

## Kinetic and thermodynamic analysis of adsorption of arsenic (III) with waste crab shells

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### ABSTRACT

Recently, pollution incidents in surface water occurred frequently all over the world, which normally caused the surface water to have lower concentrations of heavy metals. A low cost waste crab shell (WCS) has been studied for the removal of arsenic from the contaminated surface water. The adsorption kinetics of WCS for low concentration (<1 mg/L) of arsenic (III) in a controlled batch system was studied. The effects of initial arsenic (III) concentrations, temperature, pH, and WCS biomass dose on the adsorption were investigated. Under the conditions set in this research, the maximum adsorption capacity for arsenic (III) was 165.78 mg/kg at 0.928 mg/L of initial arsenic (III) concentrations, pH 7.0, 40 °C, and 2.0 g/L of WCS biomass. The kinetics fitted the pseudo-second-order model better than models, such as pseudo-first-order model, *Elovich* kinetic model, and intra-particle diffusion model, etc. An examination of thermodynamic parameters showed that the adsorption of arsenic (III) with WCS was non-spontaneous and endothermic, as well as a physical process. The results suggested that WCS adsorption may be a useful option for arsenic removal from slightly arsenic-contaminated surface water.

**Key words** | adsorption, arsenic, kinetics, thermodynamic, waste crab shells

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### INTRODUCTION

Arsenic and its compounds are well-known toxic substances in ground water, causing severe human health problems (Pena *et al.* 2005; dos Santos *et al.* 2011; Maiti *et al.* 2012). The World Health Organization recommends a standard of arsenic concentrations of 10 µg/L in drinking water (Rana *et al.* 2009; Vijayaraghavan *et al.* 2009). Adsorption is one of the popular methods to remove aqueous arsenic (Basu & Ghosh 2011). Traditional materials used in sorption methods for arsenic removal include activated alumina (Lin & Wu 2001), iron coated sand (Gupta *et al.* 2005), and ion-exchange resins (Kim & Benjamin 2004), which are all effective for arsenic removal from aqueous solution. However, researchers are still looking for cheaper adsorbents and treatment techniques (Mohan & Pittman 2007). Recent research has reported a number of economical biological materials which can be considered as biosorbents to

remove arsenic from aqueous solution, such as bacteria (Takeuchi *et al.* 2007), fungi (Murugesan *et al.* 2006), chitin and chitosan (Elson *et al.* 1980), cellulose sponge (Munoz *et al.* 2002), water hyacinth (Misbahuddin & Fariduddin 2002), *Pteris vittata* (Caille *et al.* 2004), human hair (Wasiuddin *et al.* 2002), and orange waste (Ghimire *et al.* 2003). Containing high amounts of chitin or chitosan, treated waste crab shell (WCS) represents a potential bioadsorbent due to its low cost, rigid structure, excellent mechanical strength, and ability to withstand extreme conditions, such as high-temperature regeneration processes (Niu *et al.* 2007).

Previous research has demonstrated that acid-washed crab shells (acid-WCS) have promising potential for removing Cu, Pb, Ni, Cd, Co, Au, Se, Cr, V, and Zn (An *et al.* 2001; Chu 2002; Niu & Volesky 2003a, b; Vijayaraghavan *et al.*

2004, 2006; Lu *et al.* 2007). Additionally, aqueous As(V) could be removed effectively with WCS (Vijayaraghavan *et al.* 2004, 2009; Niu *et al.* 2007; Rana *et al.* 2009). However, few studies focused on the individual As(III) removal by WCS. As(III) is more toxic than As(V), owing to the higher sulfur affinity to interrupt the intermediate metabolism (Weerasooriya *et al.* 2003). Furthermore, As(III) is more difficult to be removed than As(V) (Chowdhury & Mulligan 2011), because some methods require a preoxidation step, converting As(III) to As(V) for effective arsenic removal, such as oxidation-precipitation (Zaw & Emett 2002; Bissen & Frimmel 2003) and coagulation-coprecipitation (Khan *et al.* 2002; Wickramasinghe *et al.* 2004). This problem could be solved by direct As(III) adsorption. Since previous research on arsenic concentrations, arsenic removal with WCS focused on high initial concentrations (>1 mg/L) (Kalmykova *et al.* 2008), low concentration (<1 mg/L) arsenic removal attracts less study (Rana *et al.* 2009; Vijayaraghavan *et al.* 2009; Jeon 2011), which could not be ignored, owing to the bioaccumulation of marine animals in the long term.

