896	4.943	q_{ecal} (mg/g)
0.4733	0.357	0.3844	K_1 (1/min)
3.98	3.38	3	$q_{e.exp}$ (mg/g)
0.7753	0.9192	0.9702	R^2
Pseudo-second order kinetic model			
3.194	3.096	3.199	$q_{e.cal}$ (mg/g)
0.0676	0.0740	0.0649	K_2 (g/mg.min)
0.9681	0.9679	0.9692	R^2
0.6896	0.7097	0.664	H (mg/g.min)
3.98	3.38	3	$q_{e.exp}$ (mg/g)
Liquid film penetration kinetic model			
0.4593	0.4268	0.3841	k_f
0.9204	0.9158	0.9704	R^2

The average value of the correlation coefficient (R^2) for this model was 0.9684 for the following temperatures: 303.15 K, 313.15 K, and 323.15 K. The values of the other parameters and constants of pseudo-second order kinetic model are also presented in Table 3.

3.3.3. Liquid film penetration

In the present study, the liquid film penetration kinetic model was also used to investigate the kinetic behavior of the arsenic ion adsorption by *Chlorella vulgaris* micro algae. The linear form of this model is as given as:

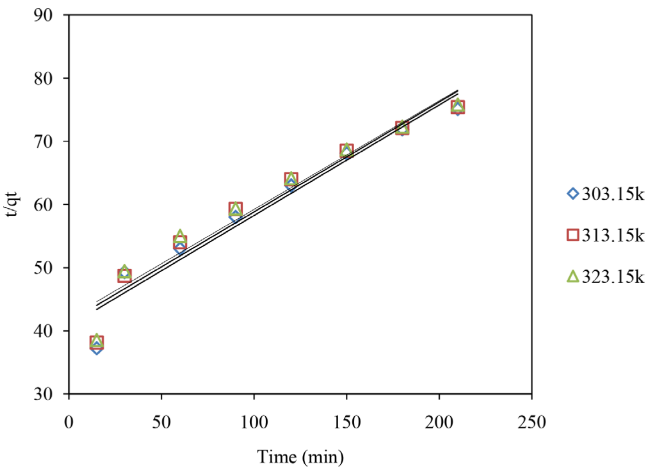

Fig. 6. The linear relation of t/q_t vs. t in the pseudo-second order kinetic model for the adsorption of arsenic ions by *Chlorella vulgaris* algae.

$$\ln\left(1-f\right)=k_{fp}t \tag{5}$$

where k_{fp} is the mass transfer coefficient (min^{-1}) and f is the ratio of q_t/q_e. The parameters of the liquid film penetration kinetic model are also given in Table 3. Based on the data in this table, the liquid film penetration model cannot describe the adsorption kinetics better than the pseudo-second order kinetic model. According to k_f values, mass transfer rate decreases with temperature. The linear relation between *ln(1–f)* and *t* can be observed in Fig. 7.

3.4. Adsorption isotherm

3.4.1. Langmuir isotherm model

Langmuir isotherm model is the most used model for the description equilibrium in the adsorption processes. The linear form of this isotherm is as Eq. (6) [26]:

$$\frac{t}{q_e}=\frac{1}{k_L\times q_{\max}{}^2}\times\frac{1}{C_e}+\frac{1}{q_{\max}} \tag{6}$$

where q_{max} and k_L, which are the Langmuir model constants, are the adsorption capacity (mg/g) and the adsorption energy (L/g), respectively. R_L is another important and effective parameter that expresses the main features of the Langmuir equation. This parameter indicates the state and the quality of the adsorption isotherm model. It is calculated by Eq. (7):

$$R_L=\frac{1}{1+K_LC_0} \tag{7}$$

In this equation, C_0 is the arsenic ion initial concentration (mg/L) in the aqueous solution. The linear relation between l/q_e vs. l/c_e for Langmuir model is depicted in Fig. 8. The results obtained for the adsorption isotherm models for the arsenic ion adsorption are presented in Table 4. According to the obtained results, the maximum value of the adsorption capacity specified for the micro algae used in the current study was 13.07 mg/g and the Langmuir constant was 0.022 g (k_1). Additionally, R_l is equal to 0.645 which indicates that the current adsorption process is in a linear and optimum manner. The correlation coefficient (R^2) for Langmuir isotherm model was 0.8197 which reflects the fact that the aforementioned isothermal model is capable of describing the equilibrium behavior of the process.

