

Arsenic removal from an aqueous solution by modified *A. niger* biomass: Batch kinetic and isotherm studies

D. Pokhrel, T. Viraraghavan*

Faculty of Engineering, University of Regina, 3737 Wascana Parkway, Regina, SK, S4S 0A2, Canada

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Abstract

Batch studies were conducted to examine the adsorption kinetics and adsorption capacity of iron oxide-coated biomass (IOCB) for As(III) and As(V). The optimum pH for As(V) and As(III) removal was found to be 6. The equilibrium time for removal of arsenic was found to be approximately 7 h. The adsorption of As(V) on IOCB was rapid compared to that of As(III) adsorption. An increase in temperature (from 5 to 30 °C) was found to increase As(III) removal, whereas in the case of As(V), the removal increased with temperature from 5 to 10 °C, but remained relatively constant thereafter up to 30 °C. The pseudo-second order rate equation was found to describe better the kinetics of arsenic adsorption than other equations. The isotherm data for As(V) removal fitted better with the Langmuir equation compared with other tested models and the isotherm data for As(III) removal fitted better with Redlich–Peterson equation than other tested models. Iron oxide-coated fungal biomass (*A. niger*) was found to be efficient in removing arsenic from an aqueous solution.

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1. Introduction

Arsenic in groundwater has become a serious problem to humanity because of its toxicity. Chronic arsenic poisoning of drinking water is reported to cause numerous health disorders [1]. Therefore, the World Health Organization (WHO) in 1993 [2] and the United States Environmental Protection Agency (US EPA) in 2001 reduced the limit of arsenic in drinking water to $10 \mu\text{g l}^{-1}$ from an earlier value of $50 \mu\text{g l}^{-1}$ [3]. It was estimated that some 35–77 million people were at extreme risk of groundwater arsenic poisoning in Bangladesh [4]. Arsenic exists in natural waters in both inorganic as well as organic forms. The inorganic form of arsenic is more toxic than its organic form. Inorganic arsenic exists in natural waters in two oxidation states: As(III) and As(V). As(III) is dominant in more reduced conditions whereas As(V) is dominant in an oxidizing environment.

Arsenic can be removed by coagulation and filtration, ion exchange, membrane and adsorption technologies. Coagulation and filtration is the most commonly used technique. Ion

exchange resins are effective in removing arsenate [As(V)] but raw water may contain arsenite [As(III)]. So use of resin as an arsenic removal method may not be suitable for certain raw water sources which are dominant in As(III). Use of membrane as an arsenic removal method is quite expensive compared to other methods [5]. Arsenic removal by adsorption on activated alumina, granular ferric hydroxide (GFH) and manganese green sand filtration were proven to be effective. Iron oxide based adsorbents are classified as emerging technologies for arsenic removal [6]. Iron oxide-coated sand was reported to be efficient to remove arsenic from water [7–9]. Other iron oxide-coated or loaded materials were also reported to be effective in removing arsenic [10–12]. Loukidou et al. [13] obtained enhanced arsenate removal using chemically modified [polyelectrolyte (magnafloc), dodecylamine and cetyl trimethyl ammonium bromide] *P. chrysogenum* compared with the unmodified biomass. Pokhrel and Viraraghavan [14] investigated arsenic removal potential of chemically modified *A. niger* biomass because preliminary studies showed that arsenic removal was less than 20% using non-viable *A. niger* biomass. Among the various pretreatment studies, iron oxide-coated *A. niger* biomass was found to be the best in terms of arsenic removal efficiency [14]. Further, iron oxide-coated biomass may be a better option to use in the case

* Corresponding author. Tel.: +1 306 585 4094; fax: +1 306 585 4855.
E-mail address: t.viraraghavan@uregina.ca (T. Viraraghavan).

of drinking water compared to other chemical modifications. A factorial design study identified temperature and the mass of adsorbent as important factors in the removal of arsenic by iron oxide-coated *A. niger* biomass [15]. In this study, iron oxide-coated *A. niger* biomass was used in batch studies to examine the feasibility of adsorption of As(III) and As(V).

2. Kinetic and isotherm models

2.1. Kinetic models

The most common kinetic models available for the evaluation of the adsorption data are discussed further.

2.1.1. Lagergren model

Lagergren [16] showed that the rate of adsorption of pollutants on the adsorbent followed a pseudo-first order equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where q_e and q_t are the sorption capacity ($\mu\text{g g}^{-1}$) of the adsorbent at equilibrium and at time t (h), respectively and k_1 is the pseudo-first order sorption rate constant (h^{-1}).

