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Effects of Common Competing Anions on the
Adsorption of As(III) by δ-MnO₂ and Goethite

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Batch experiments had been conducted to study the effects of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, SiO_3^{2-}, SO_4^{2-} and Cl^- on the adsorption of As(III) by the δ-MnO₂ and the goethite. Moreover, the influential mechanisms of anions had been discussed. First, when the concentration of As(III) was low (10 mg/L), the effects of PO_4^{3-} and SiO_3^{2-} on the adsorption of As(III) by the δ-MnO₂ were notable and relative small effects of HPO_4^{2-} and $H_2PO_4^-$ were suggested. PO_4^{3-}, SiO_3^{2-} and $H_2PO_4^-$ could affect the adsorption of As(III) by the goethite and the effect of HPO_4^{2-} could be negligible. Both SO_4^{2-} and Cl^- had negligible competing adsorption to As(III) by the δ-MnO₂ and the goethite. The effects of anions on the As(III) adsorption by the δ-MnO₂ were more severe than that by the goethite. Then, when the concentration of As(III) varied from 0-85 mg/L, compared to the blank, all the anions performed their effects to As(III) absorption by the δ-MnO₂ and the goethite and the effects were more severe in high concentration than that in low concentration. The effects to the goethite were also obvious than that to the δ-MnO₂ in high concentration. Lastly, for the δ-MnO₂ and the goethite, SiO_3^{2-} magnified the effect of PO_4^{3-}. For the goethite, the combined effect of SiO_3^{2-} and PO_4^{3-} was more remarkable. The difference was decided by the structure characteristic of sorbent themselves, the δ-MnO₂ had more adsorptive capacity while the goethite had strong adsorptive affinity to As(III).

Key Words: δ-MnO₂, Goethite, As(III), Anions, Competing adsorption.

INTRODUCTION

Arsenic is a trace element which naturally occurs in the earth's topsoil and it's a kind of toxic elements as well as carcinogenic substance. Aqueous arsenic showed two chemical forms *i.e.*, As(III) and As(V) and As(III) is more toxic than As(V)[1]. In addition, it would lead to chronic arsenic poisoning by long-term drinking water with high concentration arsenic[2]. As(III) mainly existed in the form of arsenic oxygen anions (such as AsO_2^-, AsO_3^{3-}, AsO_3^- and AsO_4^{3-}) in soils, the arsenic content in the none-contaminated soils[3] was commonly less than 6 µg/g. Arsenic presented in soils due to natural factors such as natural rock weathering, geological activities, as well as anthropic activities, including pesticide application, burning coals and discharging of industrial castoff, which caused the arsenic contamination in soils all over the world[4-7]. People came to emphasis on the effects on human health caused by soil arsenic contamination. To lower and control the contamination, studies concerning arsenic migrating process and the effects of other competing anions, the pH value and organic matter on migrating processes in soils, had become the research hot spot[8].

To some extent, arsenic content was affected by adsorption and desorption equilibrium in the soil's solid-liquid interface. Arsenic could be typically associated with soil clay minerals[8,9]. Soil silicate clay minerals had small effect on the adsorption of arsenic. In contrast, metal hydroxides with high surface charge, big surface area and other features could remove many organic or inorganic contaminations effectively, including arsenic[10-12]. During the past decades, a lot of effort had devoted to the work about arsenic adsorption by iron oxides[13-18], manganese oxides[19] and aluminum oxide[16,20]. The adsorption included electrostatics, ion exchange, complexation and precipitation[21].

The arsenic coexisted with other anions in soils, so the adsorption of arsenic was influenced by other anions in soils. So far, some researches had studied the effect of anions on the adsorption of As(V) and As(III). Livesey and Huang[4] had designed the competing adsorptive experiments about the effects of chloride, sulfate, nitrate and phosphate on the adsorption of As(V) by soils and discovered that chloride, sulfate and nitrate hadn't affected As(V) adsorption, the adsorption was largely inhibited by phosphate. Waltham and Eick[22] had

found that silicate exhibited great influence on the adsorption of As(V) by the goethite through competitive adsorptive site and electrostatic repulsion. The experimental results of Liang *et al.*[19] had indicated that competing adsorptions between sulfate, phosphate and arsenic(III) on the surface of manganese oxide made the removal rate of arsenic(III) decrease obviously. Meng *et al.*[23] had discussed the combined effects of PO_4^-, SiO_3^{2-} and HCO_3^- on As(III) and As(V) removal from iron hydroxides and found that the presence of SiO_3^{2-} and HCO_3^- magnified the effect of PO_4^-. However, previous research about anion effect on As adsorption mostly focus on arsenic(V) and the anion species is not wide enough. Furthermore, the influential mechanism needs to be further discussed.