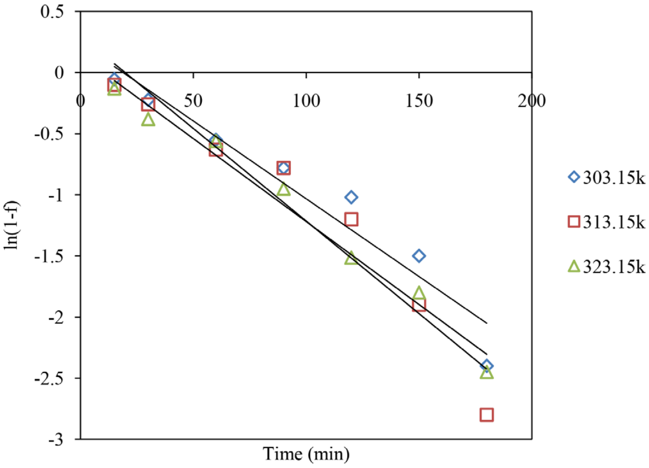

Fig. 7. The linear relation between In(1-*f*) and *t* for the liquid film penetration kinetic model for the adsorption of arsenic ions by *Chlorella vulgaris* algae.

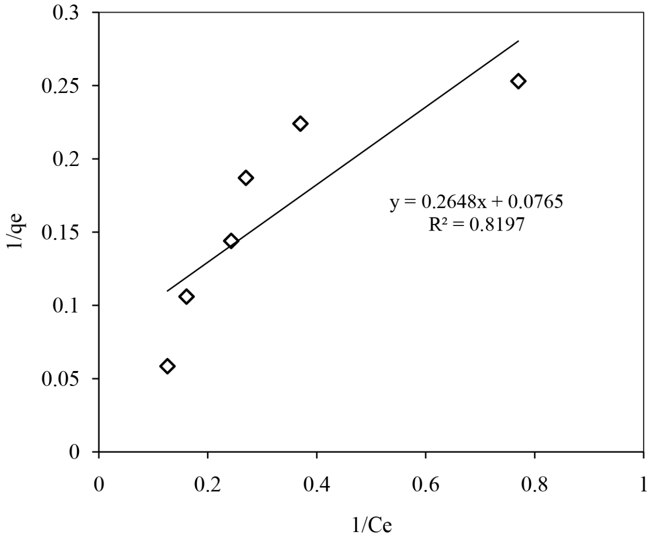

Fig. 8. Linear form of Langmuir model for the adsorption of arsenic ions by *Chlorella vulgaris* algae.

3.4.2. Freundlich isotherm model

Freundlich isotherm model is another isotherm which is frequently used in adsorption studies. It is an empirical model which is applied to describe the organic and inorganic compounds adsorption via various adsorbents. The linear form of this model is as presented in Eq. (8):

$$\ln q_e=\ln k_f+\frac{1}{n}\ln c_e \tag{8}$$

Table 4
Parameters of Langmuir, Freundlich, and Temkin isotherm models for the adsorption of arsenic ions by *Chlorella Vulgaris* algae

Adsorption isotherm	Isotherm constants	Results
Langmuir	K_L (L/g)	0.022
	q_{max} (mg/g)	13.07
	R_L	0.645
	R^2	0.8197
Freundlich	K_f (mg/g)(L/mg)$^{1/n}$	2.515
	n	1.296
	R^2	0.8207
Temkin	A (L mg^{-1})	2.9542
	B_1	0.4554
	R^2	0.918

where k_f and n are the Freundlich model constants that demonstrate the relationship between the adsorption capacity and intensity. Fig. 9 illustrates the results of the linear form of the Freundlich isotherm model for the process of pseudo-metal arsenic ion adsorption by *Chlorella vulgaris* micro algae. The slope value is equal to *1/n* and its intercept determines k_f. The *n*-value in the most of the studies is reported in a range from 1–10. Large *n* values indicate the intensive reaction between the adsorbent and the metal ion, and if *n* is found equal to 1, there is a linear adsorption for the entire adsorbent's active sites [27]. In fact, *n* describes the manner in which the adsorbed material attached to the surface of the adsorbent. *1/n* which varies between 0 and 1 reflects the adsorbent surface heterogeneity. Near zero *n*-values show higher surface heterogeneity. When *n* is equal to 0, then the process is reversible, while $0 < 1/n < 1$ is considered as an optimum range. $1/n > 1$ is the sign of an unfavorable process. The constants and the parameters of Freundlich model are also presented in Table 4. As it can be observed, k_f and *n* are 2.515 mg/g and 1.296 mg/g, respectively. The obtained *n* value shows that the pseudo-metal arsenic ion adsorption by the *Chlorella Vulgaris* micro algae is a physical process. The correlation coefficient (R^2) was 0.8207 which is shows that Freunlich model also can describe the isothermal behavior of the process.