Integrating and applying the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to q_t :

$$q_t = q_e[1 - \exp(-k_1t)] \quad (2)$$

2.1.2. Ho model

Ho and McKay [17] proposed that the kinetics of the sorption process was best described by a pseudo-second order equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

Integrating and applying the boundary conditions $t=0$ to t and $q_t=0$ to q_t and rearranging:

$$q_t = \frac{k_2tq_e^2}{1 + k_2tq_e} \quad (4)$$

where k_2 is the pseudo-second order sorption rate constant ($\text{g h } \mu\text{g}^{-1}$) and, t time (h).

2.1.3. Elovich equation

The Elovich equation is described as follows [18]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (5)$$

where α is the initial sorption rate constant ($\mu\text{g g}^{-1} \text{h}^{-1}$) and β is the desorption constant ($\text{g } \mu\text{g}^{-1}$).

Chien and Clayton [19] simplified the equation assuming $\alpha\beta t \gg 1$ and applying the boundary conditions $t=0$ to t and $q_t=0$ to q_t :

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (6)$$

2.1.4. Weber and Morris model

Weber and Morris [20] described the intraparticle uptake of the sorption process to be proportional to the half-power of time:

$$q_t = k_w t^{1/2} \quad (7)$$

where k_w is sorption constant ($\mu\text{g g}^{-1} \text{h}^{-1/2}$).

2.2. Equilibrium isotherm models

The equilibrium isotherm models describe the adsorption process in terms of mathematical equations. Normally, the experimental data and the model predicted values are plotted in terms of adsorption density versus the equilibrium concentration. The Langmuir, Freundlich and Redlich–Peterson models were tested to fit the isotherm data.

2.2.1. The Langmuir isotherm model

The Langmuir equation is expressed in the following form [21]:

$$q_e = \frac{K_L C_e}{1 + \alpha_L C_e} \quad (8)$$

where q_e is the adsorption of adsorbate to the adsorbent ($\mu\text{g g}^{-1}$) and C_e is the equilibrium solute concentration ($\mu\text{g l}^{-1}$). K_L is the solute adsorptivity (l g^{-1}) and α_L is related to the adsorption energy ($\text{l } \mu\text{g}^{-1}$). The ratio of K_L/α_L is defined as the monolayer adsorption capacity.

2.2.2. The Freundlich isotherm model

The Freundlich isotherm is of the following form [22]:

$$q_e = K_F C_e^{1/n} \quad (9)$$

where K_F is the equilibrium constant indicative of adsorption capacity (l g^{-1}), the larger the value of K_F the greater the adsorption capacity. 'n' is the adsorption equilibrium constant whose reciprocal ($1/n$) is the indicative of adsorption intensity. The reciprocal of 'n' is called heterogeneity factor and its value ranges from 0 to 1; the more the surface is heterogeneous, the value of $1/n$ is closer to zero.

2.2.3. The Redlich–Peterson model

The Redlich–Peterson equation is expressed as follows [23]:

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^\gamma} \quad (10)$$

where K_R , α_R and γ are the isotherm constants. K_R is the solute adsorptivity (l g^{-1}) and α_R related to the adsorption energy ($\text{l } \mu\text{g}^{-1}$) and γ is the heterogeneity constant ($0 < \gamma < 1$).

3. Materials and methods

3.1. Preparation of standards and reagents

Distilled deionized water (VWR International, USA) was used for the preparation of standards, modifier and wash solution [for sample dispenser of graphite furnace atomic absorption

spectroscopy (GFAAS)]. Deionized water obtained from the local supplier was used in preparation of all sample solutions. As(III) standard reference [arsenic oxide, concentration 1000 mg l^{-1}] was purchased from Fisher Scientific, Ontario. As(V) stock solution (1000 mg l^{-1}) was prepared by dissolving 4.164 g of sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$; Sigma Chemical, MO, USA) in deionized water to make a solution volume of 1 l. The stock solution was preserved with 1% trace metal grade nitric acid [14].

3.2. Preparation of biomass and modification methods

3.2.1. *A. niger*

Detailed procedure for the preparation of non-viable *A. niger* biomass has been provided elsewhere [14].

3.2.2. Iron oxide-coated biomass powder (IOCB)

A volume of 80 ml of the 2 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was prepared and 1 ml of 10 M NaOH was added in this solution and mixed thoroughly. Twenty grams of the autoclaved biomass powder were measured in a porcelain pot; the mixture of the iron oxide and NaOH solution was poured in to the porcelain pot and homogenized; kept in an oven for about 3 h at 80°C . After 3 h the oven temperature was raised to 110°C and continued for 24 h. The coated biomass powder was found to stick to each other which was separated by crushing with a mortar and pestle. The washed-coated biomass was dried and used for the experiment. This biomass is termed iron oxide-coated biomass (IOCB).

