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Biosorption of inorganic and organic arsenic from aqueous solution by *Acidithiobacillus ferrooxidans* BY-3

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ABSTRACT

The traditional techniques for removing low concentration arsenic are unsuitable. The biosorption characteristics of arsenite (iAs^{III}) and monomethyl arsonate (MMA^{V}) from aqueous solution by *Acidithiobacillus ferrooxidans* BY-3 (*At. f* BY-3) were investigated as a function of pH, contact time, initial arsenic concentration, biomass dosage and temperature in this study. Results indicated that Langmuir isotherm model fitted better than Freundlich model to the equilibrium data. Analysis of kinetic data showed that the biosorption processes of both iAs^{III} and MMA^{V} involved pseudo-second-order kinetics. The thermodynamic parameters such as ΔG^{o}, ΔH^{o} and ΔS^{o} of the biosorption process showed that the adsorption of iAs^{III} and MMA^{V} onto *At. f* BY-3 was feasible, spontaneous and endothermic under the examined conditions. The competitive biosorption of iAs^{III} and MMA^{V} in binary mixture system was evaluated, and the results indicated that *At. f* BY-3 favored MMA^{V} biosorption. Fourier-transform infrared spectroscopy (FT-IR) showed –OH and –NH groups were involved in the biosorption process.

1. Introduction

Arsenic is ubiquitous in nature and highly toxic to human. Widespread contamination of drinking water with arsenic has been a global problem and become a great challenge for the engineers, scientists and policy makers. It is estimated that there have been 150 million people at risk in over 70 countries, because of consumption of arsenic contaminated drinking water [1]. The presence of arsenic in natural water is mostly due to natural geologic processes such as weathering reactions, biological activity, and volcanic emissions, as well as anthropogenic activities [2]. Although the arsenic compounds such as additives, pesticides, herbicides, and crop desiccants have decreased significantly in the last few decades, their use is still common and will influence the environment at least locally for some years [3]. In recent years, it has been reported that long-term exposure to arsenic in drinking water can cause skin problems (lesions and keritosis), circulatory problems, degenerative diseases (targeting the respiratory, digestive and nervous systems), and even cancer (targeting bladder, kidney, liver, lungs and skin) in several parts of the world, including USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan, and India [1]. Based on the investigation of the impact of arsenic on human health, various acceptable values of arsenic in drinking water are limited to 10 μg/L (USEPA), 10 μg/L (WHO) and 7 μg/L (NHRMC) [4]. In recent years, arsenic species in environment have long been concerned, among which the inorganic forms, i.e., arsenite (iAs^{III}), arsenious acid (iAs^{III}), arsenate (iAs^{V}), arsenic acid (iAs^{V}) and the organic forms, i.e., monomethyl arsonate (MMA^{V}), dimethylarsinate (DMA^{V}) have been reported to be the main species [5]. It has been shown that iAs^{III} is more toxic than iAs^{V}, and pentavalent organic arsenicals are less toxic than inorganic forms both *in vitro* and *in vivo* [6]. Although most of the arsenic in natural waters is inorganic, the presence of MMA^{V} and DMA^{V} has also been reported [7]. Some studies have shown that organic arsenic species comprise 10–24% of the total arsenic concentration in lake water and groundwater from various places in United States [4].

Although organic forms of arsenic are considered less toxic than inorganic species, methyl arsenics have been identified as carcinogens [8]. Some reports have indicated that the pentavalent organic arsenicals are genotoxic in Chinese hamster lung (V79) cells and human lung cells [9]. Moreover, the study by Nishikawa et al. suggested that MMA^{V} may act as a promoter in liver carcinogenesis [10]. Therefore, removal of arsenic species from natural waters is necessary and important. So far, there are a number of traditional technologies for removal of arsenic from aqueous solutions, including flotation, coagulation–precipitation, adsorption, ion exchange, membrane filtration and electrochemical treatment [11]. Though simple to put into practice, several disadvantages such as high cost, incomplete removal, low selectivity, high energy consumption, and

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the difficulty in eliminating the production of toxic sludge have limited their further developments. More importantly, these methods become especially unsuitable when arsenic concentration in waters is lower than 100 mg/L [12]. Therefore, novel methods of efficient, eco-friendly and low cost for arsenic removal are necessary.

As an alternative to traditional methods, biosorption (or bioadsorption) has been recognized as an effective technique for the treatment of contaminated water. It can be defined as the passive uptake of toxicants by dead/inactive biological materials or by materials derived from biological sources [13]. Mechanisms of biosorption are independent of cell metabolism. They are based on physical or chemical interactions between contaminators and functional groups of the cell wall. The cell wall of organism mainly consists of polysaccharides, lipids and proteins, in which there are many binding sites for metals [3]. Many biosorbent materials have been intensively examined for their applications in biosorption of arsenic, such as fungal biomass, *Moringa oleifera* and green coconut shell [14,15]. *At. f* is a chemolithotrophic acidophilic bacterium that takes in ferrous or reduced inorganic sulfur compounds as energy source. In addition, it is an important member of microbial consortia that is used to recover metals via a process known as bioleaching or biomining [16]. It is resistant to heavy metals and metalloids at concentration in the milligram per liter range, which is considered toxic for other microorganisms. Indeed, some works have suggested that this bacterium has tolerance to arsenic, and the arsenic resistance genes have been found in the chromosome of *At. f* [16]. Although the potential of *At. f* as a biosorbent for various metals, including Ni (II), Cd (II), Zn (II), Pb (II) and Cu (II) has been reported [17–19], there is a remarkable lack of information about the removal of negatively charged arsenic species by *At. f*.

The goal of the present work is to evaluate the feasibility of removal of inorganic and organic arsenic compounds from aqueous solution by a natural biosorbent, *At. f* BY-3. The influences of different factors on arsenic species uptake such as pH of solution, contact time, aqueous arsenic concentration, biomass dosage and temperature were investigated in a series of batch experiments. Various models were tested to investigate the sorption behavior of kinetics and equilibrium. In addition, thermodynamics of the biosorption at various temperatures were also evaluated. FT-IR was used to analyze the interaction of the arsenic species (iAs^{III}, MMA^{V} and iAs^{III}/MMA^{V}) and the cell surface wall. The competitive biosorption of iAs^{III} and MMA^{V} in binary mixture system was also investigated.

