Thermodynamics of As(V) Adsorption onto Treated Granular Zeolitic Tuff from Aqueous Solutions

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The adsorption of As(V) ions from aqueous solution onto treated granular zeolitic tuff (TZT) has been investigated. In this study, the effects of adsorbent dose, solution pH, initial concentration, contact time, and temperature were examined. Thermodynamic analysis revealed that the adsorption behavior of As(V) ions onto the TZT adsorbent was an endothermic process, resulting in higher adsorption capacities at higher temperatures. Thermodynamic parameters, the negative values of ΔG^o and positive values of ΔH^o, revealed that the adsorption process was spontaneous and endothermic. The Langmuir and Freundlich isotherm models were employed to fit the isothermal adsorption. The results revealed that the Langmuir isotherm model is the best-fit model to predict the experimental data.

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1. Introduction

Arsenic is a toxic trace element occurring in natural water and wastewaters mainly in the inorganic trivalent As(III) and pentavalent As(V) oxidation states. The toxicity of arsenic depends on its oxidation state and trivalent As has been reported to be more toxic than pentavalent As.[1] It has been reported[2] that the long-term uptake of arsenic-contaminated drinking water produced gastrointestinal, skin, liver, and nerve tissue injuries. The presence of arsenic in water and wastewaters is mostly due to biological and mining activities, geochemical reactions, arsenic additives, pesticides, and herbicides; crop desiccants make the problem more serious for animals and human beings.[3]

Various treatment methods have been reported for the removal of arsenic from aqueous solutions, precipitation/coagulation processes using metal salts such as those of iron and aluminum,[4] precipitation/adsorption processes on activated alumina and oxides/hydroxides of mainly iron,[5] ion exchange,[6] and desalting techniques such as reverse osmosis or electrodialysis.[7] The adsorption technique is generally considered to be a promising method and has been studied for arsenic removal from aqueous solutions. So far, various adsorbents for arsenic removal have been developed which include granular ferric hydroxide,[8] titanium dioxide,[9] natural zeolites,[10] zeolitic volcanic rocks,[11] activated bauxite,[12] activated carbon,[12] activated alumina,[13] and aluminum-loaded shirasu zeolite.[14]

In this work, a new adsorbent, treated granular zeolitic tuff (TZT), was developed for the adsorption and removal of As(V) from aqueous solution. The TZT was found to work as an excellent adsorbent for As(V).

2. Experimental Section

2.1. Preparation of As(V) Stock Solution. An As(V) stock solution of 1000 mg·L^{-1} was prepared by dissolving 4.1645 g of sodium arsenate ($NaH_2AsO_4 \cdot 7H_2O$, Merck, Germany) in 1000 mL of double-distilled water. A working solution for the experiments was freshly prepared from the stock solution. The working solutions with different concentrations of As(V) ions were prepared by appropriate dilutions of the stock solution immediately prior to their use. Standard acid of 0.1 M HNO_3 and a base solution of 0.1 M NaOH were used for pH adjustment. All of the reagents were of analytical grade and used without further purification.

2.2. Preparation of Adsorbent. Zeolitic tuff (ZT) samples were collected from Jabal Aritayn, 30 km northeast of Azraq, Jordan. ZT was rolled crushed by a jaw crusher to obtain grains of ZT with dimensions between (0.08 and 2.5) mm and then sieved to obtain (0.5 to 2) mm sized fraction. The (0.5 to 2) mm sized fraction of ZT was washed with distilled water to remove soluble elements and dried at 378 K. Dried ZT was treated with concentrated hydrochloric acid (0.32 mass fraction purity) with agitation from time to time and left overnight. An aqueous colored acid solution which formed was separated from grains of zeoltic tuff by decantation and filtration. Grains of TZT were washed with distilled water and dried at a temperature of 378 K. The TZT samples from volcanic tuffs were examined by X-ray fluorescence (XRF), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR).