3.2.3. Characterization of the adsorbent

The IOCB used for the adsorption experiments was of sizes passing through $400 \mu\text{m}$ sieve. The IOCB was found to have a surface area of $2 \text{ m}^2 \text{ g}^{-1}$, a density of 0.7188 g cm^{-3} and an iron content of 254 mg g^{-1} . The surface potential of the IOCB was negative from a pH of 3–9 whereas it was positive at pH 2 [14].

The iron content of the biomass was determined by the following method [24]: 1 g of the IOCB was added to 50 ml of 10% HNO_3 in a beaker and the solution was boiled for 2 h. The iron oxide detached completely from the IOCB turning the solution color yellow. The solution was allowed to cool down and filtered. The solution was made up to 1 l with distilled deionized water. The iron content of the solution was determined by graphite furnace atomic absorption spectroscopy.

3.2.4. Batch kinetic and isotherm studies

A volume of 100 ml of the arsenic solution of a concentration [As(III) and As(V)] of $100 \mu\text{g l}^{-1}$ was contacted with 0.1 g of the biomass in a series of conical flasks at various pHs (pH 4–8.5) and samples were collected at every 15 min for the first 1 h and at every hour then after for kinetic studies. The mass of the biomass was varied from 0.01 to 0.1 g in the isotherm studies keeping all other parameters constant (equilibrium contact time 7 h and pH 6). The arsenic solutions and the adsorbent (IOCB) were mixed thoroughly at a speed of 175 rpm in a platform shaker, (model: Classic C2), manufactured by New Brunswick Scientific, New Jersey, USA. pH was kept constant during each run using 0.1 M tris buffer (Invitrogen life technologies, USA) for

pH 6 and above. The initial pH of the 0.1 M tris buffer was 10 and it was reduced to pH 6 by adding 0.5 M HNO_3 . For pH 4 and 5, a mixture of acetic acid (0.2 M) and acetate (0.2 M) was used [25]. All experiments were conducted in duplicate and average values were used in data analysis.

3.2.5. Arsenic analysis

The sample preservation and arsenic analysis procedures had been detailed in earlier publications [14,15].

3.2.6. Evaluation of data

The kinetic and isotherm data were fitted to various models described earlier by non-linear regression analysis using the software package STATISTICA (release 5.0) for Windows. The significance of the data fit by various models was conducted by *t*-test. The paired comparison of *t*-test is a meaningful method of judging significance of the data fit. However, only the *t*-value obtained by *t*-test cannot be considered as the judging parameter to accept the significance of the data fit. The probability of the *t*-test result is one of the major parameters to be considered to reject or accept the significance of the data fit. The data were judged based on the *t*-value obtained from the *t*-test and also with the probability of the test result. The standard deviations of the fit are also shown in the figures.

3.2.7. Spectroscopic studies

In order to investigate the chemical change in the *A. niger* biomass after coating with iron oxide, Fourier Transform Infrared (FT-IR) spectra were obtained. The samples were analyzed qualitatively on a Bio-Rad FTS-60 infrared system using a potassium bromide (KBr) pellet technique (6 mg sample per 400 mg KBr).

4. Results and discussion

4.1. Batch kinetic studies [As(V)]

The rate of adsorption of As(V) was evaluated using various kinetic models. The goodness of fit was evaluated by the least square method. The residual As(V) versus time is shown in Fig. 1 with error bars; the kinetic models for the data at pH 6.0 (optimum pH) are presented in Fig. 2 with standard deviation of fit.

The optimum pH for As(V) removal was found to be pH 6. The analysis of the kinetic data showed that As(V) was poorly adsorbed at pH values of 4 and 5 (Fig. 1). The equilibrium adsorption q_e , ($\mu\text{g g}^{-1}$) of As(V) on IOCB, predicted by pseudo-second order equation [17] is presented in Table 1. Table 1 shows kinetic parameters at different pH values. The equilibrium adsorption was found to be highest at pH 6 and decreased as the pH increased or decreased (Table 1). The equilibrium time of adsorption was considered to be 7 h (Fig. 1) as the adsorption of As(V) beyond 7 h was insignificant. Pseudo-second order [17] rate equation best described the kinetic data with a higher R^2 value (0.974 at pH 6). The equilibrium adsorption of As(V) on IOCB at pH 6 was found to be $96.9 \mu\text{g g}^{-1}$. The pseudo-first order rate equation [16] and Elovich equation [18] described