2. Materials and methods

2.1. Biosorbent preparation

At. f BY-3 (CCTCC-M203071), which was isolated from the acidic mine drainage at an abandoned copper mine in Baiyin of Gansu, China, was used as a biosorbent in adsorption experiments. The batches were cultured in 9 K medium [20] at pH 2.0, 30 °C, and 150 rpm. After oxidizing 90% of ferrous ions, bacterial culture reached the beginning of the stationary phase [21]. The cultures were centrifuged at 2000 rpm for 15 min to remove the precipitated iron and were centrifuged again at 8000 rpm for 20 min to condense or amplify the concentration of bacteria. Finally, the cells were washed with dilute sulfuric acid (at a pH of 2.0) and deionized doubly distilled water. The cellular quantification was determined by measuring the dry weight of cells, following the procedure reported by Liu et al. [18].

2.2. Solution preparation

Sodium arsenite ($NaAsO_2$, iAs^{III}) was purchased from J.T. Baker (NJ, USA). Sodium monomethyl arsonate ($CH_4AsNaO_3 \cdot (3/2)\ H_2O$, MMA^{V}) was purchased from Quandao Scientific Trade Co. Ltd. (Shanghai, China). Stock solutions (1000 mg/L) of iAs^{III} and MMA^{V} were prepared by dissolving appropriate amounts of $NaAsO_2$ and CH_4AsNaO_3 in distilled deionized water. Solutions requiring lower concentrations were prepared daily by diluting the stock solutions and the pH was adjusted with either 0.1 M HCl or 0.1 M NaOH. All other reagents used in this work were of analytical grade.

2.3. Batch biosorption experiments

All batch experiments were carried out with microorganism suspension in Erlenmeyer flasks on a horizontal water-bath shaker, operating at 150 rpm. To observe the influence of pH, contact time, initial arsenic concentration, biosorbent dose and temperature on biosorption of iAs^{III} and MMA^{V} by *At. f* BY-3, different conditions of pH (2.0–8.0), contact time (10–120 min), initial concentration (500–3000 μg/L), biosorbent dose (2–8 g/L), and temperature (20, 30, 40 °C) were evaluated in this study. The pH of the solutions was adjusted by adding 1.0 M HCl or 1.0 M NaOH. Each experiment was run for 120 min to establish biosorption equilibrium. A control was also run under similar conditions with the aqueous solutions. After the isothermal equilibration, 1 mL biosorption suspension samples were centrifuged at 10,000 rpm for 10 min and the supernatant liquid was analyzed for residual arsenic content. All experiments were performed in triplicate and the average values were reported.

Competitive biosorption of iAs^{III} and MMA^{V} by *At. f* BY-3 in binary arsenic mixture system was investigated at six different initial concentrations of iAs^{III} and MMA^{V}; namely, 500, 1000, 1500, 2000, 2500, and 3000 μg/L. All the experiments were conducted at pH 4.0, 30 °C, and biomass dose 2 g/L for 120 min.

2.4. Analysis

The concentration of arsenic (iAs^{III} or MMA^{V}) in the single-component solution before and after the equilibrium was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES, IRIS Advantage ER/S, Thermo Jarrell Ash, USA).

Species-specific analysis of iAs^{III} and MMA^{V} concentrations in binary mixture system were performed by Capillary Electrophoresis System (CE, P/ACE MDQ, Beckman Coulter, USA) equipped with a reversible-polarity power supply (0 to (±30) kV) and a photodiode-array detector coupled to the 32 Karat software for data acquisition and evaluation. The separation and determination of iAs^{III} and MMA^{V} were achieved by capillary zone electrophoresis (CZE) using an uncoated fused-silica capillary (60 cm by 75 μm i.d.) with a buffer consisting of 20 mM borate and 0.5 mM cetyltrimethylammonium bromide (CTAB) at pH 9.5 and direct UV detection at 195 nm. The applied voltage was −20 kV and the capillary temperature was kept constant at 25 °C [22].

The adsorption capacity of the biomass at the corresponding equilibrium conditions was obtained by a mass balance equation as in Eq. (1) and the removal efficiency of arsenic ion was calculated by Eq. (2).

$$q_e = \left[\frac{C_i - C_e}{m}\right] V \quad (1)$$

$$R = \left[\frac{C_i - C_e}{C_i}\right] \times 100\% \quad (2)$$

where q_e and R are the equilibrium arsenic uptake capacity (μg/g) and removal efficiency (%), respectively, C_i and C_e are the initial and equilibrium arsenic concentrations (μg/L), m is dry net biosorbent weight (g), and V is the working volume of the adsorption sample (mL).

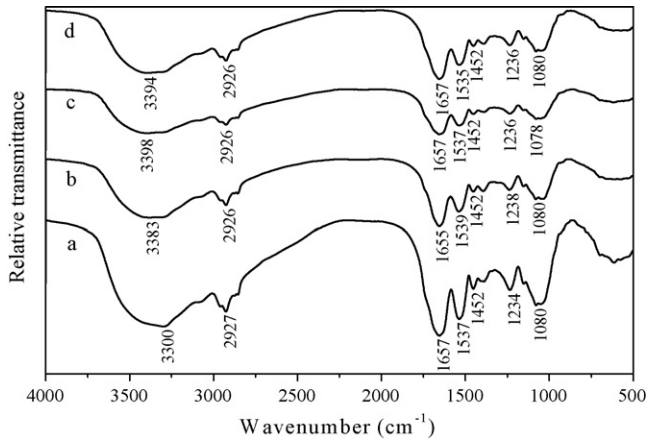

Fig. 1. FT-IR spectra of *At. f* BY-3 prepared in KBr disks: (a) pristine; (b) iAs^{III}-loaded; (c) MMA^{V}-loaded; (d) iAs^{III}/MMA^{V}-loaded biomass.