2.3. Adsorption Isotherms. Adsorption equilibrium was obtained by shaking 1 g of dry adsorbent (TZT) in a series of 100 mL flasks containing 20 mL of initial concentration of As(V) ions ranging from (10 to 100) mg·L^{-1} for 120 min. The initial pH value of As(V) ion solutions was adjusted from 1 to 9.0 with either 0.01 M HNO_3 or 0.01 M NaOH at four temperatures, (283.15, 293.15, 303.15, and 313.15) K. Flasks were agitated on a shaker at a 350 rpm constant shaking rate for 120 min to ensure equilibrium was reached and filtered through filter paper (Schleicher and SchÜll 589), and the supernatant was analyzed for arsenic by a sequential plasma emission spectrometer (ICPS-7510, Shimadizu). Each experiment was run in triplicate, and mean values are reported.

The As(V) percent removal was calculated using the following equation

$$\text{removal (\%)} = \frac{C_o - C_e}{C_o} \cdot 100 \qquad (1)$$

where C_o and C_e are the initial and equilibrium concentrations of the As(V) ion (mg·L^{-1}).

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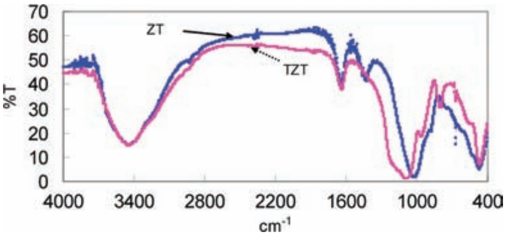

Figure 1. FTIR spectra of raw zeolitic tuff (ZT) and treated zeolitic tuff (TZT).

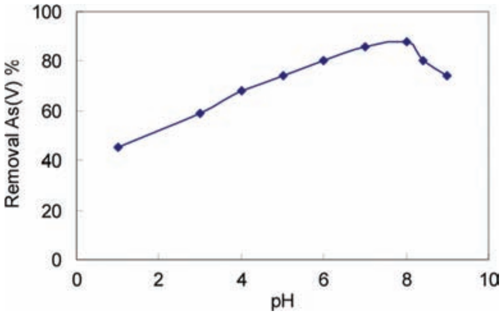

Figure 2. Effect of pH solution on the percent removal As(V) by TZT ($T = 303$ K; $C_o = 20$ mg·L^{-1}; pH = 8.0).

The amount of As(V) ions adsorbed at equilibrium q_e, which represents As(V) uptake was calculated from the following equation

$$q_e = \frac{(C_o - C_e)V}{M} \tag{2}$$

where q_e is the As(V) adsorbed (mg·g^{-1}); C_o and C_e are the same as above; V is the volume of the solution (L); and M is the weight of adsorbent (g).

3. Results and Discussion

3.1. Characterization of TZT Adsorbent. The XRD analysis indicated that the examined TZT sample is rich in phillipsite [(Ca, Na$_2$, K$_2$)$_3$ Al$_6$Si$_{10}$O$_{32}$·12H$_2$O] with some magnesium iron oxides (magnesioferrite). FTIR absorption bands of ZT and TZT are illustrated in Figure 1. The method used in this work for treating ZT allows the separation of approximately 100 w (mass fraction) = 25 to 30 of other volcanic constituents (iron, aluminum, magnesium, calcium, and sodium oxides). Figure 1 indicated that the band of ν CO$_3$ at 1426 cm^{-1} in ZT disappeared in TZT and the band of ν Si−O−Al at 1022 cm^{-1} was shifted to 1094 cm^{-1}, which appears as a strong band due mainly to phillipsite indicating that it is the major constituent of TZT. A shoulder appears at ~1200 cm^{-1} which is due to the presence of faugasite and chabasite, with a possible contribution of amorphous silica. XRF analysis showed that the TZT is rich in SiO$_2$ and Al$_2$O$_3$ with a percent oxide composition of 48.70 and 7.83, respectively. The moderate to high SiO$_2$/Al$_2$O$_3$ ratio of 6.98 gives rise to good selectivity.[15] Mineralogical characterization studies[16,17] of some Jordanian ZT showed that the main constituents are phillipsite, chabasite, and faujasite.

