Effect of Ca^{2+} and PO_4^{3-} on As(III) and As(V) adsorption at goethite-water interface: Experiments and modeling

Y.X. Deng, L.P. Weng & Y.T. Li

Agro-Environmental Protection Institute, Ministry of Agriculture, Tianjin, P.R. China

ABSTRACT: Adsorption process is a key reaction that controls the bioavailability and mobility of arsenic in the environment. So far, studies regarding As adsorption to minerals in multiple component systems are still limited. In this study, we investigated the effect of Ca^{2+} as the major cation and PO_4^{3-} as the major anion on As(III) or As(V) adsorption at goethite-water interface over a wide pH range. Data of the adsorption experiments were compared to those calculated with the CD-MUSIC model. Results show that Ca^{2+} promoted As(V) adsorption at high pH, but slightly influenced (increased or decreased) As(III) adsorption. Phosphate competed strongly with the adsorption of both As(III) and As(V), especially at relatively low pH for As(III) and high pH for As(V). The combined effect of Ca^{2+} and PO_4^{3-} on As adsorption results in an increased As(III) adsorption with the increase of pH (3–10), whereas for As(V) a maximum adsorption can be seen around pH 6. The CD-MUSIC model can predict As adsorption in the complex systems by considering electrostatic interactions and site competition. Competition with PO_4^{3-} leads to a decrease of the bidentate As(III) and As(V) surface species. Our results can provide understanding needed in the risk assessment and remediation of As contaminated soils and water.

1 INTRODUCTION

The predominant As species in water and soil are As(III) and As(V). Arsenic adsorption to minerals controls to a large extent its bioavailability and mobility. The adsorption process is significantly influenced by pH and co-occurrence of other ions such as Ca^{2+} and PO_4^{3-} (Kanematsu *et al.*, 2008, Stachowicz *et al.*, 2010). However, there are so far very few studies that investigate simultaneously the effect of Ca^{2+} and PO_4^{3-} on As(III) or As(V) adsorption under different pH. Similarly, the ability of the CD-MUSIC model, which is an advanced surface complexation model (Hiemstra & Van Riemsdijk, 2006), to predict As adsorption in multiple component systems has not been sufficiently tested. The objectives of this study are: (1) to reveal the effect of Ca^{2+} and PO_4^{3-} on As(III) or As(V) adsorption to goethite under various pH; (2) to validate the reliability of CD-MUSIC model prediction for the above-mentioned systems; and (3) to discuss Ca^{2+} and PO_4^{3-} effect on the surface speciation of adsorbed As on goethite based on the CD-MUSIC model.

2 METHODS

Goethite material was prepared according to Hiemstra *et al.* (1999). The specific surface area and PZC of goethite are $89 \text{ m}^2 \text{ g}^{-1}$ and 9.2 respectively.

Adsorption experiments were carried out in gas-tight polyethylene centrifuge tubes, to which appropriate amounts of stock solutions were added under

N_2 atmosphere. For all treatments, the final concentration of goethite was 1.1 g L^{-1} , of NaCl was 0.1 M . For both As(III) and As(V), treatments of As, As + Ca, As + P and As + Ca + P were prepared and the pH was adjusted with acid and base to a range between 3.5 and 11.5. The prepared suspensions were equilibrated on a horizontal shaker at 25°C for 3 days. The suspensions final pH was measured, then centrifuged and filtered through $0.45 \mu\text{m}$ membranes. The filtrates were analyzed on ICP-MS for As concentration and on ICP-OES for Ca and P concentrations. The CD-MUSIC model parameters were adopted from the literatures (Stachowicz *et al.*, 2007, 2008), except that the logK values for As(III), As(V), Ca^{2+} and PO_4^{3-} were optimized in the current study using data of single adsorbate experiments. The model calculations were carried out using the computer program ECOSAT.

3 RESULTS AND DISCUSSION

In the As(III)-Ca-P system, the competitive effect of PO_4^{3-} on As(III) adsorption is very strong especially at $\text{pH} < 10$, whereas the Ca^{2+} effect is only visible at $\text{pH} > 6$ (Fig. 1a). Interestingly, there is a decrease rather than an increase of As(III) adsorption at pH about 6–10, when Ca^{2+} is added to the As(III)-P system. This phenomenon can be attributed to the increase of PO_4^{3-} adsorption in the presence of Ca^{2+} as a result of synergistic electrostatic interactions, which consequently leads to a decrease of As(III) adsorption due to site competition between As(III) and PO_4^{3-} .

Figure 1. Influence of Ca^{2+} and PO_4^{3-} on the adsorption (a, b) and surface speciation (c, d) of As(III) or As(V) to goethite. (a, b) Symbols are experimental data, and lines are CD-MUSIC model predictions; (c, d) all lines are calculated with the CD-MUSIC model.

