

## REMOVAL OF ARSENIC FROM AN AQUEOUS SOLUTION BY PRETREATED WASTE TEA FUNGAL BIOMASS

<sup>1</sup>S. Mamisahebei, <sup>\*</sup><sup>1</sup>Gh. R. Jahed Khaniki, <sup>2</sup>A. Torabian, <sup>1</sup>S. Nasseri, <sup>1</sup>K. Naddafi

<sup>1</sup>Department of Environmental Health Engineering, School of Public Health, Medical Sciences/University of Tehran, Tehran, Iran

<sup>2</sup>Department of Civil Environmental Engineering, Faculty of the Environment/University of Tehran, Tehran, Iran

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### ABSTRACT

Arsenic contamination in water poses a serious threat on human health. The tea fungus known as Kombucha is a waste produced during black tea fermentation. The objective of this study was to examine the main aspect of a possible strategy for the removal of arsenates employing tea fungal biomass. The pretreatment of biomass with FeCl<sub>3</sub> was found to improve the biosorption efficiency. Arsenic uptake was found to be rapid for all concentrations and reached to 79% of equilibrium capacity of biosorption in 20 min and reached equilibrium in 90 min. The pseudo second-order and first-order models described the biosorption kinetics of As (V) with good correlation coefficient ( $R^2 > 0.93$ ) and better than the other equations. The data obtained from the experiment of biosorption isotherm were analyzed using the Freundlich and Langmuir isotherm models. The equation described the isotherm of As (V) biosorption with relatively high correlation coefficient ( $R^2 > 0.93$ ). According to the Langmuir model, the maximum uptake capacities ( $q_m$ ) of tea fungal biomass for As (V) were obtained  $3.98 \times 10^{-3}$  mmol/gr. The effect of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>+2</sup> and Ca<sup>+2</sup> on equilibrium capacities of As was not significant. The variation of sorption efficiency with pH showed that optimum biosorption takes place in the pH ranges of 6 to 8. Promising results were obtained in laboratory experiments and effective As (V) removals were observed.

**Key words:** Waste tea, fungal biomass, biosorption, arsenates isotherm, aqueous solution

### INTRODUCTION

Arsenic exists in natural waters both in inorganic and organic forms. The inorganic form of arsenic is more toxic compared to its organic form. Inorganic arsenic is the predominant form in contaminated groundwater. Arsenic exists in two oxidation states: arsenite, As (III) and arsenate, As (V) (Pokhrel and Viraraghavan, 2006). It is introduced in the aqueous system through geochemical reactions industrial waste discharge or even agricultural use of arsenical pesticides (Loukidou *et al.*, 2003). The presence of arsenic in groundwater has been a major public health concern in many countries such as Bangladesh, India, China, Kurdistan of Iran, Argentina, Canada and USA (ATSDR, 2002 and WHO, 2001). The problem of arsenic contamination in groundwater

<sup>\*</sup>Corresponding author-Email: [ghjahed@tums.ac.ir](mailto:ghjahed@tums.ac.ir)

Tel: +98 21 8895 4914, Fax: +98 21 8895 0188

poses is a serious threat in these areas because groundwater is the main source of drinking water (Pal *et al.*, 2002). Long-term exposures to arsenic levels can result in permanent and severe damage to human health. Arsenic toxicity causes skin lesions, damage mucous membranes, digestive, respiratory, circulatory and nervous system (Murugesan *et al.*, 2006). According to the European Commission as well as to the US Environmental Protection Agency, the acceptable value of As in drinking water is limited to 10 µg/L from an earlier value of 50 µg/L (Loukidou *et al.*, 2003). Removal of arsenic from contaminated water to satisfy the drinking water standard has been a challenge for water authorities. Iron oxides have been reported to be effective for metal ion removal. Iron oxide-coated sand was used in many studies for arsenic removal (Pokhrel and