3.2. Effect of the Initial pH. The effect of pH of the As(V) solution on the adsorption capacity of As(V) onto the TZT is shown in Figure 2. It can be seen from Figure 2 that the removal As(V) percent increases sharply with increasing pH of As(V) from 1.0 to 8.0 and then decreases to reach pH 9.0. However, a decline in removal As(V) percent occurred when the pH was lower than 8.0. The maximum adsorption was observed around pH 8.0 at all temperatures.

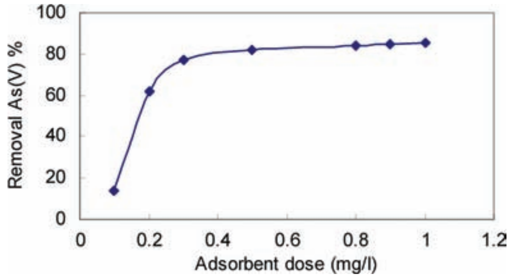

Figure 3. Effect of adsorbent dose on the percent removal of As(V) by TZT ($T = 303$ K; $C_o = 20$ mg·L^{-1}; pH = 8.0).

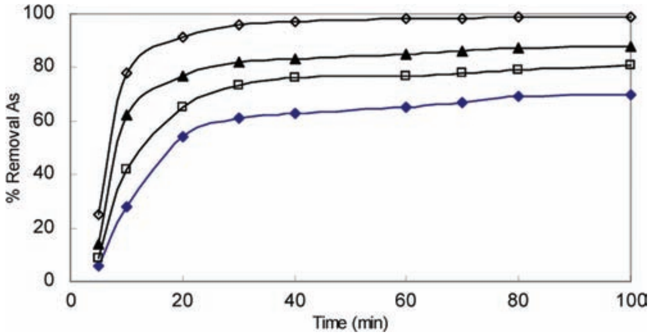

Figure 4. Effect of contact time and temperature on percent removal of As(V) by TZT. T = ♦, 283 K; □, 293 K; ▲, 303 K; ◊, 313 K.

3.3. Effect of Adsorbent Dose. The effect of adsorbent dose of TZT on the As(V) removal percent is shown in Figure 3, which shows that the removal percent of As(V) increased very rapidly with an increase in dosage of TZT from (0.1 to 0.9) g·L^{-1} and a marginal increase was observed on further increase in the adsorbent dose. At an adsorbent dose of 0.9 g·L^{-1} TZT, maximum removal efficiencies of 84.12 % were observed at 303.15 K. The increase in efficiency of As(V) removal may be attributed to the fact that, with an increase in the adsorbent dose, more adsorbent surface or more adsorption sites were available for the metal ions to be adsorbed.

3.4. Effect of Contact Time and Temperature. The effect of contact time and temperature on the adsorption of As(V) onto TZT is shown in Figure 4. It can be seen from Figure 4 that the removal percent of As(V) increases with contact time until equilibrium is attained between the amount of As(V) on TZT and the remaining As in solution. Figure 4 shows that the removal percent of As(V) increases with contact time from (0 to 60) min and then becomes almost constant up to the end of the experiment. It can be concluded that the binding of As(V) with TZT is high at initial stages and becomes almost constant after an optimum contact time of 100 min. As temperature increases from (283 to 313) K, As(V) removal percent increased from (70.0 to 98.8) % for an initial concentration of 50 mg·L^{-1} at pH 8.0. Similar trends were observed for other concentrations. This indicated that the adsorption process is endothermic in nature. The As(V) removal percent versus time curves are smooth and continuous leading to saturation, suggesting possible monolayer coverage of As(V) ions on the surface of the TZT.

