A preliminary investigation on adsorption behavior of As(III) and As(V) in Jiangnan Plain

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ABSTRACT: High arsenic groundwater has posed a severe health threat to the local people in Jiangnan Plain. Several studies have been conducted to illuminate the factors and mechanism controlling seasonal variations in As concentrations. However, the quantitatively description of As adsorption has not been studied and this impedes the explanation of As reactive transport and fate in the study area. In this study, a series of adsorption experiments on natural sediments were conducted to investigate the characteristics of surface complexation reactions. The results showed that As(III) and As(V) have different adsorption behaviors on natural sediments. The HCO_3^- competitive adsorption has negligible effect on As(V) adsorption in artificial groundwater (AGW), while it has significant influences on As(III) adsorption. With the increase of pH, adsorbed As(III) concentration increased and As(V) concentration decreased. The results from this study strongly suggested that different adsorption behavior of As(III) and As(V) should be considered as a important process for controlling the seasonal variation in arsenic concentration in Jiangnan Plain.

1 INTRODUCTION

Jiangnan plain, which is located in the middle reaches of Yangtze River, was found to be widely distributed with high-arsenic groundwater. This posed a severe health threat to local people. Several studies have been conducted to investigate the distribution of high arsenic (As) groundwater and explore the factors and mechanism that control the seasonal variations in As concentrations. However, the As reactive transport has not been qualitatively simulated until know, which impedes the further understanding of As reactive transport processes. Adsorption and desorption play an important role in controlling the arsenic reactive transport. The behavior of adsorption/desorption and its quantitatively modeling is of great importance for the coupled flow- reactive transport modeling of arsenic and thus understanding its fate in Jiangnan Plain.

Hence, the aims of this research is to characterize the surface complexation behavior of As(III) and As(V) on natural sediments in Jiangnan Plain by laboratory batch experiments, and to develop the surface complexation model.

2 METHODS/EXPERIMENTAL

2.1 Study site and sediments collection

Jiangnan Plain is an alluvial plain created by Yangtze and Han rivers. It is comprised of the central and southern regions of Hubei Province. Arsenic concentration measured in the sediments and groundwater is much

Figure 1. Location of the monitoring site and the sediments is collected at SY07 (cited from Duan *et al.*, 2015).

higher than the global average. Meanwhile, adsorption and desorption are main factors for controlling arsenic concentrations under various geochemical conditions (Duan *et al.*, 2015; Rathi *et al.*, 2017). The study site, Shahu site, is located within the Jiangnan Plain as shown in Figure 1.

2.2 Adsorption experiments

A series of batch experiments were conducted to investigate the adsorption/desorption behavior of As(III) and As(V) on sediments in Jiangnan Plain with varying

Figure 2. Adsorption isotherm for As(III) and As(V) on sediments in NaCl and AGW solution.

initial arsenic concentration, solution pH and HCO_3^- concentration. Sediments were mixed with solutions which were representative of in-situ groundwater geochemistry, and then were placed on a rotating mixer for an equilibration time of 168 hours. All As(III) adsorption experiments were conducted in an anaerobic environment.

2.3 Geochemical modeling

A generalized surface complexation model was proposed to model the arsenic adsorption and desorption. PHREEQC (version 3) software was employed to simulate the equilibrium surface complexation reactions and other related reactions (Davies *et al.*, 1998). All ions, As(III), As(V) and some related minor elements such as Fe and Mn were taken into consideration during modeling (Rathi *et al.*, 2017).

3 RESULTS AND DISCUSSION

3.1 Arsenic adsorption

The As(III) adsorption was greater than As(V) in NaCl solution as shown in Figure 2. In comparison, more As(V) was absorbed than As(III) in AGW solution. The As(V) adsorption in AGW was similar to that in NaCl, while more As(III) was adsorbed in NaCl solution. This may be caused by competitive adsorption. The results from HCO_3^- competitive adsorption experiments further evidenced this hypothesis. Figure 3 shows that the adsorbed As(III) increased with the increase in HCO_3^- concentration, while the adsorbed As(V) almost remained unconstant with the increase in HCO_3^- concentrations. The degree of the influences of HCO_3^- competitive adsorption on As(V) and As(III) was different.

The reactions for major ions were directly taken from PHREEQC standard database and the water complexation reactions and their equilibrium constants were taken from Watq database. A non-electrostatic generalized composite surface complexation model (GC-SCM) is proposed as shown in Table 1. The model

Figure 3. Effect of bicarbonate on adsorption of As(III) and As(V) on different sediments surface.

Table 1. Parameters for SCM of experimental data.

Solution species	Reactions	Equilibrium constant
H^+ and OH^-	$\text{Jh_cOH} + \text{H}^+ = \text{Jh_cOH}_2^+$	pK_c^1
	$\text{Jh_cOH} + = \text{Jh_cO}^- + \text{H}^+$	pK_c^2
As(III)	$\text{Jh_cOH} + \text{AsO}_3^{3-} + 3\text{H}^+ = \text{Jh_cH}_2\text{AsO}_3 + \text{H}_2\text{O}$	$\log K_c^1$
	$\text{Jh_cOH} + \text{AsO}_3^{3-} + 2\text{H}^+ = \text{Jh_cHAsO}_3^- + \text{H}_2\text{O}$	$\log K_c^2$
	$\text{Jh_cOH} + \text{AsO}_4^{3-} + \text{H}^+ = \text{Jh_cAsO}_3^{2-} + \text{H}_2\text{O}$	$\log K_c^3$
As(V)	$\text{Jh_sOH} + \text{AsO}_4^{3-} + 3\text{H}^+ = \text{Jh_sH}_2\text{AsO}_4 + \text{H}_2\text{O}$	$\log K_c^4$
	$\text{Jh_sOH} + \text{AsO}_4^{3-} + 2\text{H}^+ = \text{Jh_sHAsO}_4^- + \text{H}_2\text{O}$	$\log K_c^5$
	$\text{Jh_sOH} + \text{AsO}_4^{3-} + \text{H}^+ = \text{Jh_sAsO}_4^{2-} + \text{H}_2\text{O}$	$\log K_c^6$
HCO_3^-	$\text{Jh_sOH} + \text{CO}_3^{2-} + 2\text{H}^+ = \text{Jh_sCO}_3^- + \text{H}_2\text{O}$	$\log K_c^7$
	$\text{Jh_cOH} + \text{CO}_3^{2-} + 2\text{H}^+ = \text{Jh_cHCO}_3 + \text{H}_2\text{O}$	$\log K_c^8$

Figure 4. Effect of pH on adsorption of As(III) and As(V) on different sediments surface.

was preliminarily developed and ran to obtain the equilibrium constants.

3.2 Effects of pH

pH has a relatively significant influence on both As(III) and As(V) adsorption as indicated in Figure 4. While

the more As(III) was absorbed as the pH increased, the adsorbed As(V) become less with the increase in pH.

4 CONCLUSIONS

The different adsorption behaviors of As(III) and As(V) was shown by this study. The experimental results showed that effect of the HCO_3^- competitive adsorption on As(V) adsorption was minor. However, it has a significant impact of As(III) adsorption. While the increase in pH enhances the As(III) adsorption, it has negative influences on As(V) adsorption. The seasonal variation in arsenic concentration was observed in the study area and the different valence state of As dominated at different seasons. The results from this study strongly implied that different adsorption behavior of As(III) and As(V) should be considered as an important process for controlling the seasonal variation in arsenic concentration in Jiangnan Plain.

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