δ-MnO$_2$ and goethite are the common manganese and iron oxides, which take the important roles on arsenic immobility in soils. This paper devotes to argue the importance of the effect of common anions in soils including PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, SiO_3^{2-}, SO_4^{2-} and Cl⁻ on As(III) adsorption by δ-MnO$_2$ and goethite and attempt to provide useful information for explaining As(III) remaining in soils. Firstly, the δ-MnO$_2$ and goethite were artificially synthesized, then the competing adsorption tests between the common anions (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, SiO_3^{2-}, SO_4^{2-} and Cl⁻) and As(III) by δ-MnO$_2$ and goethite were conducted. Moreover, the influential mechanisms of anions on the As(III) adsorption were discussed. The results reported in the present study will benefit environmental contamination applications concerning arsenic mobility, arsenic transformation and other possible applications in various fields (*e.g.* soil decontamination, agriculture irrigation and water treatment).

EXPERIMENTAL

The instruments used in experiments were AFS-2202 Atomic Fluorescence Spectrometer (Beijing Kechuang Haiguang Instrumental Co., Ltd.), Z-323 Freezing Centrifuge (Jintan Medical Equipment Factory in Jiangsu), SHZ-82 Swing-type water circulation bath oscillator (Jintan Jincheng Guosheng Experimental Equipment Factory in Jiangsu) and XD-3 diffractometer (Beijing Puxi general Co., Ltd.).

All the chemicals were analyzed grade reagents and were used without further purification, including $MnSO_4$, $KMnO_4$, $Fe(NO_3)_3 \cdot 9H_2O$, NaOH, HCl, As_2O_3, KBH_4, thiourea, ascorbic acid and the water was the first deionized water. δ-MnO$_2$ and goethite used in this study were synthesized following the procedure adapted from Liang *et al.*[24] and Ye *et al.*[15], with a few deviations, respectively.

Batch experiments: All batches of adsorptive experiments were carried out in the 50 mL conical flasks. 0.1 g sorbent, As(III) and a competing anion were simultaneously added to the conical flask, the ratio of solid to liquid was 1:200. The conical flask was shaken for 60 min at a constant temperature of 25 ± 0.5 ºC in the thermostatic water-circulate bath oscillator. Subsequently, the suspension was centrifuged for 20 min. The adsorbed amount of As(III) was calculated by finding the difference between the initial and residual concentration of As(III) in the solution. The concentration of As(III) was fixed at 10 mg/L with the concentrations of anions varying from 0 to 180 mg/L. In contrast, the concentrations of anions were fixed (as the same average concentration in soils: SiO_3^{2-} 50 mg/L, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-} 30 mg/L, Cl⁻ 4 mg/L)[25] with the concentrations of As(III) varying from 0 to 85 mg/L.

Operating conditions of AFS: Negative pressure was 280 V, main lamp current was 60 mA, furnace temperature was 300 ºC, atomized instrumental height was 8 mm, flow velocity of carrier gas was 400 mL/min, flow velocity of shielded gas was 900 mL/min.

RESULTS AND DISCUSSION

X-ray diffraction spectrogram of δ-MnO$_2$ and goethite and transmission electron microscope image of δ-MnO$_2$: The XRD spectrograms of the two samples are shown in Fig. 1. It is obvious that the crystal peak at 37.26º is low and broad, which is the δ-MnO$_2$ (card number 13-0162) by retrieving XRD graph. The δ-MnO$_2$ is amorphous. The main component of iron oxide are Fe_2O_3 (card number 33-0664) and the goethite (card number 29-0713) by retrieving XRD graph. The crystallinity of the goethite is better than δ-MnO$_2$.
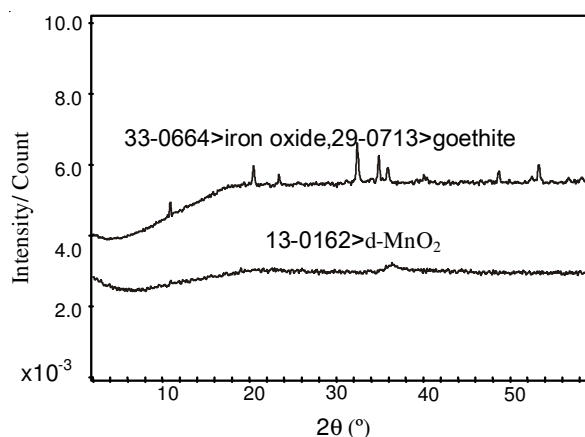