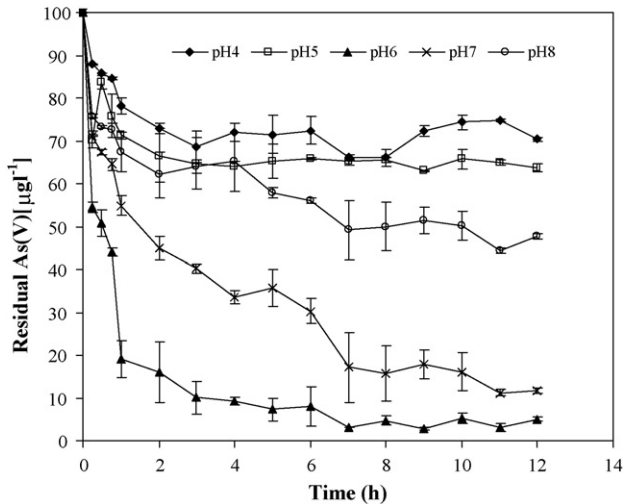


Fig. 1. Residual As(V) at different time intervals [initial As(V) concentration $100 \mu\text{g l}^{-1}$, adsorbent (IOCB) dose 1 g l^{-1} and error bars are shown in the figure].

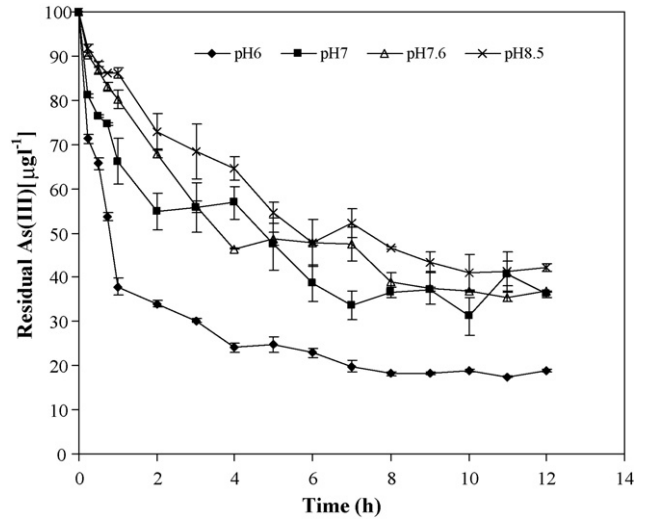


Fig. 3. Residual As(III) at different time intervals [initial As(III) concentration $100 \mu\text{g l}^{-1}$, adsorbent (IOCB) dose 1 g l^{-1} and error bars are shown in the figure].

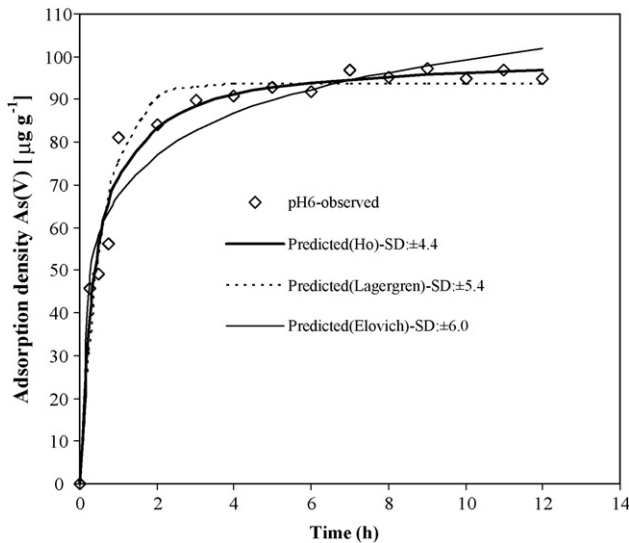


Fig. 2. The rate of adsorption of As(V) on IOCB predicted by various models [initial As(V) concentration $100 \mu\text{g l}^{-1}$, adsorbent dose 1 g l^{-1} and standard deviations (S.D.) of fit are shown in the figure].

Table 1
Kinetic parameters for arsenic removal by IOCB as estimated by Ho model

Description	As(V)			As(III)		
	q_e	K_2	R^2	q_e	K_2	R^2
pH 4	31.2	0.066	0.898	–	–	–
pH 5	35.9	0.137	0.849	–	–	–
pH 6	100.0	0.025	0.974	85.9	0.020	0.987
pH 7	91.2	0.010	0.950 ^a	70.1	0.012	0.944 ^a
pH 7.6	–	–	–	78.4	0.005	0.987
pH 8	50.6	0.037	0.942	–	–	–
pH 8.5	–	–	–	80.5	0.003	0.986 ^a

^a Model parameters are not statistically significant (*t*-test) at 95% confidence level for pH 7. Model parameters at other pH values are statistically significant at 95% confidence level.

the kinetic data with R^2 value of 0.960 and 0.883, respectively. Weber and Morris [20] model ($R^2 = 0.260$) did not fit adequately the experimental adsorption data for As(V) removal by IOCB. The *t*-test results showed that all the tested models adequately described the kinetic data at 95% confidence level except Weber and Morris model.