Viraraghavan, 2006; Joshi and Chaudhuri, 1996). Huang and Vane (1989) treated activated carbon by various cationic metal salt solutions, such as  $\text{Ba}(\text{ClO}_4)_2$ ,  $\text{Cu}(\text{ClO}_4)_2$ ,  $\text{FeSO}_4$ ,  $\text{FeCl}_2$ ,  $\text{Fe}(\text{ClO}_4)_2$ ,  $\text{Fe}(\text{ClO}_4)_3$ ,  $\text{Fe}(\text{ClO}_4)_2$ ,  $\text{Fe}(\text{ClO}_4)_3$  and  $\text{FeCl}_3$ . They found that arsenate removal by activated carbon pretreated with the ferrous salt was the best among other solutions (almost ten times greater than untreated activated carbon). In Bangladesh, groundwater rate of As (V)/As (III) is variable from 1.1 to 10, but the usual rate of this index is 1.66 to 2 (Smedley and Kinniburgh, 2002). The research for highly biomass sorption is expected to improve the potential for the introduction of new materials, which are likely to be competitive and cost-efficient for the sorption of metals. The objective of this study was to examine a possible strategy for the removal of arsenates, employing tea fungal biomass.

## MATERIALS AND METHODS

### *Preparation of tea fungus*

Tea fungus (a symbiont of two yeasts viz., *Pichia* sp. NRRL Y-4810 and *Zygosaccharomyces* sp. NRRL Y-4882 and a bacterium *Acetobacter* sp. NRRL B-2357) was obtained from perfumery of Tehran city. The fungus was grown in tea medium. To 1 L of water, two tea spoons (10.5 g) of tea powder was mixed and boiled for 5 min. Then 100 g of sucrose was added. The tea extract was filtered and used as a medium. It was incubated at  $28 \pm 2^\circ\text{C}$  statically for ten days. New fungal mat was produced over the mother culture (Murugesan *et al.*, 2006).

### *Biosorbent preparation*

The tea fungal mat was washed with an adequate amount of deionized water until free media components. The washed fungal mat was dried at  $75^\circ\text{C}$  for 24 h and the dried biomass was ground in a laboratory blender. Then a portion of the dried and ground mat was immersed in  $\text{FeCl}_3$  solution (15 mg/L) for 60 min. These two modified fungal mats were then tested for efficacy to remove As (V) from an aqueous solution.

### *Chemicals*

Synthetic solutions were prepared by the use of deionized water and salts including NaCl, KCl,

$\text{MgCl}_2$  and  $\text{CaCl}_2$  (Merck supplied). Initial pH of the solutions was adjusted with electrical pH meter (CAMLAB Lts, Model CG 842) to the desired values by using 0.1 to 1 mol/L HCl and 0.1 to 1 mol/L NaOH.

### *Equilibrium experiments*

The optimum speed of agitation was adjusted about (50-250 rpm). The solution volume was 100 mL in all batch equilibrium experiments. The sample was agitated in a rotary shaker at 160 rpm. All experiments were conducted at room temperature ( $22 \pm 4^\circ\text{C}$ ). The initial pH of solutions was adjusted to desired values and then the final pH was measured.

### *Biosorption isotherms*

Biosorption isotherm experiments were conducted in a single-component system. The initial As (V) concentration was 1 mg/L and biosorbent doses varied from 0.1 to 1 g. Also, the initial pH of solutions was adjusted to 6.

### *Effect of pH on biosorption*

The effect of pH on equilibrium capacities of As (V) biosorption was studied in a single-component system. The initial As (V) concentration was 1 mg/L and the pH of solutions had some variations from 2 to 9. After pH adjustment, 100 mg of tea fungus biomass was added to experiment vessels.

### *Effect of background ions*

Ionic species such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$  are usually present in drinking water and groundwater contaminated with arsenic (Smedley and Kinniburgh, 2002). These ions may interfere in the uptake of arsenic by adsorbent through competitive binding or complexation.

### *Metal analysis*

The biomass was removed by filtration through  $0.45 \mu\text{m}$  membrane filters (Mixed cellulose esters). Then the filtrates were analyzed for residual As (V) concentration by ICP model AMS 100 "I-speeder".