Fig. 1. XRD spectrogram of δ-MnO$_2$ and goethite

XRD spectrogram indicates that the δ-MnO$_2$ is amorphous, so the TEM is further done to identify the structure of the δ-MnO$_2$. Fig. 2 is the TEM image of the δ-MnO$_2$, the particle is ball, it disperses well and has a little reunion, the size of particle is about 250 nm.
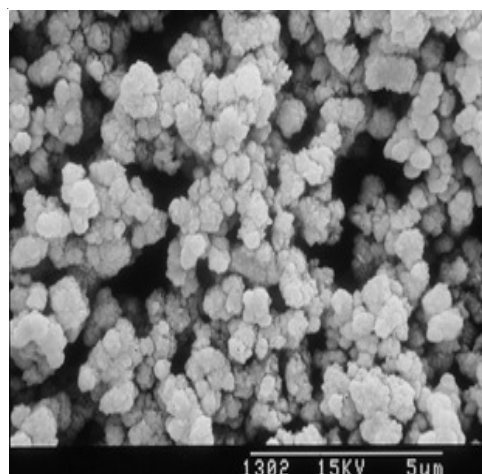

Fig. 2. TEM image of δ-MnO$_2$

Effects of anions on the As(III) adsorption by δ-MnO₂:
The effects of competing anions on the As(III) adsorption by the δ-MnO₂ in the same concentration of As(III) are dramatically shown in Fig. 3. When the concentration of As(III) is fixed at 10 mg/L, the adsorption capacity of As(III) by the δ-MnO₂ decrease and then come to balance with the concentrations of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$ and SiO_3^{2-} varying from 0 to 180 mg/L. The curves of PO_4^{3-} and SiO_3^{2-} decrease dramatically, while the curves of HPO_4^{2-} and $H_2PO_4^-$ decline slightly. It indicates that the effects of PO_4^{3-} and SiO_3^{2-} on the As(III) adsorption by the δ-MnO₂ are stronger than that of HPO_4^{2-} and $H_2PO_4^-$. It should be noted that SO_4^{2-} and Cl^- have no effect on the As(III) adsorption by the δ-MnO₂. The As(III) adsorption by the δ-MnO₂ is seriously restrained in the presence of PO_4^{3-}, SiO_3^{2-}, $H_2PO_4^-$ and HPO_4^{2-}. When the concentration of $H_2PO_4^-$ and HPO_4^{2-} are larger than 120 mg/L and the concentration of PO_4^{3-} and SiO_3^{2-} are larger than 140 mg/L, the effects become insufficient.
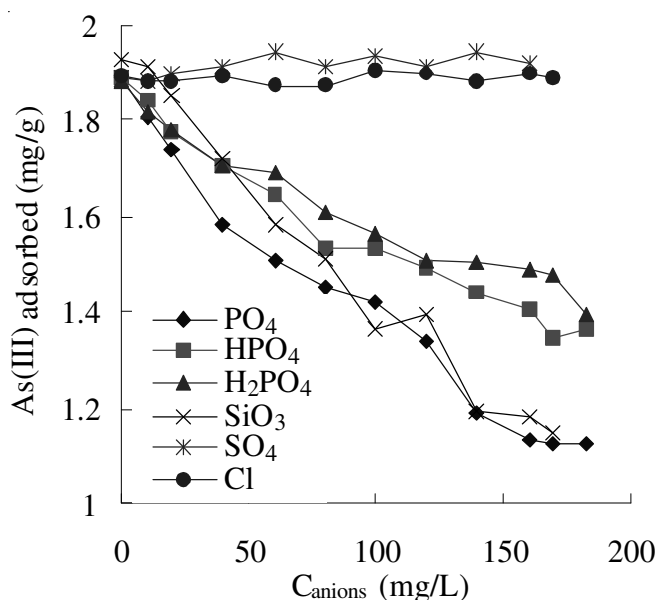