3.5. Thermodynamics. In the present work, the thermodynamic behavior of the adsorption of As(V) ions onto TZT is evaluated as follows. The changes in Gibbs energy, ΔG^o, of the adsorption process is related to the equilibrium constant by the following equation

$$\Delta G^{\mathrm{o}} = -RT \ln K_{\mathrm{c}} \tag{3}$$

where K_c is the equilibrium constant calculated from the following equation

$$K_{\mathrm{c}} = \frac{C_{\mathrm{Ae}}}{C} \tag{4}$$

where C_{Ae} and C_e are the equilibrium concentration of As(V) ($\mathrm{mg \cdot L^{-1}}$) on TZT adsorbent and in solution, respectively.

The enthalpy change, ΔH^o, and entropy change, ΔS^o, were obtained from the van't Hoff equation

$$\log K_{\mathrm{c}} = \frac{\Delta S^{\mathrm{o}}}{2.303R} - \frac{\Delta H^{\mathrm{o}}}{2.303RT} \tag{5}$$

where T is the absolute temperature (K); R is the gas constant ($8.314\ \mathrm{J \cdot mol^{-1} \cdot K}$). ΔH^o ($\mathrm{kJ \cdot mol^{-1}}$) and ΔS^o ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$) were calculated from the slope and intercept of a linear plot of $\log K_c$ versus $1/T$. The plot shown in Figure 5 is linear over the entire range of temperatures investigated.

The thermodynamic parameters were evaluated at four operating temperatures, (283, 293, 303, and 313) K, at an initial As(V) concentration of $10\ \mathrm{mg \cdot L^{-1}}$. The values of K_c, ΔH^o, ΔS^o, and ΔG^o at the investigated temperatures are listed in Table 1. The obtained negative values of ΔG^o at all temperatures studied revealed the fact that the adsorption process was spontaneous. Positive values of ΔH^o indicate the endothermic nature of the adsorption process. The positive value of ΔS^o suggests increased randomness of the solid−solution interface during the adsorption of As(V) ions onto TZT adsorbent.

3.6. Adsorption Isotherms. Adsorption data for a wide range of adsorbate concentration are most conveniently described by adsorption isotherms. The experimental data for the removal of As(V) by TZT were processed using the Langmuir and Freundlich isotherm models (Figures 6 and 7). The data were found to fit both models.

The Langmuir isotherm model is given by the following equation

$$\frac{C_{\mathrm{e}}}{q_{\mathrm{e}}} = \frac{1}{Q_{\mathrm{m}} b} + \frac{1}{Q_{\mathrm{m}}} C_{\mathrm{e}} \tag{6}$$

where q_e is the milligrams of arsenic adsorbed per gram of the adsorbent; C_e is the arsenic concentration in the final solutions ($\mathrm{mg \cdot L^{-1}}$); and Q_m ($\mathrm{g \cdot g^{-1}}$) and b ($\mathrm{L \cdot g^{-1}}$) are the Langmuir constants related to sorption capacity and sorption energy, respectively. The maximum adsorption capacity denoted by Q_m represents monolayer coverage of As(V) with adsorbent, and b implies the enthalpy of adsorption which should vary with temperature. A linear plot, Figure 4, is obtained by plotting C_e/q_e against C_e over the entire range of arsenic concentration investigated. Langmuir parameters Q_m and b, together with the regression coefficients R^2 determined from the plot given in Table 2, confirm a good agreement between the theoretical model and the experimental results obtained. Q_m values are computed from the slope and b values from the intercept. Langmuir Q_m and b values increased with temperature, showing that the adsorption capacity and intensity of adsorption are enhanced at higher temperatures.

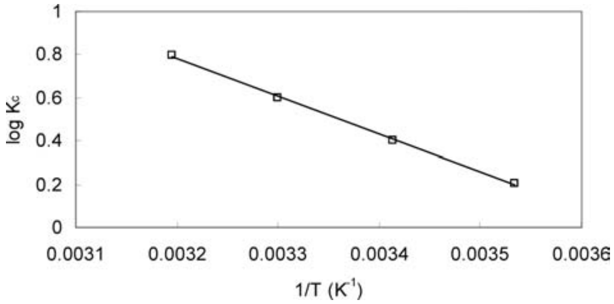

Figure 5. log K_c vs $1/T$ for the adsorption of As(V) by TZT.