### *Kinetic modeling*

Kinetic of As (V) biosorption was modeled by the pseudo first-order (Langergren), pseudo second-order, saturation (mixed-order) and second-order rate equations, presented as equations 1 to 4, respectively:

$$\ln \frac{(q_e - q_t)}{q_e} = -k_1 t \quad (1)$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

$$\frac{1}{t} \ln \frac{C_o}{C_t} = -\frac{k_o}{k} - \frac{1}{k} \left( \frac{C_o - C_t}{t} \right) \quad (3)$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + Kt \quad (4)$$

Where  $q_e$  and  $q_t$  are the amount of metal ion sorbed (mmol/g) at equilibrium at any time, respectively;  $K_1$  is the pseudo first-order rate constant of adsorption (1/min);  $K_2$  is the pseudo second-order rate constant of adsorption (g/mol/min),  $C_o$  and  $C_t$  are the metal concentrations.

#### Isotherm modeling

In order to estimate the maximum capacities of adsorbents, it is necessary to know the quantity of adsorbed metal as a function of metal concentration in the solution.

Typically two models can be applied as Freundlich and Langmuir isotherms.

#### - Freundlich isotherm

The Freundlich equation serves as a tool for simulating adsorption processes and equation is given by equations 5 and 6.

$$q = K \cdot C^n \quad (5)$$

$$\text{or } \log q = \log K + n \log C \quad (6)$$

Where  $q$  (mg/g) and  $C$  (mg/mL) are the equilibrium concentrations of solute in solid and liquid phases, respectively. The Freundlich constants  $K$  (mg/g) and  $n$  (value between 0 and -1) represent the adsorption capacity and adsorption intensity of the adsorbent, respectively.

#### - Langmuir isotherm

The Langmuir equation is based on the assumption that maximum adsorption corresponds to a saturated monolayer of salute on the adsorbent surface, and that the energy of adsorption is constant and there is no transmigration of adsorbate in the plane of the surface. The Langmuir equation is given by equations (7).

$$q = q_{\max} C / (C + K_d) \quad (7)$$

Constants  $q_{\max}$  (mg/g) and  $K_d$  (mg/mL) are the Langmuir parameters. The constant  $q_{\max}$  represents the maximum adsorption capacity and  $K_d$  is the dissociation coefficient of the solute-adsorbent complex, which represents the affinity between the solute and the adsorbent. The Langmuir isotherm has been widely accepted as a practical method for integrating experimental data of adsorption processes. Rearranging equations. (8), a linear expression can be derived as a function of  $C$ :

$$C/q = K_d/q_{\max} + (1/q_{\max})C \quad (8)$$

## RESULTS

### Kinetic study

The kinetic profile of As (V) biosorption by tea fungus is shown in Fig. 1.

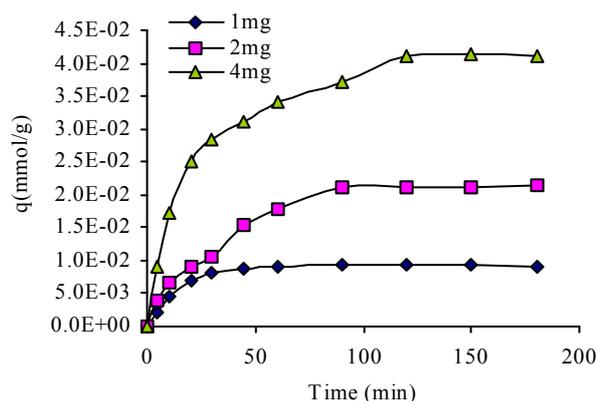


Fig.1: Kinetic profile of As (V) biosorption by tea fungus biomass

Kinetic parameters of rate equations for biosorption of As (V) by tea fungus biomass are shown in Tables 1 and 2.