Fig. 3.   Effects of anions on the As(III) adsorption by δ-MnO₂ in the same concentration of As(III) ($C_{Cl^-} \times 10$)

All the anions perform their effects to As(III) absorption by the δ-MnO₂ when the concentration of As(III) vary from 0-85 mg/L compared to the blank (no disturbance anions) (Fig. 4). The adsorption capacity of As(III) by the δ-MnO₂ raise dramatically with the increase of As(III) concentration. The influence difference of different anions on the As(III) adsorption capacity is less and the effects are mostly determined by the initial As(III) concentration, when initial As(III) concentration is larger than 20 mg/L, the effects become obvious less and less, the effects are relative severe in high concentration than that in low concentration. When the As(III) concentration get to 85 mg/L, the adsorption capacities are not saturated, it indicates that the δ-MnO₂ has enough adsorption capacity to As(III) due to its big surface area and more active adsorption sites. Although the influence difference of different anions on the As(III) adsorption is less, the effect curves also show anions disturbance with the following order: PO_4^{3-}, SiO_3^{2-} > $H_2PO_4^-$, HPO_4^{2-} > SO_4^{2-}, Cl^-.
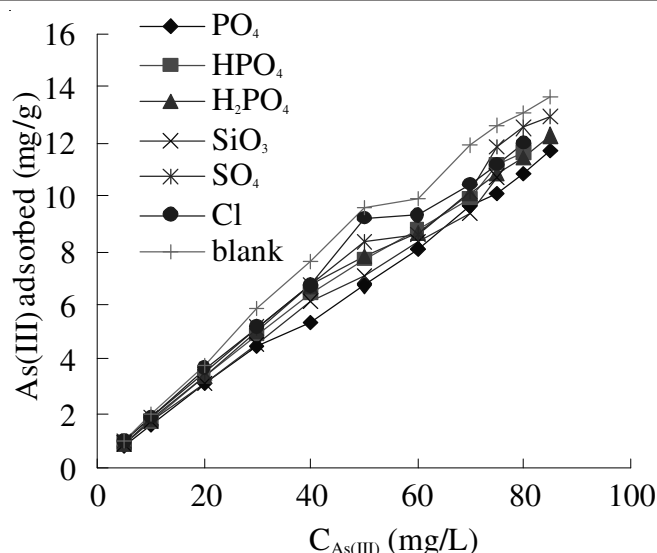

Fig. 4.   Effects of anions on the As(III) adsorption by δ-MnO₂ in the different concentration of As(III)

There were many hydroxyl on the surface of the δ-MnO₂. The results suggested that coexistence anions occupy the surface active sites (hydroxyl) through ion exchange. The more ion valence was, the more exchange ability was. The structure of PO_4^{3-} and SiO_3^{2-} were more similar to AsO_2^- and AsO_3^{3-}, so the effects of PO_4^{3-} and SiO_3^{2-} were the most. $H_2PO_4^-$ and HPO_4^{2-} had stronger interference than SO_4^{2-} and Cl^- owing to forming hydrogen bond with hydroxy of the δ-MnO₂ surface. SO_4^{2-} and Cl^- only competed the active adsorption site through ion exchange, the effects of them were the least.

The ion exchange function between active site and As(III) was dominant when the As(III) concentration was low. But the mechanism of As(III) adsorption by the δ-MnO₂ were surface diffusion except for ion exchange when As(III) concentration was relatively high. The concentration of As(III) took an important role, especially when the concentration of As(III) surpassed 20 mg/L, the surface diffusion was dominating.

Effects of anions on the As(III) adsorption by goethite:
As shown in Fig. 5, when the As(III) concentration is fixed at 10 mg/L and anions concentration varies from 0-180 mg/L, HPO_4^{2-}, SO_4^{2-} and Cl^- have negligible effects on the As(III) adsorption capacity by the goethite. $H_2PO_4^-$ shows effect when the concentration is more than 160 mg/L. For SiO_3^{2-} and PO_4^{3-}, there are no effects on the adsorption of As(III) yet, until the concentration of SiO_3^{2-} and PO_4^{3-} are more than 50 mg/L and 80 mg/L, respectively. In a word, when the As(III) concentration is low, the effect of anions is very limited and the effect extent is less than that by the δ-MnO₂. It indicates that the As(III) have stronger affinity to the goethite than other anions.