The objective of this study is to investigate the potential of WCS on removal of aqueous As(III) at low concentrations. Parameters affecting the biosorption potential, kinetics, and thermodynamics of biosorption were also determined and demonstrated.

## MATERIALS AND METHODS

### Biosorbent and solution preparation

Raw WCS: WCS obtained from a seafood market in Jinan, Shandong, China, was treated as follows: washed by deionized water, fully dried, and crushed and sieved into 0.35–0.5 mm particles. Then, the particles were rinsed in 1 N HCl (55 g dry shells/L HCl) for 6 h in order to eliminate minerals before being washed with deionized water until the pH was stabilized at approximately 6.0. The washed material was dried at 55 °C overnight.

As(III) solutions were prepared with solid NaAsO<sub>2</sub> and deionized water. The pH values of aqueous samples were adjusted with 0.1 M HCl or 0.1 M NaOH if necessary. All the reagents used in this study were of analytical grade.

### Experimental procedure

In the batch adsorption experiments, each 250 mL conical flask contained 100 mL of As(III) solution and 0.2 g WCS, being shaken with bath shakers for 10 h at 120 rpm. Then, mixed solution was filtered through 0.22 μm polytetrafluoroethylene membranes and the filtrate was kept for As(III) analysis. In the experiment, for effect of the initial As(III) concentrations, 100 mL of arsenic solutions were prepared with different known initial concentrations (0.032, 0.051, 0.088, 0.491, and 0.928 mg/L). To determine the effects of pH and temperatures on adsorptions, tests were conducted at different pH values (1.0, 3.0, 5.0, and 7.0) and temperatures (13, 20, 30, and 40 °C). To evaluate the influence of biomass doses, a series of WCS mass (0.08, 0.12, 0.20, 0.28, and 0.40 g) were added to 100 mL of As(III) solution (0.928 mg/L), respectively. In kinetic studies, 1.0 g of WCS was added to 1.0 L of 0.928 mg/L As(III) solution (pH = 7.0) at 13 °C, shaken at 120 rpm and sampled at 15, 30, 60, 180, 300, 600 and 1440 min, respectively. In addition, the same kinetic experiment procedures were carried out at 20, 30, and 40 °C for thermodynamic studies, respectively.

Each test was run in triplicate with a blank control under the same condition. The As(III) concentrations were determined by atomic fluorescence spectrometry (AFS-930) (Beijing Titan Instruments Co., Ltd). The As(III) adsorption capacity can be calculated using Equation (1)

$$Q_e = (C_0 - C_e)V/m \quad (1)$$

where  $Q_e$  is the metal adsorption capacity (mg arsenic/kg WCS);  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of As(III) in the solutions (mg/L), respectively;  $V$  is the solution volume (L); and  $m$  is the biomass dose of WCS (g).

## RESULTS AND DISCUSSION

### Effect of initial As(III) concentrations

The effect of initial As(III) concentrations on adsorption (pH = 7.0, temperature = 13 °C, WCS biomass = 2.0 g/L) is

shown in Figure 1. The adsorption capacity ( $Q_e$ ) increased with the initial As(III) concentrations, and its maximum value was  $162.70 \pm 11.31$  mg/kg when the concentration was 0.928 mg/L within the tested concentration range (0.032–0.928 mg/L). Considering the trend of curve, the adsorption capacity was assumed to keep increasing if higher initial concentration was involved. However, the equilibrium As(III) removal efficiency decreased from 64.9% at initial As(III) concentrations of 0.032 mg/L to 35.1% at initial As(III) concentrations of 0.928 mg/L. A possible explanation may be that As(III) adsorption sites on WCS became increasingly saturated with higher initial As(III) concentrations (Kalmykova *et al.* 2008).