Table 1: Kinetic parameters of the pseudo first-order and pseudo second-order rate equations for biosorption of As (V) by tea fungus biomass

C <sub>0</sub> (mg)	Pseudo-first order model			Pseudo-second order model		
	q <sub>e</sub>	k <sub>1</sub>	R <sup>2</sup>	q <sub>e</sub>	k <sub>2</sub>	R <sup>2</sup>
1	0.00945	0.02	0.97	0.0099	10.38	0.994
2	0.0212	1.31	0.816	0.0257	1.26	0.988
4	0.0412	1.51	0.954	0.046	1.14	0.998

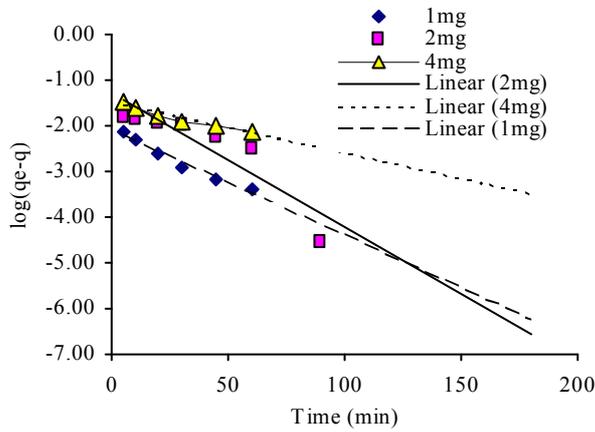
C<sub>0</sub>= initial concentration of metal ion; R=Correlation coefficient

Table 2: Kinetic parameters of the saturation second-order rate equations for the bio sorption of As (V) by tea fungus biomass

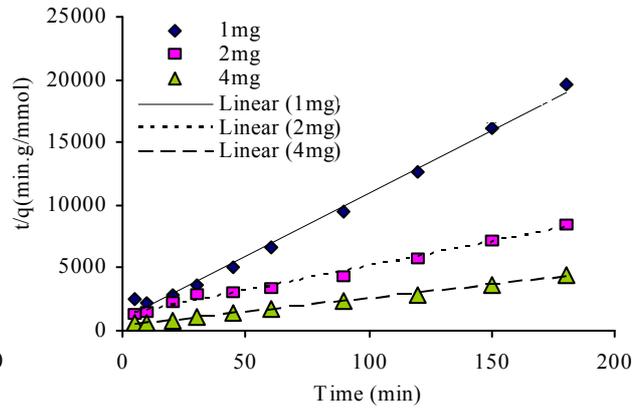
C <sub>0</sub> (mg)	Saturation model			Second order model		
	K	K <sub>0</sub>	R <sup>2</sup>	K	K <sub>0</sub>	R <sup>2</sup>
1	-0.01	0.0001	-0.01	0.0001	-0.01	0.0001
2	-0.03	0.0002	-0.03	0.0002	-0.03	0.0002
4	-0.05	0.0003	-0.05	0.0003	-0.05	0.0003

C<sub>0</sub>= initial concentration of metal ion; R=Correlation coefficient

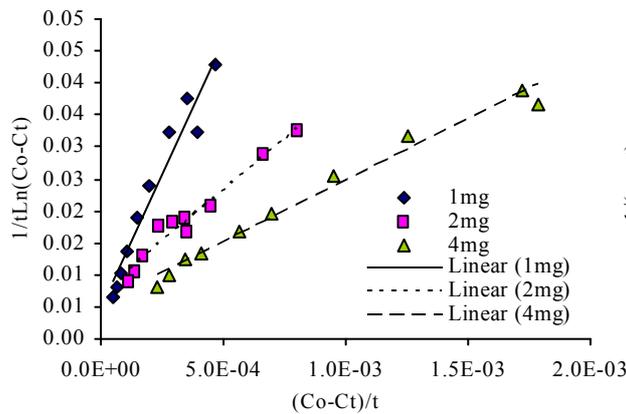
Fig. 2. (a)-(d) show kinetic modeling of As (V) biosorption by linear plots of the pseudo first-order, pseudo second-order, saturation and second rate equation (Equations 1 to 4).