To investigate the main functional groups involved in arsenic biosorption using the IR spectroscopy, bacteria were pelleted by centrifugation at 10,000 rpm for 10 min and dried in an oven at 50 °C for 24 h. Approximately 1 mg of finely crushed sorbent was encapsulated in 300 mg of KBr (Sigma, USA). The FT-IR spectra were recorded in KBr disks using a Fourier-Transform Infrared Spectrometer (FT-IR, NEXUS 670, Thermo Nicolet, USA) over the wave number range of 500–4000 cm^{-1} under ambient conditions. Infrared spectra of *At. f* BY-3 with or without adsorbed arsenic were obtained.

3. Results and discussion

3.1. Fourier-transform infrared (FT-IR) spectra

The FT-IR spectra of *At. f* BY-3 in virgin form and loaded with arsenic were taken to obtain information on the nature of the possible cell–arsenic ions interactions (Fig. 1). The FT-IR spectrum at 3300 cm^{-1} was indicative of the existence of –OH and –NH groups of the biomass [23]. The group of bands at 2927 and 1452 cm^{-1} were attributable to –CH stretching modes, which indicate the presence of $–CH_2$ and –CH groups [24]. The peaks observed at 1657 cm^{-1} (mainly C=O stretching) and 1537 cm^{-1} (mainly –NH stretching) can be attributed to amide I and amide II bands of protein peptide bonds [25]. The bands centered around 1234 cm^{-1} can be assigned to the $–SO_3$ stretching and the bands observed at 1080 cm^{-1} can be attributed to the –CN stretching vibration of the protein fractions [26].

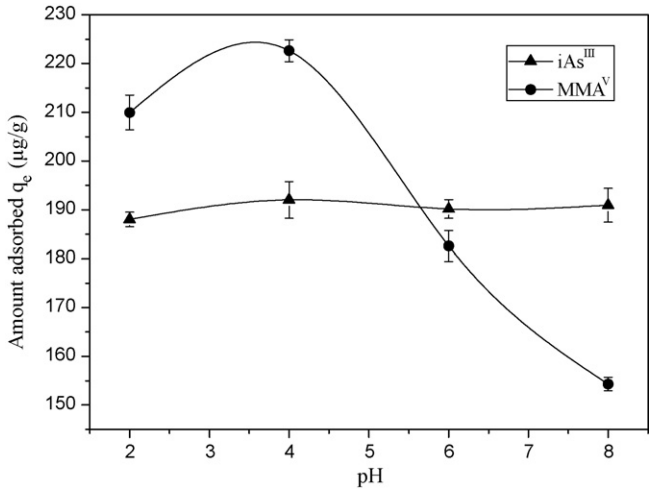

Fig. 2. Effect of pH on biosorption capacity of *At. f* BY-3 for iAs^{III} and MMA^{V} (arsenic concentration: 500 μg/L; biomass dose: 2.0 g/L; contact time: 120 min; temperature: 30 °C). Error bars indicated standard deviation.

Fig. 1 (spectra b–d) shows the changes in the FT-IR spectrum of the biomass after adsorption of iAs^{III}, MMA^{V} and iAs^{III}/MMA^{V}, respectively. After loading with iAs^{III}, the peaks at 3300, 2927, 1657, 1537 and 1234 cm^{-1} were shifted to 3383, 2926, 1655, 1539 and 1238 cm^{-1}, respectively. After interaction with MMA^{V}, the transmittance at 3300, 2927, 1234 and 1080 cm^{-1} were shifted to 3398, 2926, 1236 and 1078 cm^{-1}, respectively. After being loaded with iAs^{III}/MMA^{V}, the bands at 1657, 1234 and 1080 cm^{-1} groups were almost invariant, while the peaks at 3300, 2927 and 1537 cm^{-1} were shifted to 3394, 2927 and 1535 cm^{-1}. It was found that the FT-IR data did not show any significant change except at 3300 cm^{-1}. These results indicate that the presence of functional groups on the surface of the biomass able to interact with arsenic ions, and the mechanism of iAs^{III}, MMA^{V} and iAs^{III}/MMA^{V} adsorption was dependent on functional groups especially the –OH and –NH groups.

3.2. Effect of pH

Earlier studies have shown that pH is a critical parameter affecting the biosorption process [27]. It is well known that the pH can strongly influence the solution chemistry of the sorbates, the activity of functional groups on the biomass cell walls, as well as the competition of sorbates for the binding sites. The effect of pH on the biosorption of iAs^{III} and MMA^{V} by *At. f* BY-3 is graphically presented in Fig. 2. It can be seen from the figures that the adsorption of iAs^{III} did not vary significantly over a pH range of 2.0–8.0, whereas the adsorption of MMA^{V} attained a maximum value at pH 4.0. This was attributed to the properties of both biomass and arsenic.

The cell wall matrix of *At. f* contains complex heteropolysaccharides that can provide amino, amide and carboxyl groups, and its structure is intact compared with other biomass in acidic environment [28]. *At. f* grown with ferrous ion exhibited an isoelectric point (IEP) at about pH 2.0 [29]. At pH values below the IEP, it is expected that the bacterial cells would be positively charged, and the cells could became increasingly negative as the pH increased [29]. However, arsenic biosorption was determined not only by the properties of functional groups present on the biomass surface, but also by the chemical speciation of arsenic in the solution, arsenic in aqueous solution tends to hydrolyze depending on the solution pH. In the experimental pH range of 2.0–8.0, the predominant form of iAs^{III} is uncharged H_3AsO_3 [30]. Although this species cannot undergo electrostatic interaction with the adsorbent, it can interact with the unprotonated amino groups [31]. Below pH 4.0, adsorption decreased slightly, as shown in Fig. 2. This can be correlated to the maximum dissociation of arsenic acid at pH equal to the pK_a value of 2.2, and the adsorption capacity usually decreased at pH values less than pK_a [32]. Below pH 2.6, the predominant MMA^{V} was $CH_3AsO(OH)_2$, while $CH_3AsO(OH)O^-$ dominated at a pH range between 2.6 and 8.2 [33]. As displayed in Fig. 2, it was observed that MMA^{V} uptake increased with decreasing pH values within the range of 4.0–8.0. This was attributed to the interaction between the negatively charged arsenate ion and the positively charged amino acids and hydroxyl groups on the surface of biomass. At pH 2.0, the adsorptive capacity decreased, even though the biomass surface was positively charged and the arsenate species were negatively charged. This was attributed to a lack of electrostatic attraction between the biomass surface and the protonated arsenate species in the pH below 4.0. With the increase of pH, the biomass may be negatively charged by adsorbing hydroxyl ions or by ionization of acidic functional groups such as $–SO_3$ groups on the surface, or both. So a repulsive force, which results in a decrease in adsorption, may