### Temperature effect

The influence of temperature on adsorption (pH = 7.0) is shown in Figure 2. The adsorption capacity increased slightly with the increase of water temperature from 13 to 40 °C, with a maximum value of  $165.78 \pm 15.33$  mg/kg under the conditions of initial arsenic (III) concentrations of 0.928 mg/L, pH 7.0, 40 °C, and WCS biomass of 2.0 g/L. The results demonstrated that temperature is not the main influencing factor of As(III) adsorption. Similar behavior was observed in the adsorption of aqueous phosphate on WCS (Jeon & Yeom 2009). The thermal stability of WCS favored to As(III) adsorption could benefit its application to the

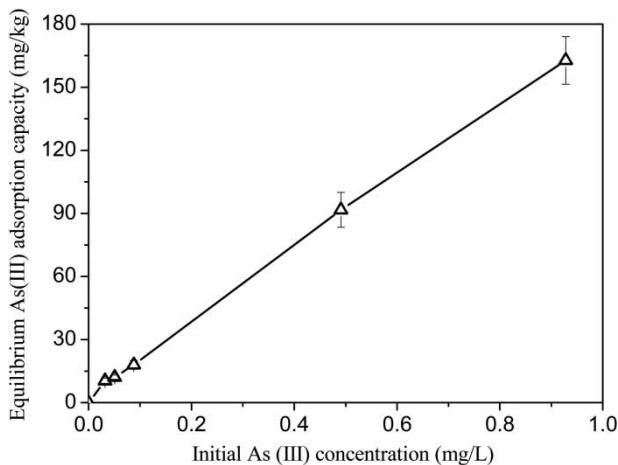


Figure 1 | Effect of initial As(III) concentrations on adsorption (pH 7.0, 13 °C, WCS biomass of 2.0 g/L).

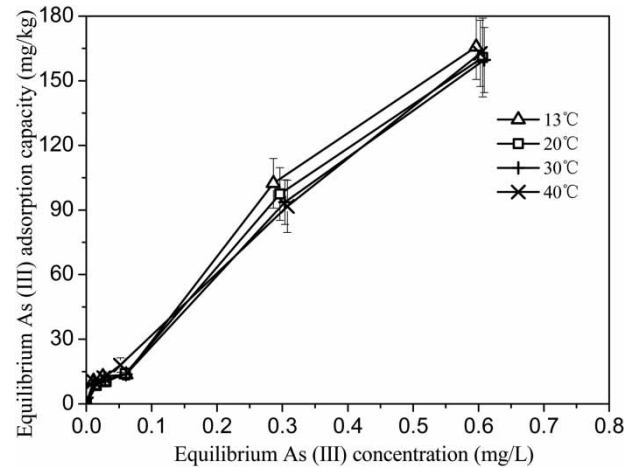


Figure 2 | Influence of temperature on adsorption (pH = 7.0, initial As(III) concentrations of 0.928 mg/L, WCS biomass of 2.0 g/L).

treatment of natural waters polluted with arsenic, especially resisting the temperature shifting at the transition of seasons.

### pH effect

Figure 3 shows adsorption isotherms obtained for As(III) on WCS at equilibrium pH values of 1.0, 3.0, 5.0, and 7.0. As pH increases at the initial As(III) concentrations of 0.928 mg/L, the adsorption capacity for As(III) uptake on WCS increased from  $109.10 \pm 8.12$  to  $162.70 \pm 15.32$  mg/kg. This could be attributed to the fact that the arsenic dominant species is  $H_3AsO_3$  ( $pK_a = 9.2$ )

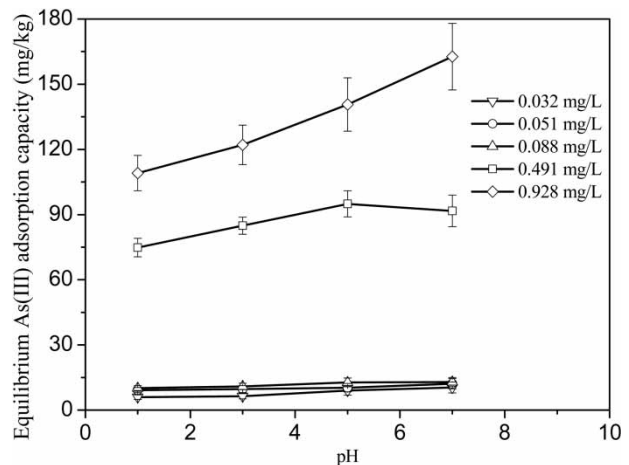


Figure 3 | Influence of pH on adsorption ( $T = 13$  °C; WCS biomass of 2.0 g/L).