In the As(V)-Ca-P system, the magnitudes of the competitive effect of PO_4^{3-} and the synergistic effect of Ca^{2+} on As(V) adsorption are comparable at pH 5–9, whereas the Ca^{2+} effect is more significant at higher pH and PO_4^{3-} effect is more significant at lower pH (Fig. 1b). When PO_4^{3-} is present, the influence of Ca^{2+} appears at a lower pH compared with the As(V)-Ca system, which is caused by the more negative charge and potential at goethite surface in the presence of PO_4^{3-} .

The CD-MUSIC model well predicted adsorption features of both As(III) and As(V) in different systems (Figs. 1c, d). However, in order to achieve good agreements between calculated and measured soluble Ca^{2+} and PO_4^{3-} concentrations, two types of calcium phosphate precipitates need to be included, i.e. $\text{Ca}_2\text{HPO}_4(\text{OH})_2$ (hydroxysphodiosite) and $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (hydroxyapatite) with fitted solubility product ($\log K_{\text{so}}$) of -32.9 and -47.0 respectively. The Ca^{2+} and PO_4^{3-} effect on As(III) and As(V) adsorption is accounted in the model via electrostatic interactions and site competition. The weaker Ca^{2+} effect on As(III) than on As(V) adsorption can be explained by the weaker electrostatic interactions between Ca^{2+} and As(III).

In the CD-MUSIC modeling, adsorbed As(III) is represented using two inner-sphere complexes, i.e., a bidentate $\equiv\text{Fe}_2\text{O}_2\text{AsOH}$ and a monodentate $\equiv\text{FeOAs}(\text{OH})_2$ surface species; and adsorbed As(V) is represented using three inner-sphere complexes, i.e. a bidentate $\equiv\text{Fe}_2\text{O}_2\text{AsO}_2$, a protonated bidentate $\equiv\text{Fe}_2\text{O}_2\text{AsOOH}$, and a protonated monodentate $\equiv\text{FeOAsO}_2\text{OH}$ surface species (Stachowicz *et al.*, 2008). Our model calculations show that the bidentate surface complex of adsorbed As(III) and As(V) is greatly suppressed in the presence of PO_4^{3-} (Fig. 1c, 1d), whereas the effect of Ca^{2+} on the surface speciation of As(III) or As(V) in the As-Ca systems is

quite slight (in Fig. 1c and 1d, the lines of As-Ca treatments coincide with those of As treatments). In the As(III)/As(V)-P systems, the presence of Ca^{2+} decreased the bidentate complex of As(III) and As(V), especially for As(V) due to site competition as a result of enhanced As(V) and PO_4^{3-} adsorption.

4 CONCLUSIONS

This study demonstrated that the presence of PO_4^{3-} and Ca^{2+} influences not only the magnitude of adsorption of As(III) and As(V), but also their adsorption pH dependency. In the natural environment (pH 3.5–8.5), when As is in the form of As(III), the adsorption of As will increase with the increase of pH; When As is present in the form of As(V), a maximum adsorption around pH 6 can be expected when Ca^{2+} is present. The increase of PO_4^{3-} concentration will decrease both As(III) and As(V) adsorption, whereas an increase of Ca^{2+} concentration will increase As(V) adsorption, but it may increase or decrease As(III) adsorption depending on conditions. Increasing soil pH by liming is an effective approach to decrease the mobility and bioavailability of heavy metals such as Cd. Our analysis indicates that the mobility and bioavailability of As can possibly be decreased by liming in dry land soils when the pH remains below 6, whereas the opposite effect may take place when the pH is above 6.

The CD-MUSIC model is a reliable tool to understand and predict the adsorption behavior of As on iron (hydr)oxide minerals.

ACKNOWLEDGEMENTS

This work was supported by the National Key Research and Development Program of China (2016YFD0800304), and the National Natural Science Foundation of China (No. U1401234).

REFERENCES

- Hiemstra, T. & Van Riemsdijk, W.H. 1999. Surface structural ion adsorption modeling of competitive binding of oxyanions by metal (hydr)oxides. *J. Colloid. Interf. Sci.* 210(1): 182–193.
- Hiemstra, T. & Van Riemsdijk, W.H., 2006. On the relationship between charge distribution, surface hydration, and the structure of the interface of metal hydroxides. *J. Colloid. Interf. Sci.* 301(1): 1–18.
- Kanematsu, M., Young, T.M., Fukushi, K., Green, P.G. & Darby, J.L. 2010. Extended triple layer modeling of arsenate and phosphate adsorption on a goethite-based granular porous adsorbent. *Environ. Sci. Technol.* 44(9): 3388–3394.
- Stachowicz, M., Hiemstra, T. & van Riemsdijk, W.H. 2007. Arsenic-bicarbonate interaction on goethite particles. *Environ. Sci. Technol.* 41(16): 5620–5625.
- Stachowicz, M., Hiemstra, T. & van Riemsdijk, W.H. 2008. Multi-competitive interaction of As(III) and As(V) oxyanions with Ca^{2+} , Mg^{2+} , PO_4^{3-} , and CO_3^{2-} ions on goethite. *J. Colloid. Interf. Sci.* 320(2): 400–414.