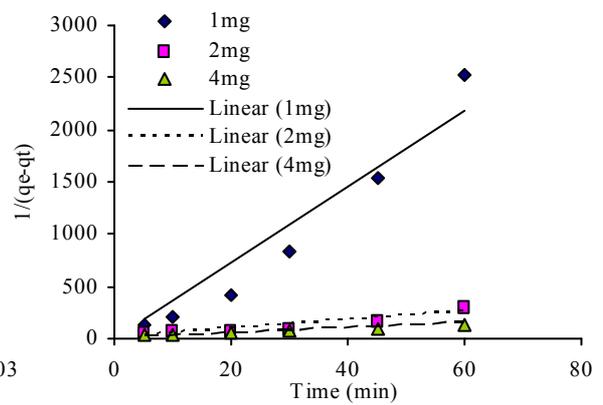
(a)



(b)



(c)



(d)

Fig. 2: Kinetic analysis of As (V) biosorption by linear plots of (a) the pseudo first-order, (b) pseudo second-order, (c) saturation and (d) second order rate equation

*Isotherm study*

Fig. 3. (a)-(b) shows isotherm modeling of As (V) biosorption by linear plot of the Freunlich and Langmuir models (Equations 5 to 8).

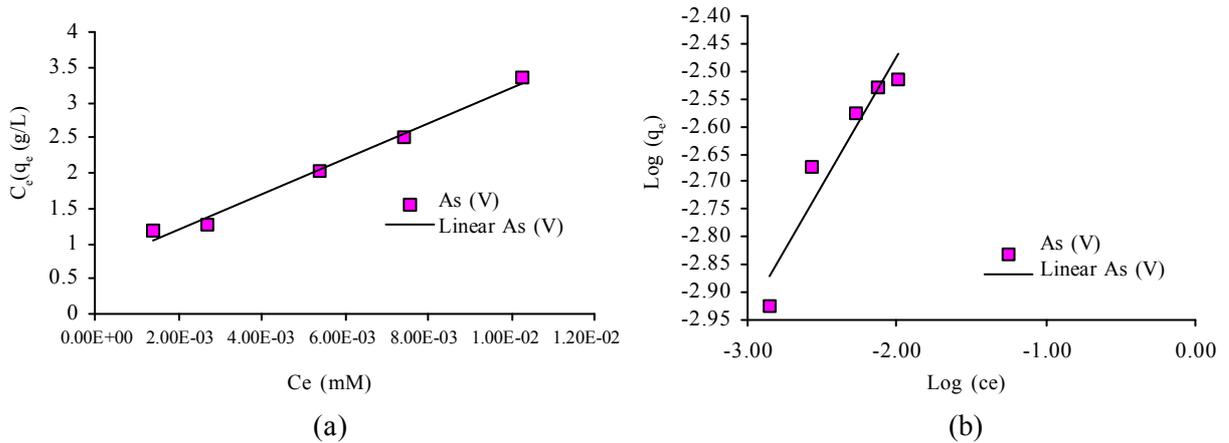


Fig. 3: Isotherm analysis of As (V) biosorption by linear plots of (a) Freundlich and (b) the Langmuir models

*Effect of pH on biosorption*

Fig. 4 shows the effect of pH on equilibrium uptake capacities of tea fungus biomass for As (V).

*Effect of light metal ions on biosorption*

The effect of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  on equilibrium capacities of As (V) biosorption by tea fungus

biomass is shown in Fig. 5.

*Effect of agitation speed*

The influence of agitation speed on adsorption of As (V) on tea fungal biomass was studied by changing the speed of agitation from 50 to 250 rpm and result are shown in Fig. 6.