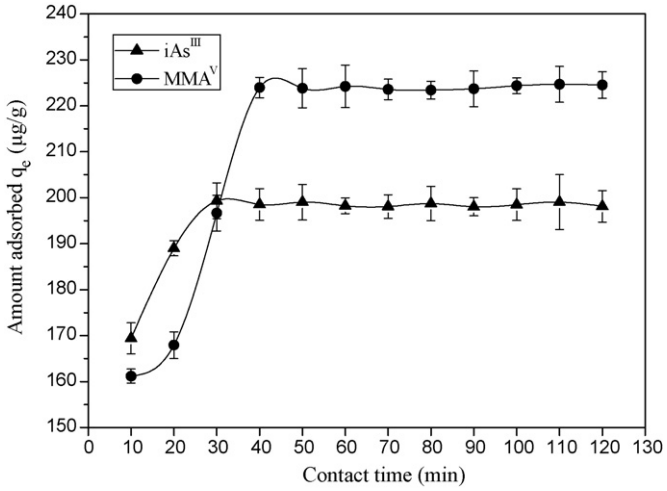

Fig. 3. Effect of contact time on biosorption capacity of *At. f* BY-3 for iAs^{III} and MMA^{V} (arsenic concentration: 500 μg/L; biomass dose: 2.0 g/L; pH 4.0; temperature: 30 °C). Error bars indicated standard deviation.

develop between the negatively charged surface and the anions. The effect of pH may be further explained in relation to the competition effect between OH^- and arsenic ions. As pH increases, the competing effect of OH^- increases and OH^- occupies the binding sites on the cell walls. As a result, the arsenic biosorption capacity is decreased. The same trend has been observed by several researchers who investigated the effect of pH on biosorption of As(III) and As(V) with use of different kinds of sorbents [31,34]. Fig. 2 shows that the greatest biosorption capacity for iAs^{III} and MMA^{V} was 192.02 and 222.64 μg/g at pH 4.0, respectively. The higher adsorption capacity for MMA^{V} may be attributed to the stronger interaction between arsenic ions and biosorbent through electrostatic attraction with each other.

3.3. Effect of contact time and sorption kinetics

A high efficient sorbent can be characterized by a rapid uptake rate that gives a short equilibrium time indicating its potential for successful practical application. Fig. 3 shows the effect of contact time on arsenic biosorption capacity by *At. f* BY-3. It has been observed that adsorption capacity increased with increasing reaction time, until the state of equilibrium was reached due to the saturation of available sites present on biomass surface. The maximum uptake took place within 60 min and the adsorption capacity were 199.34 and 223.97 μg/g for iAs^{III} and MMA^{V}, respectively. The data obtained from this experiment showed that a contact time of 30 min for iAs^{III} and 40 min for MMA^{V} was sufficient to achieve equilibrium.

In order to investigate the mechanism of the biosorption process, the Lagergren pseudo-first-order and Ho's pseudo-second-order [35] models were introduced to analyze adsorption kinetic data in this study. Base on the poor values of correlation coefficient R^2, the results of the Lagergren pseudo-first-order were not included in this paper. The linear equation of the Ho's pseudo-second-order model is given in Eq. (3):

$$\frac{t}{q_t} = \frac{1}{K_{2,\mathrm{ads}} q_\mathrm{e}^2} + \frac{t}{q_\mathrm{e}} \tag{3}$$

where q_e is the amount of adsorbate adsorbed from aqueous solution at equilibrium (μg/g), q_t is the mass of adsorbate sorbed on the biomass at any time t (min), and $K_{2,ads}$ is the pseudo-second-order rate constant (g/μg min).

The kinetic parameters were obtained from pseudo-second-order kinetic model by linear regression analysis using Origin Pro

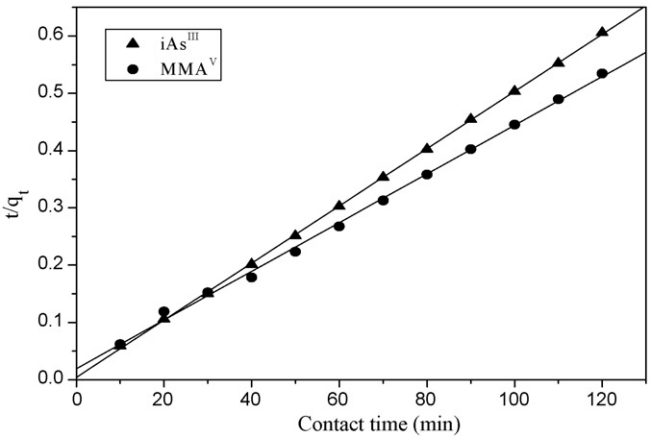

Fig. 4. Linearized pseudo-second-order kinetic plots for iAs^{III} and MMA^{V} biosorption onto *At. f* BY-3.