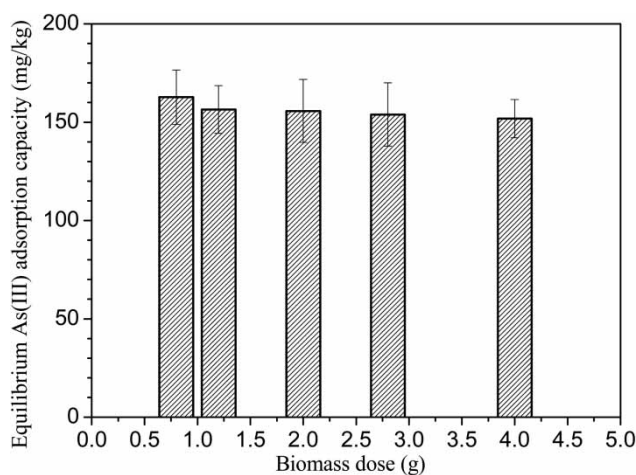
when pH is far less than 7.0, and van der Waals force could play an important role between the solute and adsorbent (Weerasooriya *et al.* 2003). With pH increasing, more  $\text{H}_2\text{AsO}_3^-$  would form and benefit arsenic uptake to WCS, due to more electrostatic attraction (Liu *et al.* 2012).

### Effect of WCS dose

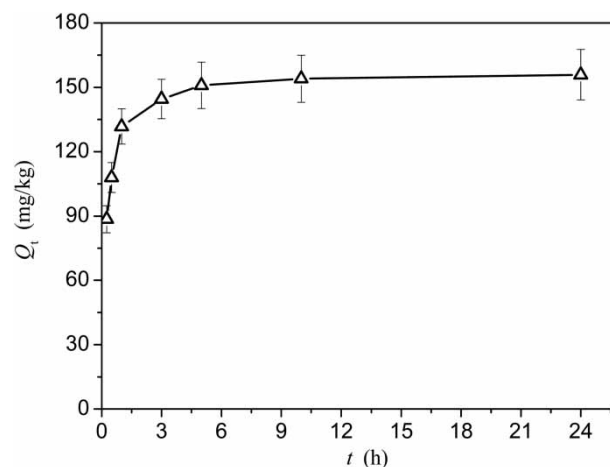
Generally, the metal adsorption capacity increases with biomass dose. However, Figure 4 shows that the As(III) adsorption capacity slightly decreased from  $162.70 \pm 13.87$  to  $151.83 \pm 9.71$  mg/kg with the biomass dose increasing from 0.8 to 4.0 g/L, which resulted from the effective active area reducing, caused by biomass particle aggregating at a high biomass dose (Miretzky *et al.* 2010). Similar results were reported for As(V), Cu, and Co on WCS (Vijayaraghavan *et al.* 2006).

### Kinetics

Kinetic study was conducted to investigate As(III) adsorption rate and to determine the rate-limiting step within the ion transport mechanism. The kinetic curve of aqueous As(III) adsorption on WCS ( $T = 13^\circ\text{C}$ ,  $\text{pH} = 7.0$ ) is shown in Figure 5, including three time phases. For the first 15–60 min, the increasing of metal



**Figure 4** | Influence of WCS biomass dose on As(III) adsorption ( $\text{pH} = 7.0$ ,  $T = 13^\circ\text{C}$ , initial As(III) concentrations of 0.928 mg/L).



**Figure 5** | Kinetics of As(III) adsorption onto WCS from aqueous solution ( $T = 13^\circ\text{C}$ ,  $\text{pH} = 7.0$ , WCS biomass of 1.0 g/L).

adsorption capacity and rate resulted from the dominant van der Waals force between sorbents and sorbates. The second phase was from 60–300 min, where the slope of the curve became lower, meaning the metal adsorption capacity increased more slowly. This could be attributed to gradual saturation of the active site on the WCS surface. The third phase started from 300 min to the end. In this phase, the adsorption reached equilibrium when the curve tended to be level. Generally, the transport of metal ions on porous media includes four steps: transport of the sorbate in the bulk solution, film diffusion from the bulk solution through the boundary layer of fluid immediately adjacent to the external surface of the biosorbent particle, diffusion through the particle, and intra-particle diffusion (Lodeiro *et al.* 2006). The last two steps are slower, so they are usually considered as rate-limiting steps.