3.4.3. Temkin isotherm model

The main Idea of Temkin isotherm model is that the adsorption energy decreases with the surface coverage. This model is presented in Eqs. (9) and (10):

$$q_e = \frac{RT}{b} \ln AC_e \tag{9}$$

$$q_e = B_1 \ln A + B_1 \ln C_e \tag{10}$$

In these equations B_1, *A*, *R*, and *T* are the Temkin constant which is related to the heat of adsorption (J/mol), Temkin isotherm equilibrium binding constant (L/g), universal gas constant (8.314 J/mol·K), and absolute temperature (*K*), respectively. B_1 and *A* can be determined from the slope and intercept of q_e vs. $\ln C_e$ plot [28].

Fig. 10 and Table 4 reveal the R^2 and the constants of Temkin isotherm model. It can be observed that the correlation coefficient of the current isotherm was higher than R^2 of Langmuir and Freundlich isotherm models, therefore this model is able to describe the adsorption equilibrium of arsenic ions by *Chlorella vulgaris* algae.

3.5. The thermodynamics of adsorption process

In order to investigate the thermodynamic behavior of the arsenic ions adsorption by *Chlorella vulgaris* micro algae, thermodynamic parameters, including enthalpy, entropy, and Gibb's free energy were evaluated. Gibbs free energy is calculated via Eq. (11):

$$\Delta G^\circ = -RTLnK_D \tag{11}$$

Additionally, the enthalpy (ΔH°) and entropy (ΔS°) of the adsorption process can be calculated using Eq. (12):

$$LnK_D = \frac{\Delta s^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{12}$$

where

$$K_D = \frac{q_e}{c_e} \tag{13}$$

where K_D is the distribution coefficient. The findings of thermodynamic study of arsenic ions adsorption by *Chlorella vulgaris* algae are set out in Fig. 11.

As it can be seen, Gibbs free energy was obtained –2.095 kJ/mol, –2.858 kJ/mol, and –3.415 kJ/mol in 303.15K, 313.15K, and 323.15K, respectively. The negative values obtained for Gibbs free energy indicate that the arsenic ions adsorption process by *Chlorella vulgaris* micro algae was a spontaneous process. Since Gibbs free energy increases with temperature, the process was more spontaneous in higher temperatures. The adsorption enthalpy was 1.32 kJ/mol for this process. The positive value obtained for the enthalpy shows that the current adsorp-

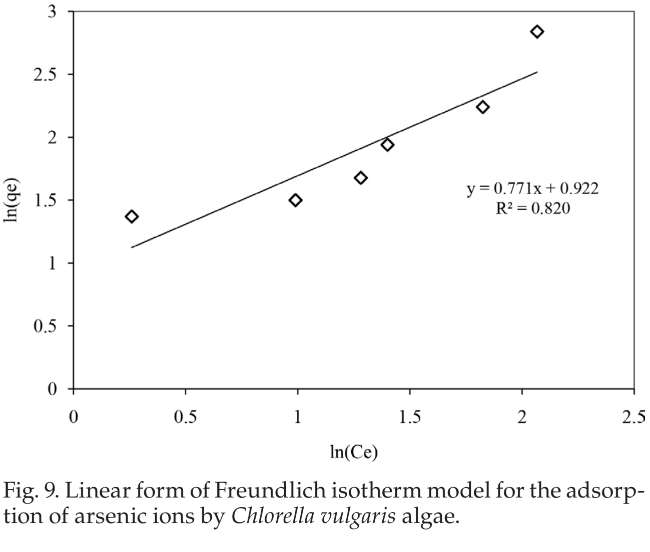

Fig. 9. Linear form of Freundlich isotherm model for the adsorption of arsenic ions by *Chlorella vulgaris* algae.