Table 1. Thermodynamic Parameters of TZT for As(V) Adsorption

T		ΔG^o	ΔH^o	ΔS^o
K	K_c	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
283	1.599	−1.106	9.459	121.887
293	2.506	−2.239	9.794	
303	3.990	−3.486	10.128	
313	6.223	−4.758	10.462	

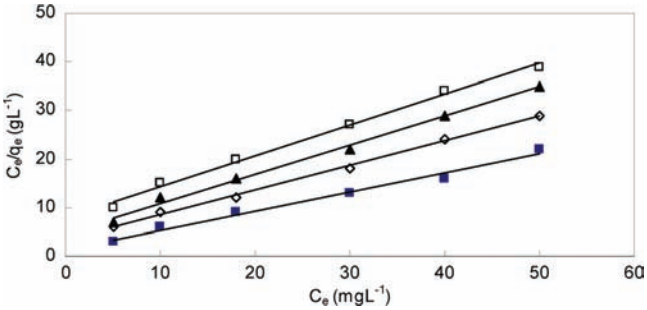

Figure 6. Langmuir plots for As(V) onto TZT at T = ■, 283 K; ◊, 293 K; ▲, 303 K; □, 313 K.

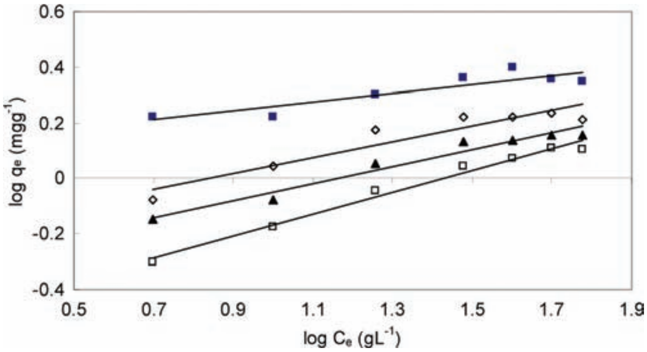

Figure 7. Freundlich plots for As(V) onto TZT at T = □, 283 K; ▲, 293 K; ◊, 303 K; ■, 313 K.

Table 2. Langmuir and Freundlich Adsorption Constants Obtained from Adsorption Isotherms of As(V) Ions at Different Temperatures

T	Langmuir constants			Freundlich constants		
K	Q_o	b	R^2	n	K	R^2
283	15.723	0.077	0.998	2.538	0.274	0.983
293	16.313	0.132	0.998	3.268	0.439	0.955
303	18.349	0.201	0.992	3.521	0.578	0.885
313	23.866	0.377	0.995	6.289	1.256	0.809

The Freundlich isotherm model could be applied to the sorption process which describes the physical adsorption of As(V) only. In contrast to the Langmuir monolayer model, the Freundlich isotherm is a consecutive layer model which does not predict any saturation of the adsorbent by As(V). The linearized form of the Freundlich isotherm used to evaluate the different sorption parameters is

$$\log q_{\mathrm{e}} = \log K + \frac{1}{n} \log C_{\mathrm{e}} \tag{7}$$

where C_e is the equilibrium concentration ($\mathrm{mg \cdot L^{-1}}$); q_e is amount adsorbed at equilibrium ($\mathrm{mg \cdot L^{-1}}$); and K and n are the isotherm constants are calculated from the intercepts and slopes of the Freundlich plots of log q_e against log C_e (Figure 5). Freundlich parameters K and n together with the regression coefficients R^2 determined from the plot are given in Table 2 and confirmed a good agreement between the theoretical model and experimental results obtained.

The Langmuir model is more suitable than the Freundlich model for the representation of the adsorption data because it has higher R^2 values.