4.2. Batch kinetic studies [As(III)]

The residual As(III) versus time is shown in Fig. 3 with error bars in it. The kinetic models are presented in Fig. 4. The effect of pH on As(III) adsorption can be observed from Fig. 3 and Table 1. The equilibrium adsorption of As(III) on IOCB at pH 6 was found to be $80.1 \mu\text{g g}^{-1}$.

The equilibrium time of adsorption was considered to be 7 h (Fig. 3). The kinetic data were fitted to various kinetic mod-

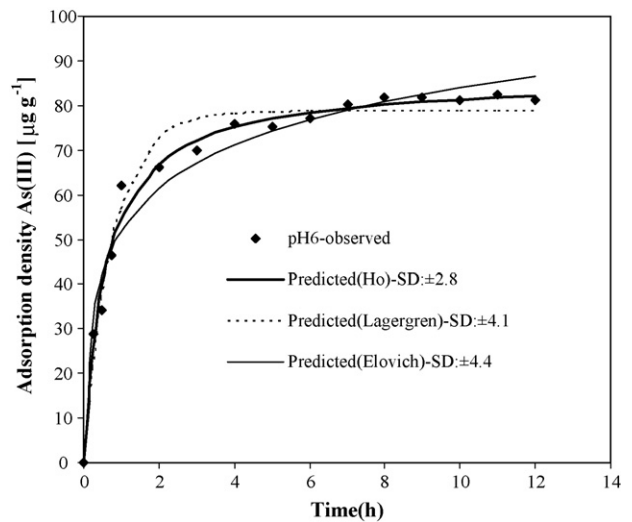


Fig. 4. The rate of adsorption of As(III) on IOCB predicted by various models [initial As(III) concentration $100 \mu\text{g l}^{-1}$, adsorbent dose 1 g l^{-1} and standard deviation (S.D.) of fit are shown in the figure].

Table 2
Best fit model equations for kinetic and isotherm data for As(V) and As(III) removal using IOCB at pH 6

Description	As(V)	R^2	As(III)	R^2
Ho model (kinetic data) (pseudo-second order)	$q_t = \frac{0.025 \times 100^2 t}{1 + 0.025 \times 100t}$	0.974	$q_t = \frac{0.020 \times 86^2 t}{1 + 0.020 \times 86t}$	0.987
Langmuir model (isotherm data)	$q_e = \frac{58.55C_e}{1 + 0.060C_e}$	0.948	–	–
Redlich–Peterson model (isotherm data)	–	–	$q_e = \frac{0.844C_e}{1 + (-0.00093)C_e^{1.479}}$	0.810

Note: Model parameters are statistically significant (*t*-test) at 95% confidence level.

els. Among the models tested, pseudo-second order [17] rate equation was found to fit better compared with other models. The pseudo-first order [16], pseudo-second order [17] and the Elovich equation [18] described the kinetic data with R^2 values greater or equal to approximately 0.95. Weber and Morris [20] model (R^2 value 0.537) exhibited a poor fit to the kinetic data for As(III) removal using IOCB. The *t*-test results showed that all the tested models other than Weber and Morris model described the kinetic data at 95% confidence level for As(III) removal by IOCB. The best fit kinetic model equations for As(III) and As(V) removal by IOCB are presented in Table 2.

4.3. Isotherm studies for As(V) and As(III)

The equilibrium time for As(V) and As(III) removal by IOCB was considered to be 7 h. The optimum pH for both As(V) and As(III) removal was found to be pH 6. Therefore, the isotherm studies were conducted at pH 6 for these two species of arsenic. The experimental data were tested for fit with commonly used models such as the Langmuir, Freundlich and Redlich–Peterson. The isotherm plots for As(V) and As(III) removal are presented in Figs. 5 and 6, respectively. The best fit model equations for As(V) and As(III) adsorption isotherms are shown in Table 2. The isotherm data for As(V) were better fit with the Langmuir equation with R^2 value of approximately 0.95 and As(III)

isotherm data were better represented by the Redlich–Peterson equation (R^2 value 0.810).

The shape of the isotherm curve is considered to predict whether a sorption process is ‘favorable’ or ‘unfavorable’. Hall et al. [26] defined a dimensionless number K_H (separation factor), to indicate whether the isotherm is favorable.

$$K_H = \frac{1}{1 + \alpha_L C_0} \quad (11)$$

where α_L = Langmuir constant, $l \mu\text{g}^{-1}$, C_0 = initial concentration of solution, $\mu\text{g} l^{-1}$. According to the value of K_H , the isotherm is considered to be of the following types: $K_H > 1$, unfavorable. $K_H = 1$, linear. $0 < K_H < 1$, favorable. $K_H = 0$, irreversible.