7.5. The linear plots of t/q_t versus t for the pseudo-second-order model for the biosorption of iAs^{III} and MMA^{V} are shown in Fig. 4. The values of parameters for the biosorption of iAs^{III} and MMA^{V} are given in Table 1. It was observed that the values of correlation coefficient R^2 for the pseudo-second-order model for iAs^{III} and MMA^{V} adsorption were 0.9999 and 0.9989, respectively. Moreover, the calculated $q_{e2,cal}$ values of the pseudo-second-order kinetic model for the *At. f* BY-3 were close to the experimental $q_{e,exp}$ values. Therefore, it can be concluded that the pseudo-second-order adsorption model is suitable to describe the adsorption kinetics of iAs^{III} and MMA^{V} onto *At. f* BY-3. It has also been reported that the experimental data well fit the pseudo-second-order adsorption model on the biosorption of arsenic on the different biosorbent such as coryneform mutant strains and macrofungus (*Inonotus hispidus*) [23,36].

3.4. Effect of initial arsenic concentration and biosorption isotherms

The effects of initial arsenic concentration on biosorption capacity of biomass and removal efficiency of arsenic by *At. f* BY-3 are shown in Fig. 5. The data showed that, with the increase of initial concentration from 500 to 3000 μg/L, the amount adsorbed increased from 194.26 to 277.22 μg/g for iAs^{III} and from 225.05 to 323.85 μg/g for MMA^{V}, respectively. However, the removal efficiency decreased from 77.7 to 18.48% for iAs^{III} and from 90.02 to 21.59% for MMA^{V}. Slight changes in the biosorption capacity of *At. f* BY-3 were observed when the initial iAs^{III} and MMA^{V} concentration was over 2500 and 2000 μg/L, respectively. Furthermore, the extent of arsenic removal was found to change slowly. The decrease in percentage biosorption with the increase of initial concentration may be attributed to a lack of sufficient available sites present on biomass surface to accommodate much more metal in the solution. In the case of lower initial concentration, all arsenic species could interact with the active sites, and thus the removal efficiency was higher. On the other hand, the biosorption capacity showed a decreasing trend due to the decrease in diffusion coefficient and decreased mass transfer coefficient of arsenic species at lower concentration levels. With the increase of initial concentra-

Table 1
Kinetic parameters obtained from pseudo-second-order for iAs^{III} and MMA^{V} biosorption onto *At. f* BY-3.

Adsorbate	$q_{e,exp}$ (μg/g)	$q_{e2,cal}$ (μg/g)	$k_{2,ads}$ (g/μg min)	R^2
iAs^{III}	199.34	200.40	0.0009	0.9999
MMA^{V}	224.66	235.29	0.0060	0.9989

Table 2
Equilibrium constants obtained from Langmuir and Freundlich isotherms for iAs^{III} and MMA^{V} biosorption onto *At. f* BY-3.

Adsorbate	$q_{e,exp}$ (μg/g)	Langmuir			Freundlich		
		q_m (μg/g)	B (L/μg)	R^2	K_f (μg/g)	n	R^2
iAs^{III}	277.22	293.25	0.0054	0.9986	81.73	6.419	0.9901
MMA^{V}	323.85	333.33	0.0115	0.9987	148.09	9.941	0.9565

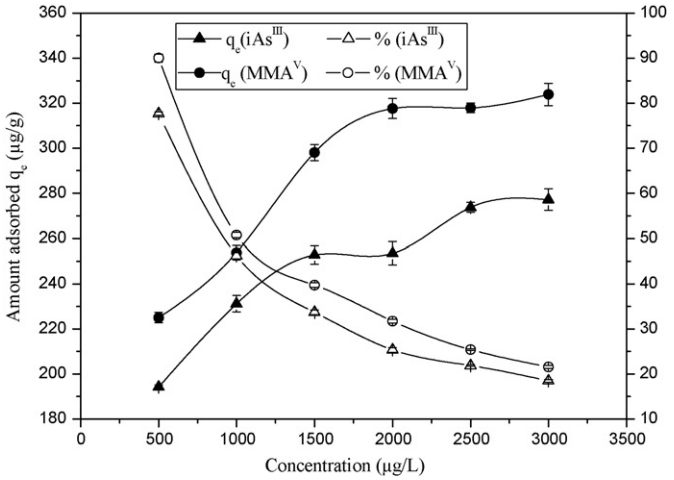

Fig. 5. Effect of initial arsenic concentration on biosorption capacity and removal efficiency of *At. f* BY-3 for iAs^{III} and MMA^{V} (biomass dose: 2.0 g/L; contact time: 120 min; pH 4.0; temperature: 30 °C). Error bars indicated standard deviation.

tions, the mass transfer driving force of the arsenic species between the aqueous solution and biosorbent phases increased, which lead to an increase in arsenic biosorption [37], while more and more unabsorbed arsenic ions were left in solution due to the saturation of active sites, resulting in a lower removal efficiency. Similar results were found by using different kinds of absorbent for the biosorption of arsenic (V) [38].

In order to examine the biosorption mechanism and surface properties of the biomass, two sorption isotherm models, i.e., Langmuir and Freundlich models were employed to analyze the experimental data.

The Langmuir model assumed a monolayer adsorption occurring on homogeneous surface of the adsorbent. Its linearized form can be represented as follows [39]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

where C_e is equilibrium concentration (μg/L), q_e is amount of arsenic adsorbed at equilibrium (μg/g) and q_m (μg/g) and b (L/μg) are Langmuir constants.

Fig. 6 shows the linear plots of C_e/q_e versus C_e for iAs^{III} and MMA^{V}, respectively. The values of the parameters were calculated from the slope and intercept of the plots were presented in Table 2. Adsorption capacity and correlation coefficients values for iAs^{III} and MMA^{V} were found to be very high (>0.998) for *At. f* BY-3 (Table 2).

Furthermore, a dimensionless parameter called separation factor (R_L) was used to test the favorability of biosorption [40].

$$R_L = \frac{1}{1 + bC_i} \quad (5)$$

where C_i is initial arsenic concentration (μg/L) and b is the Langmuir constant (L/μg). R_L values indicate whether the isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L < 0$). The values of R_L are between 0 and 1 for both iAs^{III} and MMA^{V} at different initial concentrations tested (Table 3), which confirmed the favorable adsorption of iAs^{III} and MMA^{V} by *At. f* BY-3.