4. Conclusions

The results in this paper demonstrate that TZT is an effective adsorbent and can be successfully used as an adsorbing agent for the removal of As(V) ions from aqueous solutions. The thermodynamic parameters, ΔH^o, ΔS^o, and ΔG^o values, of As(V) ion adsorption onto TZT show the endothermic heat of adsorption, favored at higher temperatures. The positive value of ΔS^o revealed an increase in randomness of the solid–solution interface during the adsorption of As(V) ions. Regression coefficients R^2 were found to be more than 0.99 and 0.98, revealing the best fit for the adsorption data by the Langmuir isotherm model over the Freundlich isotherm model.

Literature Cited

(1) Moore, J. W.; Ramamoorthy, S. *Heavy metals in natural waters*; Springer-Verlag: New York, 1984.

(2) Choong, T. S. Y.; Chuah, T. G.; Robiah, Y.; Koay, F. L. G.; Azni, I. Arsenic toxicity, health hazards and removal techniques from water: an overview. *Desalination* **2007**, *217*, 139–166.

(3) Mohan, D.; Pittman, C. U., Jr. Arsenic removal from water/wastewater using adsorbents -a critical review. *J. Hazard. Mater.* **2007**, *142*, 1–53.

(4) Gupta, V. K.; Saini, V. K.; Jain, N. Adsorption of As(III) from aqueous solutions by iron oxide-coated sand. *J. Colloid Interface Sci.* **2005**, *288*, 55–60.

(5) *WHO Guidelines for drinking Water Quality. 1. Recommendations*; World Health Organization: Geneva, 1993.

(6) USEPA. http://www.epa.gov./safewater/arsenic.html, 2004.

(7) Bissen, M.; Frimmel, F. H. Arsenic-a review, Part II. Oxidation of arsenic and its removal in water treatment. *Acta Hydrochim. Hydrobiol.* **2003**, *31*, 97–107.

(8) Guan, X.-H.; Wang, J.; Chusuei, C. C. Removal of arsenic from water using granular ferric hydroxide: Macroscopic and microscopic studies. *J. Hazard. Mater.* **2008**, *156*, 178–185.

(9) Bang, S.; Patel, M.; Lippincott, L.; Meng, X. Removal of arsenic from groundwater by granular titanium dioxide adsorbent. *Chemosphere* **2005**, *60*, 389–397.

(10) Chutia, P.; Kojima, T.; Satokawa, S. Arsenic adsorption from aqueous solution on synthetic zeolites. *J. Hazard. Mater.* **2009**, *162*, 440–447.

(11) Ruggieri, F.; Marin, V.; Gimeno, D.; Fernandez-Turiel, J. L.; Garcia-Villes, M.; Gutierrez, L. Application of Zeolitic volcanic rocks for arsenic removal from water. *Eng. Geol. (Amsterdam)* **2008**, *101*, 245–250.

(12) Gupta, K. S.; Chen, N. W. Arsenic removal by adsorption. *J. Water Pollut. Control Fed.* **1978**, *50*, 493–499.

(13) Bellock, E. Arsenic removal from table water. *J. Water Health* **1971**, *64*, 454–458.

(14) Xu, Y.-H.; Nakajima, T.; Ohki, A. Adsorption and removal of arsenic (V) from drinking water by aluminum-loaded Shirasu-zeolite. *J. Hazard. Mater.* **2002**, *B92*, 275–287.

(15) Erdem, E.; Karapinar, N.; Donat, R. The removal of heavy metal cations by natural zeolites. *J. Colloid Interface Sci.* **2004**, *280*, 309–314.

(16) Ibrahim, K. M.; Jbara, A. A. Removal of paraquat from synthetic wastewater using phillipsite-faujasite tuff from Jordan. *J. Hazard. Mater.* **2009**, *163*, 82–86.

(17) Yousif, R. I.; Tutunji, M. F.; Derwish, G. A.; Musleh, S. M. Chemical and structural properties of Jordanian zeolitic tuffs and their admixtures with urea and thiourea: potential scavengers for phenolics in aqueous medium. *J. Colloid Interface Sci.* **1999**, *216*, 348–359.

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