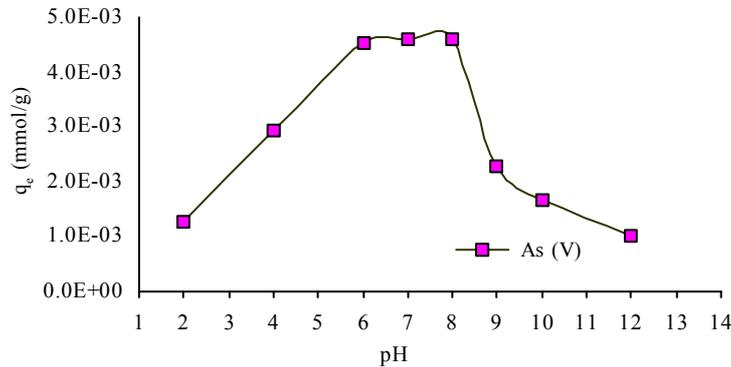


Fig. 4: Effect of pH on equilibrium capacities of As (V) biosorption by tea fungus

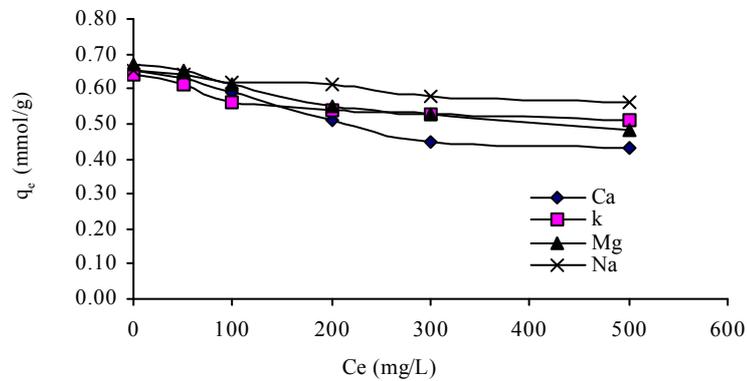


Fig. 5. Effect of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  on equilibrium capacities of As (V) biosorption by tea fungus biomass ( $C_0$ =initial concentration of light metal ion)

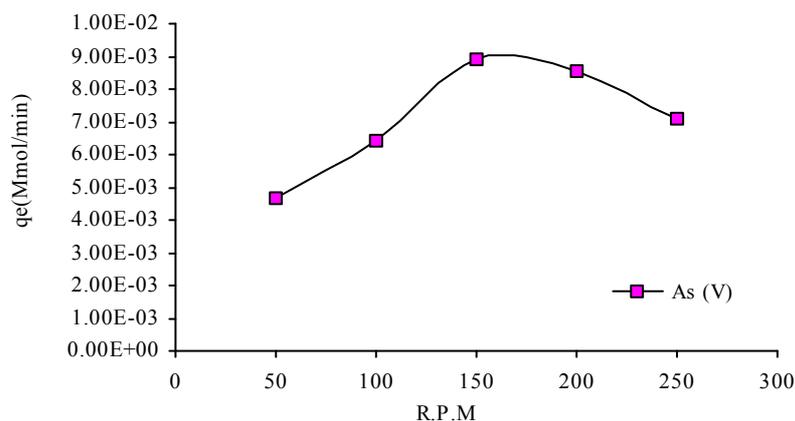


Fig. 6: Effect of agitation speed on As (V) uptake

## DISCUSSION

### Kinetic study

According to Fig. 1, As (V) uptake was relatively fast for all concentrations studied. At the initial As (V) concentration of 4 mg/L, the system reached to equilibrium within 90 min. In general the heavy metals uptake reached to 79% equilibrium capacity of biosorption in 15 min. This rapid kinetic has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy. Similar rapid metal uptake has been reported for the biosorption of As (V) using *P.chrysogenum* where in the system reached over 60-70% equilibrium uptake capacity in 10 min (Loukidou *et al.*, 2003). The biosorption of As (V) by Kombucha biomass was similar and 67% of the total uptake occurred in 70 min (Murugesan *et al.*, 2006). In present study, the pseudo first-order, pseudo second-order and saturation rate equations described the biosorption kinetic of As (V) with good correlation coefficient ( $R^2 > 0.93$ ). Kinetic analysis of As (V) biosorption by pretreated waste tea fungal biomass represented that the pseudo first-order rate equation described biosorption kinetic better than rest (Murgesan *et al.*, 2006). The rate constant of the pseudo second-order rate equation for As(V) biosorption were obtained as 10.38, 1.26 and 1.14 g/mmol/min at the initial As(V) concentrations of 1, 2 and 4 mg/L, respectively. An increase in initial concentration of As(V) led to a decrease in the rate constant value. Therefore there was not a direct relationship between initial concentration of As(V)