The adsorption curves except for blank (no disturbance anions) increase with the As(III) concentration varying from 0 to 50 mg/L and then change little (Fig. 6). All the anions perform influences to the As(III) adsorption as same as the δ-MnO₂ compared to the blank. The effects of PO_4^{3-}, $H_2PO_4^-$ and HPO_4^{2-} are stronger than that of SiO_3^{2-}, SO_4^{2-} and Cl^-. The results indicate that the effects of PO_4^{3-}, SiO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-}, SO_4^{2-} and Cl^- on the As(III) adsorption by goethite are related to the initial As(III) concentration, the effects are relatively

severe in high concentration than that in low concentration. When the initial As(III) concentration surpass some determinable value, the adsorption capacity by the goethite reach saturation, the adsorption quantity change little. At the presence of anions, the adsorption capacity by the goethite is obviously less than that by the δ-MnO$_2$.
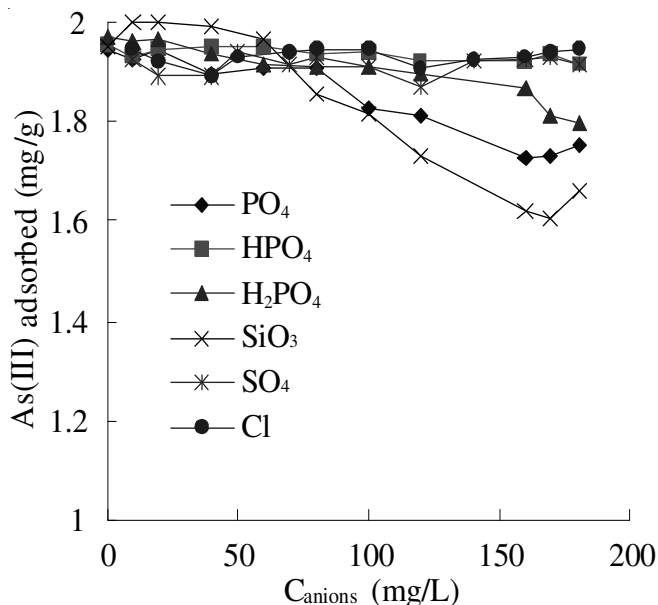

Fig. 5. Effects of anions on the As(III) adsorption by goethite in the same concentration of As(III) (C$_{Cl^-}$ × 10)
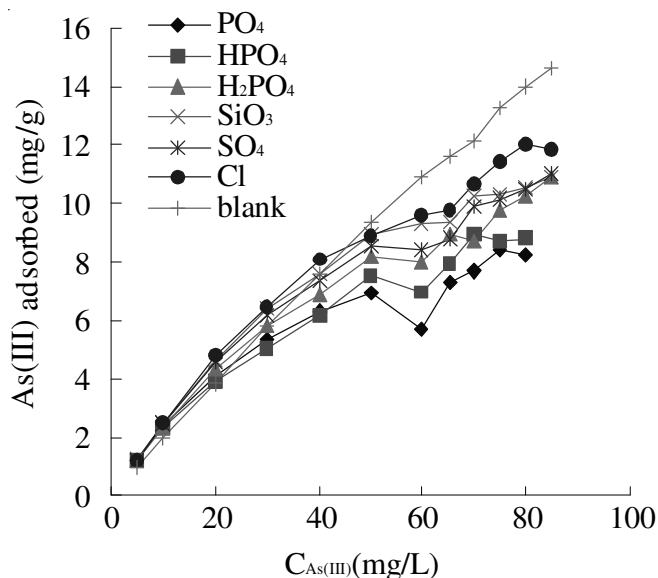

Fig. 6. Effects of anions on the As(III) adsorption by goethite in the different concentration of As(III)