Four kinetic models were used to fit the tested results of this study: the pseudo-first-order model, the pseudo-second-order model, the Elovich kinetic model and the intra-particle diffusion model. Fitting curves and model parameters are shown in Figure 6 and Table 1, respectively.

The  $Q_e$  obtained from the intercept of the plot of the pseudo-first-order model was 46.13 mg/kg, which was much lower than the experimental value of 155.89 mg/kg, which means that the kinetic process was not pseudo-first-order. The pseudo-second-order model gave a  $Q_e$  of

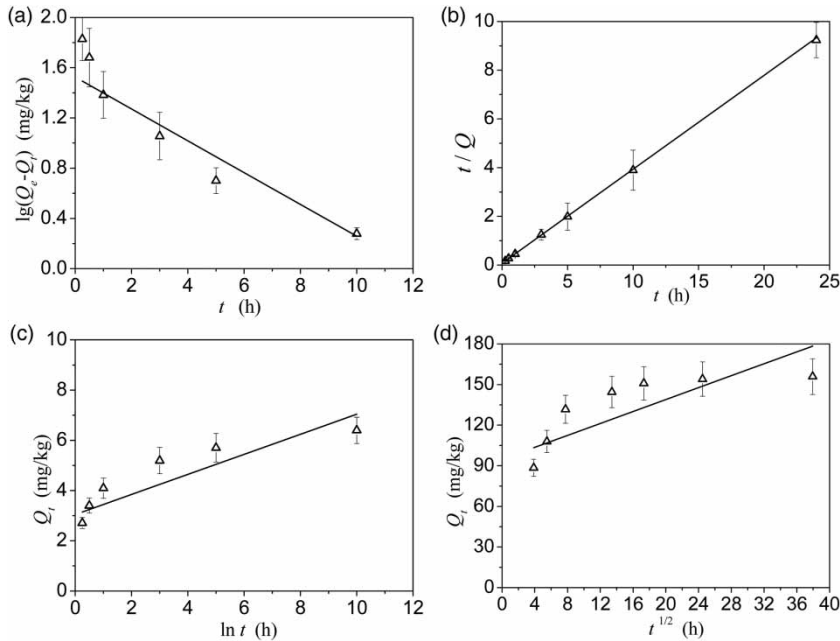


Figure 6 | Kinetic fitting curves using models: pseudo-first-order (a), pseudo-second-order (b), Elovich kinetics (c) and intra-particle diffusion (d). ( $T = 13^\circ\text{C}$ ,  $\text{pH} = 7.0$ ).

Table 1 | Fitting parameters for the pseudo-first order model, pseudo-second order model, Elovich kinetic model and intra-particle diffusion model

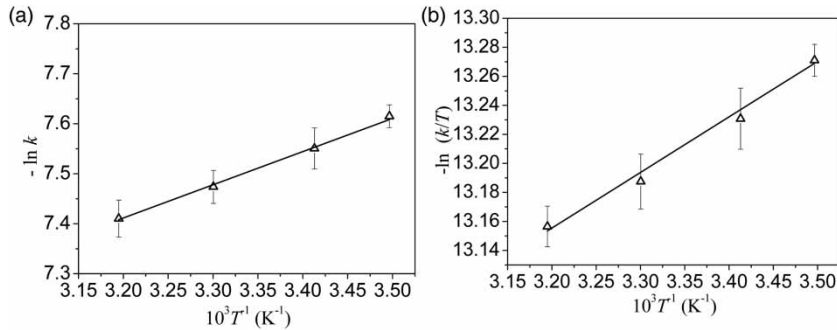
pH	T/°C	Pseudo-first order $\lg(Q_e - Q_t) = \lg Q_e - kt$ 2.303		Pseudo-second order $t/Q = 1/v_0 + t/Q_e$			Elovich kinetic $Q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$			Intra-particle diffusion $Q_t = k_d t^{1/2}$	
		$k_1$ 1/min	$r^2$	$k_2$ kg/mg·min	$v_0$ mg/kg·min	$r^2$	$\alpha$ mg/kg·min	$\beta$ mg/kg	$r^2$	$k_d$ mg/kg·min	$r^2$
7.0	13	$5.76 \times 10^{-3}$	0.92	$4.94 \times 10^{-4}$	11.67	1.00	879.52	0.07	0.88	1.68	0.63
7.0	20	$7.14 \times 10^{-3}$	0.96	$4.99 \times 10^{-4}$	12.97	1.00	963.26	0.07	0.88	1.71	0.62
7.0	30	$6.68 \times 10^{-3}$	0.94	$5.35 \times 10^{-4}$	13.91	1.00	1312.84	0.07	0.87	1.67	0.61
7.0	40	$6.45 \times 10^{-3}$	0.92	$5.76 \times 10^{-4}$	16.00	1.00	2316.90	0.07	0.84	1.61	0.58