and the rate of As(V) biosorption by tea fungal biomass. In other hand, the biosorption of As (V) tea fungal biomass was slower in high initial metal ion concentration. Analysis of equilibrium data is important for developing an equation that can be used for design purposes. Several isotherm equations have been used for the equilibrium modeling of biosorption systems (Sag and Kutsal, 1995). In this study, Langmuir and Freundlich isotherms have been applied. For each isotherm the initial As (V) concentrations was kept constant whereas the biomass concentration were varied between 0.1-1 mg in each container with 0.1L volume. The Langmuir equation described the isotherm As (V) biosorption by tea fungal biomass with high correlation coefficient ( $R^2 > 0.99$ ) and it was better than the Freundlich model ( $R^2 > 0.95$ ). According to Langmuir equation the maximum capacity of As (V) biosorption ( $q_m$ ) was obtained as  $3.98 \times 10^{-3}$  (mmol/g). The Langmuir parameters of  $q_m$  (maximum uptake capacity) is a suitable measure by comparing different sorbents for the same sorbate. Although due to the various experimental conditions employed in different studies, comparison of their results is difficult. The effect of pH on As (V) biosorption was studied in the initial pH range from 2 to 12. The optimum initial pH values for As (V) biosorption were determined as 6 to 8. The sharpest increase in As (V) uptake was obtained between pH=3 and 5. Measurement of final pH represented the simultaneous release of  $H^+$  with the uptake of arsenic ions, because final pH of solutions was

less than the initial pH. Therefore ion exchange was confirmed to be one of the biosorption mechanisms. The relative distribution of dissolved arsenic is influenced by pH and the redox conditions. Under mildly reducing conditions and at pH=6 and 9, As (V) exists predominantly as  $H_2As_2SO_4^-$  and is likely to form a complex with iron oxide-coated biomass. At higher pH, OH ions in the solution can compete with the arsenite ions and so adsorption of As (V) will be reduced (Pokhrel and Viraraghavan, 2006).

Ionic species such as  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $K^+$  are usually present in drinking water and groundwater contaminated with arsenic (Smedley and Kinniburgh, 2002). Batch equilibrium experiments were conducted to evaluate the influence of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $K^+$  on As (V) removal by pretreated tea fungal biomass. As (V) removal obtained from experiments with  $C_i=1$  mg/L and several initial concentrations of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $K^+$  are displayed in Fig. 5. Within the initial concentration range of 50-100 mg/L,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  had effect on As (V) removal by about 4-10%. Increasing the initial concentrations of background ions to 500 mg/L caused decrease on As removal. It is evident from Fig. 6 that the removal of As (V) increased with the increase in agitation speed from 50 to 150 rpm. This may be explained by the fact that the increasing agitation rate decreases the boundary layer resistance to mass transfer in the bulk and increases the driving force of As(V) ions. It may be, therefore, assumed that the film diffusion does not dominantly control the overall adsorption process (Mckay, 1981). It is further noted that there was no significant increase in uptake above 150 rpm. The results revealed that  $FeCl_3$  treated and autoclaved fungal mats are efficient in removing As (III), As (V) and Fe (II) from groundwater samples, respectively.  $FeCl_3$  treated fungal mat work better because iron has an affinity towards arsenic in forming arsenic-iron oxides. Also, some researchers had reported that iron has more affinity toward arsenic (Hodi *et al.*, 1995; Singh *et al.*, 1998; Welch *et al.*, 2000; and Thirunavukkarasu *et al.*, 2003). Hence  $FeCl_3$  pretreated fungal mat work better than nontreated mat and we achieved the same result in this study.

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