Goethite was a mineral with alterable charge. There were three groups (Fe-(OH)$_2$$^+$, Fe-(OH) and Fe-O$^-$) on the surface of goethite, the balance shifted to form Fe-(OH)$_2$$^+$ at the low pH. The pH value of the batch experiments was approximately 6, which was lower than the isoelectric point of goethite (about 8), so the mainly existing group was Fe-(OH)$_2$$^+$ on the surface of goethite. Arsenic oxygen anions (AsO$_2$$^-$, AsO$_3$$^{3-}$) were adsorbed to the goethite surface by electrostatic attraction. Meanwhile, PO$_4$$^{3-}$, SiO$_3$$^{2-}$, H$_2PO_4$$^-$, HPO$_4$$^{2-}$, SO$_4$$^{2-}$ and Cl$^-$ were

also absorbed to the surface of the goethite through electrostatic. Furthermore, the Fe-(OH)$_2$$^+$ on the surface of the goethite could complex with the AsO$_2$$^-$, AsO$_3$$^{3-}$ of solution and formed an dual-core and double-base inner complexes. Electrostatic attraction was weak while complexation was an strong adsorption. So, when the As(III) concentration was low and the concentration of anions are less than certain value, the goethite preferentially adsorbs As(III). In the other side, SiO$_3$$^{2-}$ and iron could generate precipitation, PO$_4$$^{3-}$ and iron could form complex, PO$_4$$^{3-}$ and SiO$_3$$^{2-}$ showed their disturbance when the initial As(III) concentration was low (10 mg/L) and the concentrations of PO$_4$$^{3-}$ (80 mg/L) and SiO$_3$$^{2-}$ (50 mg/L) are high.

The electrostatic attraction and complexation were the dominating function, especially the latter when the As(III) concentration was low. In the same way, there were another adsorption mechanism between the As(III) and the goethite, an iron arsenate precipitation might be formed when As(III) concentration was relatively high. The adsorption capacity mostly determined by the initial As(III) concentration.

The results also indicated that the anion effects on the As(III) adsorption by the δ-MnO$_2$ were more severe than that by the goethite when the initial As(III) concentration was low (10 mg/L). but the anion effects on the As(III) adsorption by the goethite were stronger than that by the δ-MnO$_2$ when the initial As(III) concentration was high. For the δ-MnO$_2$ and the goethite, the inflexion of As(III) concentration were 20 mg/L and 50 mg/L respectively. It was due to the structure difference of the sorbents. The δ-MnO$_2$ was amorphous, it had big surface area, there were amount of hydroxyl on the surface, so it had big adsorptive capacity, but the adsorptive affinity to As(III) was relatively weak. The goethite was crystalloid, the surface area was smaller, but the Fe-(OH)$_2$$^+$ group of the surface had strong adsorptive affinity to As(III).

Combined effects of anions on the As(III) adsorption by δ-MnO$_2$ and goethite: From the above results, it is concluded that the different kinds of anions had different effect on the As(III) adsorption by the δ-MnO$_2$ and the goethite. The anions coexisted in soils, so the disturbance tests of mixed anions were conducted. Taking into the larger impact of SiO$_3$$^{2-}$ and PO$_4$$^{3-}$ and less effect of Cl$^-$, we took the impact of PO$_4$$^{3-}$ as a reference, selected SiO$_3$$^{2-}$ and Cl$^-$ as combined ions. For δ-MnO$_2$ and goethite, the concentration of SiO$_3$$^{2-}$ fixed at 30 and 50 mg/L, respectively (the influence inflexion of SiO$_3$$^{2-}$) (Figs. 3 and 5) and the concentration of Cl$^-$ fixed at 3 and 5 mg/L, respectively.