A comparison of the maximum biosorption capacity of *At. f* BY-3 for iAs^{III} and MMA^{V} obtained in this study with other sorbents reported in the literature [23,30–32,36,41–48] is given in Table 4. The biosorption capacity of *At. f* BY-3 for iAs^{III} is of the same order of magnitude or higher than that reported for other biosorbents. Although the biosorption capacity of *At. f* BY-3 for MMA^{V} is lower than that reported for other sorbents, *At. f* BY-3 biomass was found to be promising for MMA^{V} biosorption due to its eco-friendly and low cost. These results indicate that *At. f* BY-3 has considerable potential for the bioremoval of iAs^{III} and MMA^{V} from aqueous solution.

The Freundlich isotherm used for modeling the adsorption on heterogeneous surfaces and linearized form of the model is as follows [39]:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (6)$$

where K_f is Freundlich constant indicating adsorbent capacity (μg/g dry weight) and n is related to the adsorption intensity of the adsorbent. The linear plots of $\log q_e$ versus $\log C_e$ for iAs^{III} and MMA^{V} (Fig. 7) were drawn to calculate the values of K_f, n and R^2, which were given in Table 2. The high values of K_f and n showed a high feasibility of iAs^{III} and MMA^{V} biosorption. Moreover, the K_f value for MMA^{V} was higher than that for iAs^{III}, suggesting that the arsenic binding affinity could be in the order $MMA^{V} > iAs^{III}$.

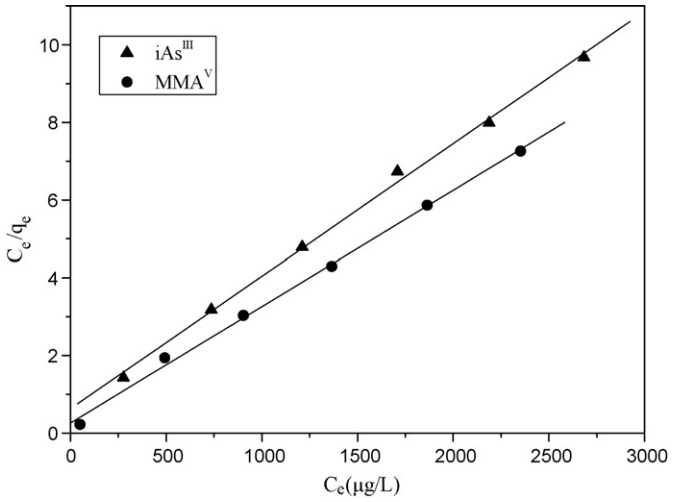

Fig. 6. Langmuir isotherms for iAs^{III} and MMA^{V} biosorption onto *At. f* BY-3.

Table 3
Values of separation factor (R_L) for iAs^{III} and MMA^{V} biosorption onto *At. f* BY-3.

Initial concentration (μg/L)	iAs^{III}	MMA^{V}
500	0.2703	0.1481
1000	0.1563	0.0800
1500	0.1099	0.0548
2000	0.0847	0.0417
2500	0.0689	0.0336
3000	0.0581	0.0282

Table 4
Comparison of biosorption capacity (mg/g) of *At. f* BY-3 for iAs^{III} and MMA^{V} with that of various sorbents.

Sorbent	iAs^{III}	pH	MMA^{V}	pH	Reference
Natural laterite	0.2000	7.2	–	–	[41]
Synthetic iron sulfide	0.3100	6.5	–	–	[42]
Degussa P25 TiO_2	12.900	6.8	6.4500	6.8	[43]
Fe-oxide impregnated activated carbon	0.0900	7.0	–	–	[30]
Hydrous ferric oxide incorporated diatomite	267.00	7.0	126.00	7.0	[44]
Iron filings	1.5000	–	0.6500	–	[45]
Ferrihydrite	–	–	233.00	4.0	[46]
Goethite	–	–	12.600	4.0	[46]
Activated alumina	–	–	15.000	5.0	[47]
Sulfate-reducing bacteria produced precipitate	0.1970	6.5	–	–	[42]
Momordica charantia	0.8800	9.0	–	–	[48]
Inonotus hispidus	51.900	6.0	–	–	[23]
Chitosan-coated biosorbent	56.500	4.0	–	–	[31]
Corynebacterium glutamicum mutant strains	0.0154	–	–	–	[36]
Atlantic Cod fish scale	0.0267	4.0	–	–	[32]
Acidithiobacillus ferrooxidans	0.2930	4.0	0.3330	4.0	This study

The high value of R^2 (>0.956) between the biosorbent-arsenic systems for two adsorption models (Table 2) indicated the high applicability of iAs^{III} and MMA^{V} biosorption by *At. f* BY-3. Between Langmuir and Freundlich models, the values of R^2 for Langmuir adsorption isotherm were greater than that of Freundlich. Furthermore, the calculated q_e values obtained from Langmuir sorption isotherm were very close to the experimental q_e. These indicated that Langmuir isotherm fitted better than the Freundlich isotherm to the experimental data. This suggests the presence of homogeneous active sites on biomass surface and biosorption process of arsenic through monolayer formation.

3.5. Effect of biosorbent dose

The influence of biosorbent dose on biosorption capacity of *At. f* BY-3 and removal efficiency of arsenic from aqueous solution was investigated by using different biomass dosage in the range of 2–8 g/L (Fig. 8). The extent of iAs^{III} and MMA^{V} removal increased with increasing biosorbent dose, while the uptake capacity decreased. The removal efficiency was found to be 69.47% for iAs^{III} and 75.6% for MMA^{V}, when the biomass dose was 2 g/L. It increased to 74.38% for iAs^{III} and 92.72% for MMA^{V}, respectively, when the biomass dose was 6 g/L. It was observed that the removal efficiency of arsenic changed slowly when the biomass concentration was over 6 g/L. However, q_e decreased from 173.68 to 61.98 μg/g for iAs^{III} and from 189 to 77.27 μg/g for MMA^{V}, respectively, when biosorbent concentration increased from 2 to 6 g/L. Although the biomass with higher concentration can provided more sites available for biosorption as well as greater surface area to interact hence removal efficiency increases, the sorption capacity was actually reduced due to partial aggregation of biomass, which resulted in a decrease in effective surface area for the biosorption [49]. Similar results have been observed in a number of studies reported previously [50].