The value of K_H for As(V) removal was calculated to be 0.14 meaning that it was a favorable isotherm. The K_H value for As(III) removal was calculated as 0.96 indicating that the isotherm was still favorable but it may be moving closer to a linear isotherm.

4.4. Effect of temperature on arsenic removal

Experiments were conducted to investigate the effect of temperature on arsenic removal efficiency. In these experiments,

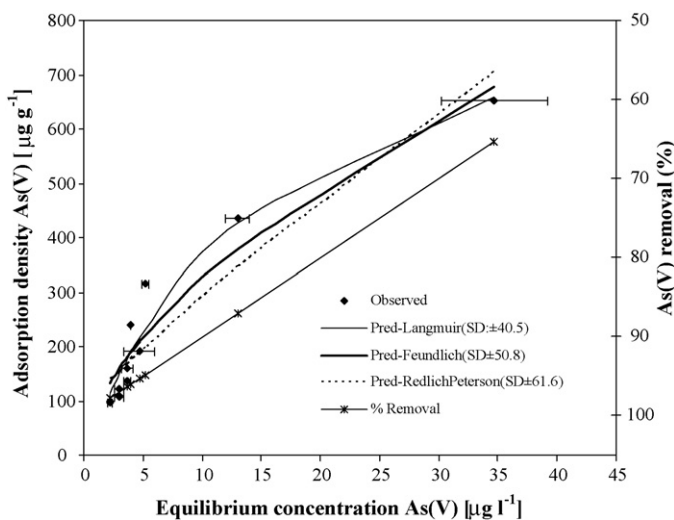


Fig. 5. Model predicted isotherm plots for As(V) using IOCB at pH 6 [initial As(V) concentration $100 \mu\text{g} l^{-1}$, equilibrium time 7 h and error bars as well as standard deviation of fit are shown in the figure].

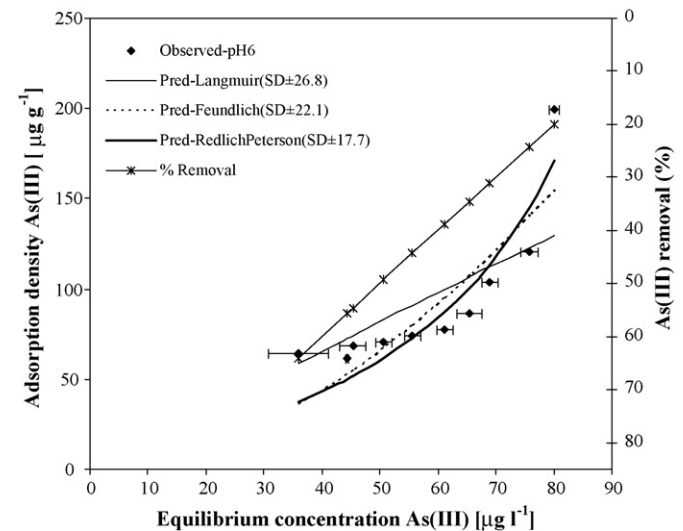


Fig. 6. Model predicted isotherm plots for As(III) using IOCB at pH 6 [initial As(III) concentration $100 \mu\text{g} l^{-1}$, equilibrium time 7 h and the error bars as well as standard deviation of fit are shown in the figure].

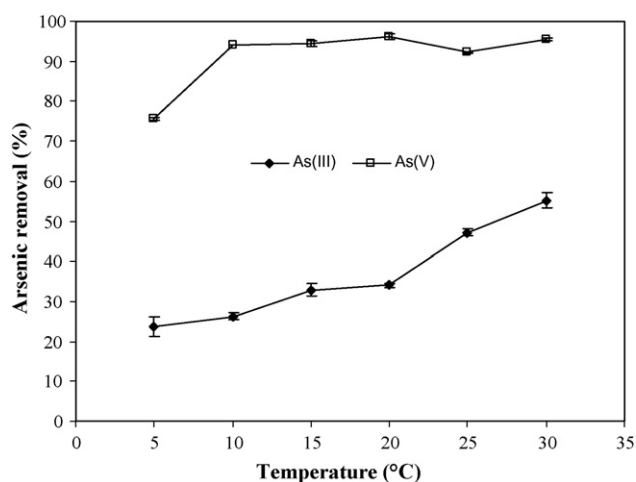


Fig. 7. Effect of temperature on arsenic removal efficiency [initial As(III) and As(V) concentration $100 \mu\text{g l}^{-1}$, adsorbent dose 1 g l^{-1} and error bars are shown in the figure].