The results are shown in Figs. 7 and 8. For the δ-MnO$_2$, Cl$^-$ do not magnify the effect of PO$_4$$^{3-}$. SiO$_3$$^{2-}$ has no combined effect yet when the concentration of PO$_4$$^{3-}$ is low. But the combined effect of SiO$_3$$^{2-}$ is obvious when the concentration of PO$_4$$^{3-}$ is greater than 50 mg/L. For example, when the concentration of PO$_4$$^{3-}$ is 80 mg/L, the adsorptive capacity of As(III) decreases from 1.42 to 1.18 mg/g (Fig. 7). For the goethite, Cl$^-$ has a few combined effect to PO$_4$$^{3-}$, SiO$_3$$^{2-}$ can magnify the effect of PO$_4$$^{3-}$. Even the concentration of PO$_4$$^{3-}$ is low, the effect is remarkable. For example, when the concentration of PO$_4$$^{3-}$ is 5 mg/L, the adsorptive capacity of As(III) decreases from 1.91 to 1.65 mg/g (Fig. 8).
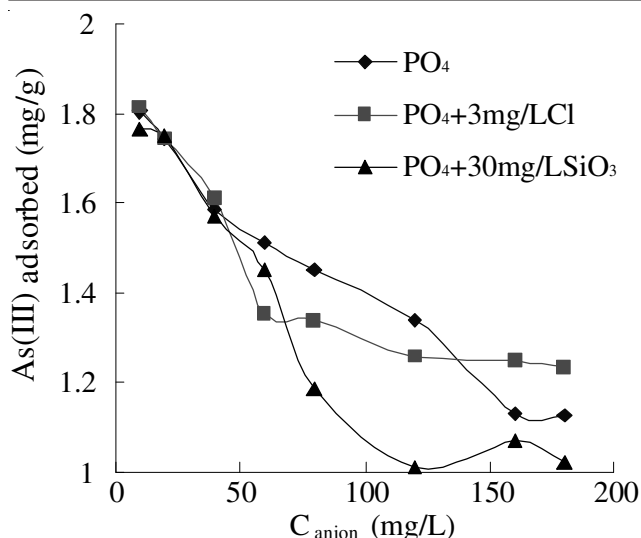
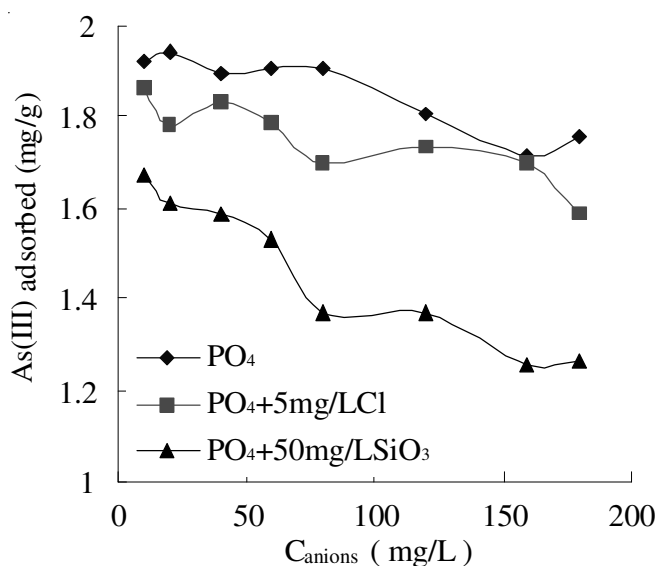Fig. 7. Combined effects of anions on the As(III) adsorption by δ-MnO₂

Fig. 8. Combined effects of anions on the As(III) adsorption by goethite

Conclusion

The δ-MnO₂ and the goethite were effective sorbents for As(III). When the As(III) concentration was fixed at 10 mg/L, the effect order of anions on the As(III) adsorption by the δ-MnO₂ was: PO_4^{3-}, SiO_3^{2-} > $H_2PO_4^-$, HPO_4^{2-} > SO_4^{2-}, Cl^- and the effect order of anions on the As(III) adsorption by the goethite was SiO_3^{2-} > PO_4^{3-} > $H_2PO_4^-$, HPO_4^{2-}, SO_4^{2-} and Cl^- had no effect to As(III) adsorption.

All the anions performed effects on As(III) adsorption by the δ-MnO₂ and the goethite when the concentration of As(III) varied from 0-85 mg/L. The effects of anions on the adsorption of As(III) by the δ-MnO₂ and the goethite were restricted by the initial As(III) concentration, the effects were relative severe in the high As(III) concentration than that in the low As(III) concentration.

Owing to the difference structure of sorbents, when the initial As(III) concentration was low (10 mg/L), the effects of anions on the As(III) adsorption by the δ-MnO₂ were more severe than that by the goethite, but when the initial As(III) concentration was high, the effects of anions on As(III) adsorption by the goethite were stronger than that by the δ-MnO₂. The δ-MnO₂ had big adsorptive capacity while the goethite had strong adsorptive affinity to As(III).

For the δ-MnO₂, when the concentration of PO_4^{3-} was greater than 50 mg/L, the combined effect of SiO_3^{2-} was obviously. For the goethite, Cl^- had a few combined effect to PO_4^{3-}, SiO_3^{2-} could magnify the effect of PO_4^{3-}, even the concentration of SiO_3^{2-} was low, the effect was remarkable.

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