3.6. Effect of temperature and thermodynamics

Fig. 9 shows the effect of temperature on the equilibrium biosorption of iAs^{III} and MMA^{V} by *At. f* BY-3 from aqueous solution at three different temperatures (20, 30 and 40 °C). As the temperature increased from 20 to 40 °C, the biosorption capacity increased from 166.89 to 205.73 μg/g for iAs^{III} and from 201.96 to 233.58 μg/g for MMA^{V}, indicating that the temperature might be an important factor for energy dependent mechanisms in metal biosorption by microbial cells. The increase in adsorption with increasing temperature may be attributed to either creation of some new sorption sites on the sorbent surface or the increase in the intraparticle diffusion rate of sorbate. Thereafter, the greater biosorption would be observed at higher temperature.

In general, the biosorption process depended on temperature is associated with several thermodynamic parameters. Thermo-

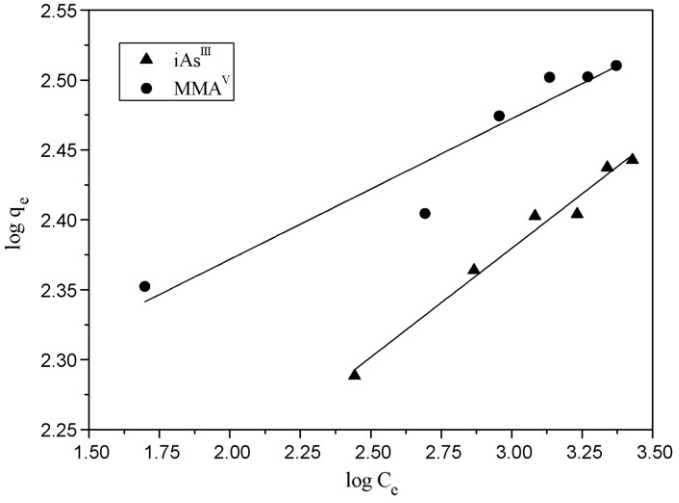

Fig. 7. Freundlich isotherms for iAs^{III} and MMA^{V} biosorption onto *At. f* BY-3.

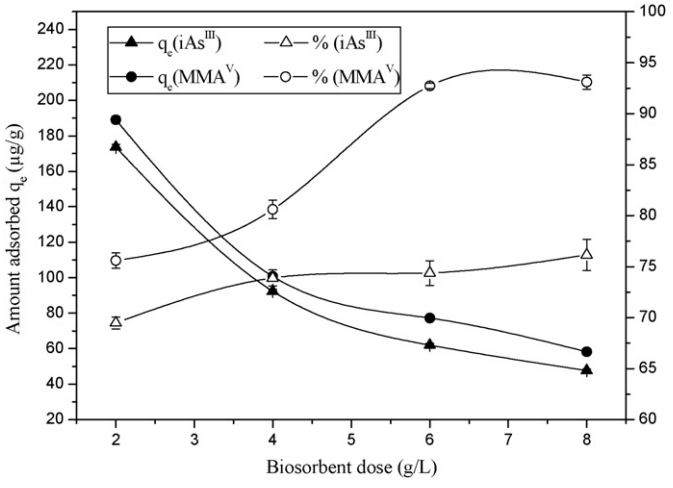

Fig. 8. Effect of biosorbent dose on biosorption capacity and removal efficiency of *At. f* BY-3 for iAs^{III} and MMA^{V} (arsenic concentration: 500 μg/L; contact time: 120 min; pH 4.0; temperature: 30 °C). Error bars indicated standard deviation.

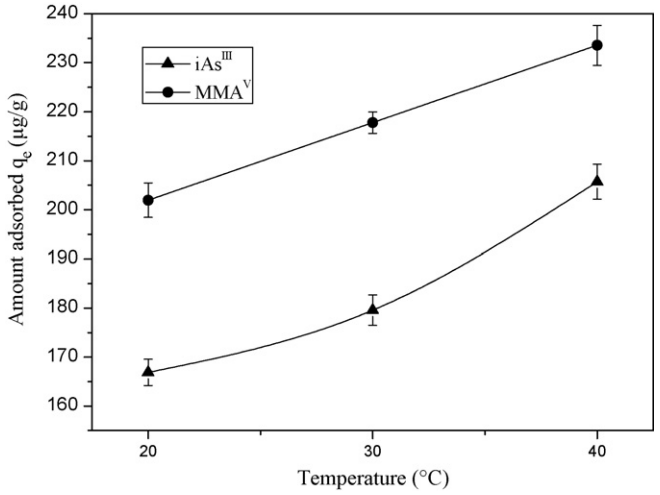

Fig. 9. Effect of temperature on biosorption capacity of *At. f* BY-3 for iAs^{III} and MMA^{V} (arsenic concentration: 500 μg/L; biomass dose: 2.0 g/L; contact time: 120 min; pH 4.0). Error bars indicated standard deviation.

dynamic parameters such as Gibbs free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were calculated from the following equations [51]:

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

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

where R is the universal gas constant (8.314×10^{-3} kJ/(mol K)); T is the absolute temperature (K); and K_D (q_e/C_e) is the distribution coefficient. ΔG^o were obtained from Eq. (7), ΔH^o and ΔS^o were estimated from the slope and intercept of the plot of $\ln K_D$ against $1/T$ (Fig. 10). The values of these parameters are given in Table 5.