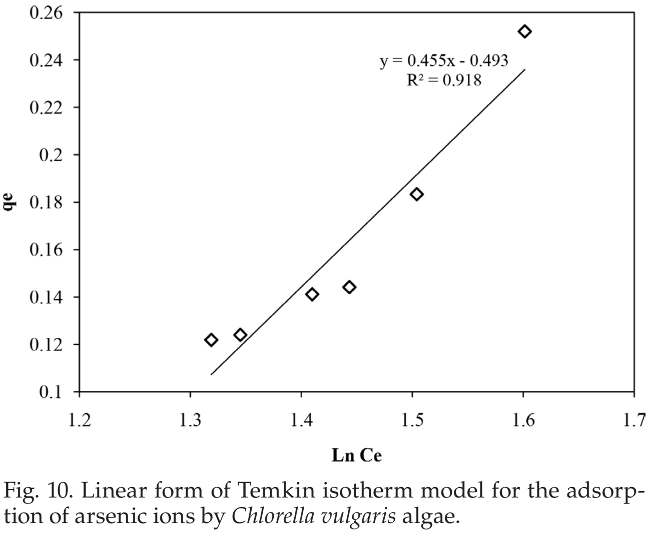

Fig. 10. Linear form of Temkin isotherm model for the adsorption of arsenic ions by *Chlorella vulgaris* algae.

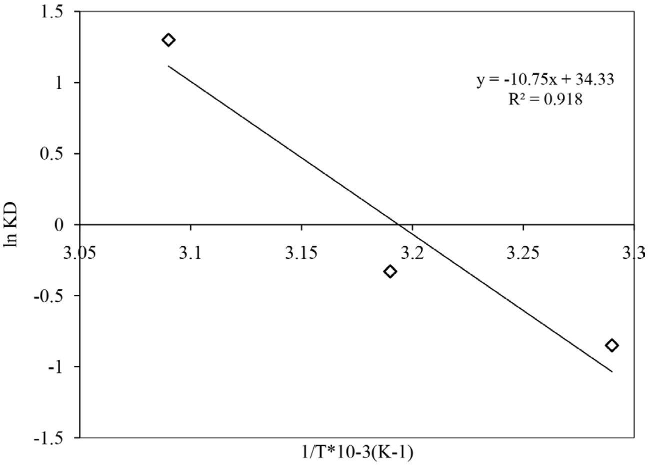

Fig. 11. Thermodynamic parameters for the adsorption of arsenic ions by *Chlorella vulgaris* algae.

tion process was endothermic in the range of 303.15–323.15 K. The positive entropy value (0.00413 kJ/mol·K) shows that the arsenic ions inside the aqueous solution have a more regular distribution compared to the ions adsorbed on the adsorbent surface.

4. Conclusion

In the present study, the adsorption of pseudo-metal arsenic ion from the sewage was conducted using *Chlorella vulgaris* micro algae. The results of the kinetic tests indicated that the adsorption efficiency increased with the contact. The maximum value of adsorption in the present study was 13 (mg/g). To evaluate the kinetic behavior of the process, pseudo-first order, pseudo-second order, and liquid film penetration kinetic models were used. Based on the results, the pseudo-second order kinetic model exhibited a higher accuracy in describing the kinetic behavior of the process in comparison with the other models. Additionally, Langmuir, Freundlich, and Temkin isotherm models were used describe the arsenic adsorption equilibrium. Based on the results, Temkin model was better than the other two models to describe the adsorption equilibrium of arsenic removal from the aqueous solutions. The thermodynamic parameters including the Gibbs free energy and enthalpy were determined, which showed that the arsenic ion adsorption process by *Chlorella vulgaris* micro algae is spontaneous and endothermic. Therefore, according to the obtained results it can be stated that *Chlorella vulgaris*is a favorable micro algae as a bioadsorbent that is highly capable of the adsorption of pseudo-metal arsenic ion from aqueous solutions.

Symbols

A — Temkin constant which is related to the heat of adsorption (J/mol)
B_1 — Temkin isotherm equilibrium binding constant (L/g)
C_0 — Arsenic ion initial concentration in the aqueous solution (mg/L)
C_e — Equilibrium arsenic concentration in mg/l
C_i — Initial and equilibrium arsenic concentration (mg/l)
f — The ratio of q_t/q_e
k_1 — Adsorption rate constant (min^{-1})
k_2 — Pseudo-second order kinetic model rate constant (g/mg·min)
K_D — Distribution coefficient
k_f — Freundlich model constant
k_{fp} — Mass transfer coefficient (min^{-1})
k_L — Adsorption energy (L/g)
n — Freundlich model constant
q_e — Equilibrium value of the adsorbed material per each gram of the biosorbent (mg/g)
q_{max} — Surficial adsorption capacity (mg/g)
q_t — Value of the metal ion adsorbed within a given period of time (mg/g)
R — Universal gas constant (J/mol·k)
R_L — Adsorption intensity
T — Absolute temperature (K)
t Time (min)
V — Solution volume (ml)
W — Mass of the nano-sorbent material (g)
ΔG° — Gibbs's free energy
ΔH° — Enthalpy
ΔS° — Entropy

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