156.25 mg/kg, which was approximately equal to the experimental data and the  $r^2$  value was 1.00, which showed that it was highly possible to be the actual adsorption process. The Elovich model ( $r^2 = 0.88$ ) did not match the experiment data as well as the pseudo-second-order model did; and for the intra-particle diffusion model the  $r^2$  value was only 0.63 and the curve obtained did not pass through the origin point, indicating that intra-particle diffusion was not the rate-limiting step.

## Thermodynamics

Assuming that the entropy ( $\Delta S^*$ ) and enthalpy ( $\Delta H^*$ ) during the adsorption process are not influenced by temperature, the  $k$  value can be obtained from the pseudo-second order kinetic model (data in Table 1) using the Arrhenius formula:

$$\ln k = -E_a/RT + c \quad (2)$$



**Figure 7** | Plots of  $1/T$  to  $-\ln k$  (a) and  $1/T$  to  $-\ln (k/T)$  (b) for As(III) adsorption on WCS.

where  $E_a$  is the adsorption activation energy (kJ/mol), which could be calculated from the curve slope in Figure 7(a).

$\Delta H^*$  and  $\Delta S^*$  were calculated by the Eyring formula (Equation (3)) and the Gibbs free energy ( $\Delta G^*$ ) was obtained by Equation (4):

$$\ln k/T = \ln k_B/h + \Delta S^*/R - \Delta H^*/RT \quad (3)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (4)$$

where  $k_B$  and  $h$  are the Boltzmann constant and the Planck constant, respectively,  $k$  is the rate constant of the pseudo-second order kinetic model. The values of  $\Delta H^*$  and  $\Delta S^*$  were the intercept and slope of the plot between  $-\ln (k/T)$  and  $1/T$  in Figure 7(b). All the thermodynamic parameters are summarized in Table 2.

Generally, when  $E_a < 40$  kJ/mol, it indicates that the reaction is a diffusion-controlled process while higher values represent a chemical reaction process. As(III) adsorption on WCS could be a diffusion-controlled rapid physical process due to  $E_a = 5.16$  kJ/mol (5–20 kJ/mol) in Table 2. Additionally, since the value is between 5 and 20 kJ/mol, the physical adsorption is the predominant adsorption mechanism for As(III) removal by WCS

(Anirudhan & Radhakrishnan 2008).  $\Delta S^* < 0$  indicates that the degree of disorder was reduced in the reaction system. Since  $\Delta H^* > 0$ , the reaction will be accelerated with increasing temperature. Also,  $\Delta G^* > 0$  demonstrates that the adsorption occurs only with when external energy is involved.

## CONCLUSIONS

The present work shows that WCS can be used to adsorb lower concentration aqueous As(III) in surface water. The maximum As(III) adsorption capacity by WCS was 165.78 mg/kg (pH = 7.0, T = 40 °C and 2.0 g/L biomass dose) from aqueous solution under the set conditions in this study. The pH and biomass dose showed significant influence on adsorption while temperature did not. Experimental kinetic data fit the pseudo-second-order model well, which indicated that it is highly possible to be the actual As(III) adsorption process. For the thermodynamic study, it was concluded that the adsorption process characterized with non-spontaneous characteristics and low adsorption activation energy favored higher temperature. All the study results will offer a reference for the application of treating slightly arsenic-contaminated natural water by WCS.

**Table 2** | Thermodynamic parameters for As(III) adsorption onto WCS

T/K	$E_a$ (kJ/mol)	$\Delta G^*$ (kJ/mol)	$\Delta H^*$ (kJ/mol)	$\Delta S^*$ (J/(mol · K))
286	5.16	31.64	2.67	-101.30
293		32.35		
303		33.36		
313		34.38		

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