adsorbent dose (1 g l^{-1}), solution pH (optimum pH 6), equilibrium time (7 h) and the rotational speed (175 rpm) were kept constant and the temperature was varied. There was an increase in As(V) removal when temperature was raised from 5 to 10°C . The reason for the increase in arsenic removal efficiency with increased temperature was not known. But in the range of $10\text{--}30^\circ\text{C}$, As(V) removal was nearly constant. It was found that As(III) removal increased as the temperature was increased. A plot of arsenic removal versus temperature is presented in Fig. 7. The effect of temperature on As(III) removal was more pronounced compared to the temperature effect on As(V) removal. Thermodynamic studies indicated the reaction mechanism between arsenic and IOCB as chemisorption (data

not shown). This was evident by the high heat of adsorption $\Delta H \approx -133 \text{ kJ mol}^{-1}$ for As(V) and 89 kJ mol^{-1} for As(III) [27]. A recent study by Mondal et al. [28] reported decrease in arsenic [As(III) and As(V)] removal efficiency using Fe^{3+} -impregnated granular activated carbon (GAC). These studies were conducted between 30 and 60°C and the decrease in removal efficiency seemed marginal.

4.5. Comparisons of arsenic removal capacity of the IOCB with other adsorbents

The arsenic removal capacity of the IOCB was compared with those of other adsorbents reported in literature (Table 3). As the adsorption capacity of the adsorbent varies with the initial arsenic concentration, solution pH and other experimental conditions, it may be difficult to compare the values directly. Since the batch study can only indicate the feasibility of adsorption, the adsorption capacity of the IOCB obtained in column study has been included as comparison in Table 3. These data has been published elsewhere [29]. The regenerated IOCB responded very well in the column study [29]. The adsorption capacities for arsenic shown by IOCB were found to be generally similar to iron oxide-coated material but much less than those shown by activated carbon and activated alumina, mostly due to the fact that the initial concentrations of arsenic in these studies were as high as 100 mg l^{-1} .

4.6. Spectroscopic observations

The reactions between the *A. niger* biomass and iron oxide with the coating process is not known. Formation of different compounds and complexes may occur. The FT-IR spectra of

Table 3
Comparison of adsorption capacity ($\mu\text{g g}^{-1}$) of various adsorbents to remove arsenic

Adsorbent	Adsorption capacity As(III)	Adsorption capacity As(V)	Reference	Remarks
Iron oxide-coated <i>A. niger</i> biomass	880*	1080*	[29]	Initial As conc. $100 \mu\text{g l}^{-1}$ and pH 6
Iron oxide-coated sand	28.6	–	[39]	Initial As(III) $400 \mu\text{g l}^{-1}$, pH 7.5
Hematite	–	218.8	[40]	Initial As(V)
Feldspar	–	207.9		10 mg l^{-1} , pH 4.2
Iron oxide-coated sand	41.1	42.6	[9]	Initial As $100 \mu\text{g l}^{-1}$ and pH 7.6
Iron oxide-coated sand	18.3**	–	[8]	Initial As $325 \mu\text{g l}^{-1}$ pH 7.4
Ferrihydrite	285**	–		
Hardened paste of Portland cement	–	12.5	[41]	Initial As(V) $200 \mu\text{g l}^{-1}$ pH 5
Natural iron ores	–	400	[42]	Initial As(V) 1 mg l^{-1} pH 4.5–6.5
Ce(IV)-iron oxide	–	16,000	[43]	Initial As(V) 1 mg l^{-1} , pH for Ce(IV)-Fe (3–7) and pH for activated alumina 5.5
Activated alumina	–	8300		
Coconut-shell carbon	–	2400	[44]	Initial As(V) varied from 50 to 200 mg l^{-1} at pH 5
Peat-based carbon	–	4910		
Coal-based carbon	–	4090		
Activated alumina	3480	15,900	[45]	Initial As(III) $0.79\text{--}4.9 \text{ mg l}^{-1}$, pH 6.9 Initial As(V) $2.85\text{--}11.5 \text{ mg l}^{-1}$, pH 5.2
Activated carbon	0	20,200	[46]	Initial As varied from 1 to 100 mg l^{-1} at pH 8
Granular ferric hydroxide (GFH)	–	8500	[47]	Initial As(V) $5\text{--}100 \text{ mg l}^{-1}$ at pH 8–9

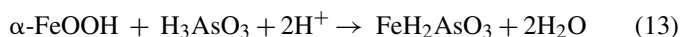
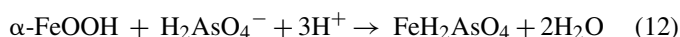
Note: (1) *The adsorption capacity of IOCB was determined by column experiment. (2) **Natural groundwater was used for the experiment. The adsorption capacity shown was for the total soluble arsenic.