The negative values of ΔG^o implied that the biosorption of iAs^{III} and MMA^{V} onto *At. f* BY-3 was spontaneous. The ΔH^o values of iAs^{III} and MMA^{V} were positive, indicating that biosorption was endothermic. This was also supported by the increase in the arsenic adsorption capacity of *At. f* BY-3 with the rise in temperature. It was observed that the ΔH^o values of iAs^{III} (32.20 kJ/mol) and MMA^{V} (46.89 kJ/mol) ranged from 20.9 to 418.4 kJ/mol [52], implying that chemisorption might be contributing to the uptake of iAs^{III} and MMA^{V} onto *At. f* BY-3. The positive value of ΔS^o suggested

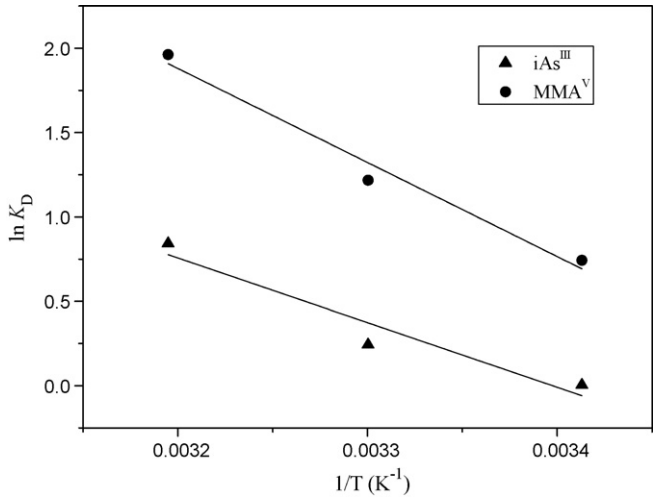

Fig. 10. Plots of $\ln K_D$ against $1/T$ for the estimation of thermodynamic parameters for iAs^{III} and MMA^{V} biosorption onto *At. f* BY-3.

Table 5
The thermodynamic parameters for iAs^{III} and MMA^{V} biosorption onto *At. f* BY-3.

Adsorbate	T (°C)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J/(k mol))
iAs^{III}	20	−0.01	32.20	0.11
	30	−0.61		
	40	−2.19		
MMA^{V}	20	−1.81	46.89	0.17
	30	−3.06		
	40	−5.10		

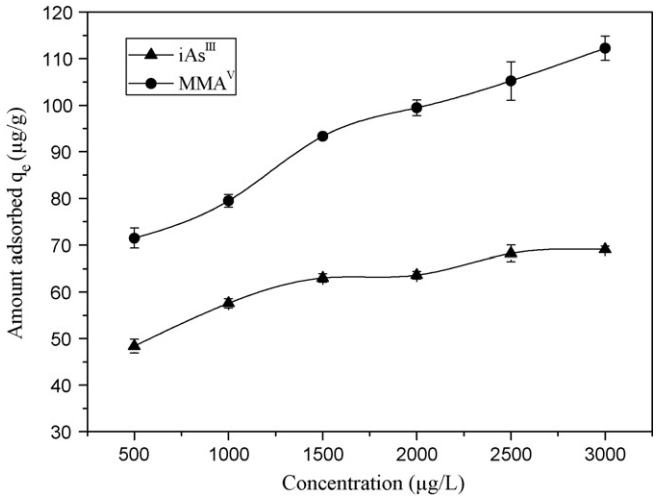

Fig. 11. Competitive biosorption in the binary mixture of iAs^{III} and MMA^{V} by *At. f* BY-3 (arsenic concentration: 500 μg/L; contact time: 120 min; pH 4.0; temperature: 30 °C). Error bars indicated standard deviation.

the increase randomness at the solid/solution interface during the biosorption of arsenic ions onto *At. f* BY-3.

3.7. Competitive biosorption for iAs^{III} and MMA^{V}

Generally, waste water contains more than single arsenic species, and the presence of more than one type of arsenic ions causes competitive sorption on sorbent [53]. The results of biosorption for the binary mixture of iAs^{III} and MMA^{V} on *At. f* BY-3 biomass are shown in Fig. 11. In this study, it was observed that the biomass was favorable to sorption of MMA^{V}. The maximum biosorption capacity of MMA^{V} adsorbed was higher than that of iAs^{III} adsorbed. At low arsenic concentrations, both iAs^{III} and MMA^{V} adsorbed to the biomass. However, with the increase of arsenic concentrations, the sorption capacity of iAs^{III} adsorbed did not increase substantially, while that of MMA^{V} increased greatly. It was also observed that when arsenic concentration exceeded 2500 μg/L, the iAs^{III} biosorption capacity no longer increased.

4. Conclusions

The biosorption process has been shown to be affected by pH, contact time, initial arsenic concentration, biomass dose, and temperature. The pH significantly influenced the biosorption of MMA^{V} whereas did not significantly affect the biosorption of iAs^{III}. The adsorption process was rapid and maximum sorption capacities were achieved within 30 min for iAs^{III} and 40 min for MMA^{V}. The iAs^{III} and MMA^{V} adsorption capacity increased with increase in initial arsenic concentration and experimental temperature, but decreased with increasing biosorbent dose. The Langmuir and Freundlich isotherm models were both introduced to interpret the experimental data. The results showed that the former fitted bet-

ter than the latter to the equilibrium data. Analysis of data showed that the biosorption of iAs^{III} and MMA^{V} onto *At. f* BY-3 fitted well the pseudo-second-order kinetic model. The negative values of Gibbs free energy change confirmed that the biosorption of iAs^{III} and MMA^{V} were spontaneous. The positive values of enthalpy change and entropy change indicated that the biosorption process was endothermic. The enthalpy change values ranged from 20.9 to 418.4 kJ/mol suggested that the adsorption of iAs^{III} and MMA^{V} onto *At. f* BY-3 was by chemisorption. The competitive biosorption of iAs^{III} and MMA^{V} in binary mixture system was evaluated and the results showed a strong preference for MMA^{V} biosorption over iAs^{III} by *At. f* BY-3. FT-IR spectrum analysis indicated that the –OH and –NH groups of the biomass were mainly involved in the biosorption process. The results of the present study reveal that *At. f* BY-3 has a potential for use in removing arsenic from aqueous solutions, especially when arsenic concentration in waters are lower than 100 mg/L.

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