A. niger biomass and the *A. niger* biomass-coated with iron oxide were obtained but these data have not been included. The form of iron oxide in the iron oxide-coated *A. niger* biomass was of iron oxyhydroxide (goethite, α -FeOOH). The IR bands for goethite were reported to be in between 797 and 890 cm^{-1} [30].

4.7. Discussion

The sorption behavior of As(V) and As(III) are quite different as can be seen from Figs. 1 and 3, respectively. The characteristics of sorption of As(V) and As(III) at the optimum pH of 6 may be different because As(V) is fully in the anionic form [dominant As(V) species H_2AsO_4^-] whereas As(III) is partially ionized at this pH [dominant As(III) species at this pH is molecular H_3AsO_3]. That may be one of the reasons why As(V) was better adsorbed compared to As(III). The reaction rate of As(V) [$0.025 \text{ g h } \mu\text{g}^{-1}$] was found to be rapid than that of As(III) [$0.020 \text{ g h } \mu\text{g}^{-1}$] with IOCB. As(III) and As(V) change into different species depending on the solution pH and the redox potential. As(III) is dominant in the form of neutral species (H_3AsO_3) below pH 9.22. It has been reported that anionic arsenic species [H_2AsO_3^- , H_2AsO_4^-] get adsorbed with the positively charged iron oxide-coated material by electrostatic attraction. On the contrary, Huang and Vane [31] reported that the surface charge of the Fe^{2+} loaded activated carbon varied according to the quantity of the iron (II) load; generally the surface potential became less negative as the iron load increased. Pokhrel and Viraraghavan [14] found that iron oxide-coated *A. niger* biomass was negatively charged from a pH of 3–9.

It is likely that the mechanism of removal of arsenic by the iron oxide-coated biomass may be complexation (sorption) reaction between the arsenic and iron oxide rather than by surface potential. As(V) and As(III) are adsorbed on oxyhydroxide by forming complexes with goethite sites by following reactions [32].



Oxides of iron, aluminum and manganese are the potential source/sink for arsenic in aquifer sediments because of their chemistry, occurrence and tendency to adsorb other particles [33]. When these metal oxides are exposed to water, metal ions on the oxide surface complete their coordination shells with OH groups [34]. These OH groups can bind or release H^+ ions depending on the pH, resulting in the development of the surface charge. The adsorption properties of oxides are due to the existence of these OH_2^+ , OH and O^- functional groups [35]. Arsenic is adsorbed by ligand exchange with OH and OH_2^+ surface functional groups forming an inner-sphere complex. This process requires an incompletely dissociated acid H_2AsO_4^- to provide a proton for complexation with the OH group, forming H_2O and providing a space for anion adsorption [34]. Spectroscopic (particularly infrared, X-ray photoelectron and X-ray absorption spectroscopy) tests conducted to understand the interfacial reactions between arsenic species and natural minerals

and other solid phase materials indicated that arsenic sorption on material surfaces may be outer-sphere (physisorbed) complexes, inner-sphere (chemisorbed) or by surface precipitation [36]. Experimental results and the various test conducted on the hydrous iron oxide indicated that adsorption of arsenate was chemisorbed on iron oxide surface [37]. Grossl and Sparks [38] also concluded that the adsorption of arsenate on goethite was an inner-sphere surface complexation. More detailed studies would be necessary to examine the reaction between iron oxide and *A. niger* biomass and nature of reaction of arsenic with iron oxide-coated biomass. A reduced removal of both As(V) and 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^- , H_2AsO_4^-].

5. Conclusions

Based on the experimental results, the following conclusions were drawn:

- (1) Iron oxide-coated *A. niger* biomass can be used to remove arsenic from water.
- (2) The optimum pH for both As(V) and As(III) removal was found to be 6. The reaction for As(V) removal was found to be more rapid compared to that of As(III) based on the reaction rate constant.
- (3) An increase in temperature from 5 to 30 °C, increased As(III) removal. There was an increase in As(V) removal when the temperature was raised from 5 to 10 °C; however, the removal remained almost constant thereafter until 30 °C.
- (4) The adsorption kinetic data for both As(V) and As(III) removal can be described better by a pseudo-second order rate equation compared to other models.
- (5) The isotherm data for As(V) fitted better with the Langmuir model and the As(III) isotherm data fitted better with the Redlich–Peterson model compared to other tested models.
- (6) The spectroscopic observations indicated that the form of the iron oxide on the iron oxide-coated biomass was of oxyhydroxide (goethite).

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