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# Mechanism of arsenate mobilization from goethite by aliphatic carboxylic acid

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ABSTRACT

Arsenic is highly toxic and therefore represents a potential threat to the environment and human health. The mobility and fixation of arsenic in natural environment is significantly affected by co-occurring dissolved natural organic acids, which are widely present in soils and sediments due to the decomposition of natural organic matters and the metabolism of plant roots and microorganisms. It was reported recently that at lower pH, citrate decreased arsenate adsorption on metal oxides as the result of competitive adsorption. This study examined the relationship between citrate-promoted goethite dissolution and citrate-suppressed arsenate adsorption in the equilibrated goethite–arsenate–citrate systems with different contact orders. The results indicated that there is obvious correlation between the suppression of arsenate adsorption and dissolution of goethite. Arsenate adsorption and goethite dissolution in the presence of citrate (1.0 mM), oxalate (1.5 mM) and acetate (3.0 mM) were compared. The results showed that arsenate adsorption was most significantly inhibited by citrate among the three organic acids. Although oxalate dissolved goethite more significantly, it inhibited arsenate adsorption much less than citrate. Hence it is proposed that the competition for binding sites rather than citrate-promoted goethite dissolution played a key role in the reduction of arsenate adsorption by citrate at lower pH.

## 1. Introduction

High concentration of arsenic in groundwaters threatens people's health and lives in many countries, especially in West Bengal, Bangladesh, and Vietnam [1]. Arsenic adsorption and desorption on the surfaces of minerals, especially iron and aluminum (hydr)oxides affects its mobility, reactivity, bioavailability, and toxicity in natural waters [2–8]. Dissolved natural organic acids (e.g., formate, acetate, lactate, oxalate, malonate, malate, succinate, and citrate) are often present in soils and sediments, especially in the microenvironment surrounding soil microbes and in the rhizosphere. Many researchers observed that low molecular-mass organic acids affected arsenic adsorption and desorption especially at acidic pH, which is generally interpreted by two mechanisms (1) competition for binding sites between arsenic and organic species and (2) arsenic release caused by organic species-enhanced dissolution of metal oxides.

Bauer and Blodau indicated that arsenic release from solid phases was controlled by the competition between arsenic and organic species for sorption sites, where redox reactions were probably of minor importance [9]. Gräfe et al. found arsenate adsorption on ferrihydrite was decreased in the presence of citric acid but little effect was observed on goethite [10,11]. Geelhoed et al. observed a decrease in the adsorption of both phosphate and citrate when the two species were brought to contact with goethite simultaneously [12]. Direct competition for binding sites was suggested to be an important factor for the decreased adsorption of phosphate and citrate [12]. Mohapatra et al. also concluded that competitive adsorption of citrate on ferrihydrite and Al-ferrihydrite resulted in the enhanced release of arsenate into solution [13]. On the other hand, the dissolution of oxide mineral surface occurs in a variety of geochemical processes, which influenced the cycling of toxic substances in aqueous environments [14]. Stumm indicated that oxides dissolution involved in the two aspects: the transfer of the chemical species between the mineral and the aqueous solution and the structure and chemical bonding at the mineral–water interface. The overall dissolution rate can be described as the sum of the rates of proton-promoted, $OH^-$-promoted, and ligand-promoted dissolution [15]. Reichard et al. also suggested that oxides dissolution is probably controlled by two independent parallel processes (i.e., proton-promoted and ligand-promoted) [16]. The dissolved organic matter (DOM)-enhanced dissolution of soil minerals is an important mechanism for the increased contaminants mobility [15]. Johnson and Loeppert observed a correlation between iron dissolution and phosphate release during the initial stages of the 24 h citrate reaction with ferrihydrite [17]. Mohapatra et al. suggested that arsenic release cannot be explained solely in terms of competitive adsorption/desorption [13]. Desorption of

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arsenic probably occurred through a complex mechanism involving competitive adsorption, dissolution of the oxide/hydroxides substrates and so on [13]. So it is necessary to further investigate the mechanism of inhibited arsenate adsorption by citrate at the water–goethite interface. The objectives of this work are (1) to investigate the relationship of goethite dissolution and suppressed arsenate adsorption by varying the contact order of citrate and arsenate with the adsorbent and (2) to shed more light on mechanism of arsenate suppression by citrate at low pH by evaluating the role of competition for binding sites on arsenate adsorption.

## 2. Materials and methods

### *2.1. Synthesis of goethite*

The goethite used in this study was synthesized from $Fe(NO_3)_3{\cdot}9H_2O$ using the method described by Schwertmann and Cornell [18]. 50 ml of 1 M $Fe(NO_3)_3$ solution was added into a 1-L polytetrafluoroethylene vessel, followed by rapid addition of 90 ml 5 M KOH solution while vigorously stirring the mixture. The precipitated ferrihydrite was immediately diluted to 1 L with DI water and held in a sealed polytetrafluoroethylene flask at 70 °C for 60 h. The solid product was separated by centrifuging, washed with DI water and dried in vacuum oven at 60 °C. X-ray diffraction analysis (on a Rigaku D/Max 2500 PC X-ray diffractometer, Japan) confirmed the identity of the solid as goethite.

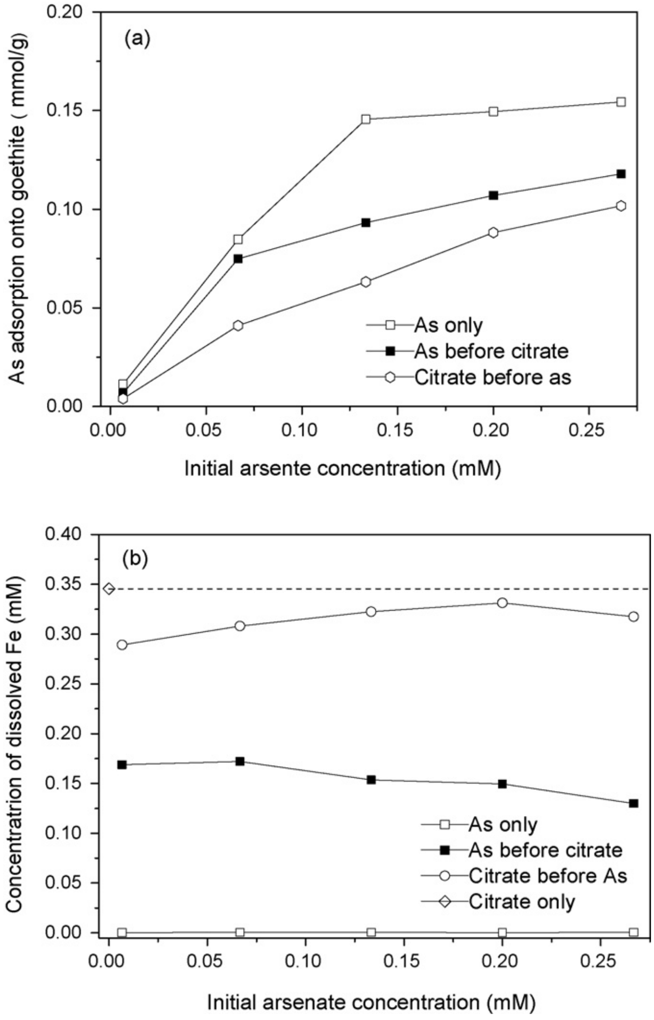

**Fig. 1.** Relationship of arsenate adsorption onto goethite (a) and dissolution of goethite (b) by different contact order of arsenate and citrate at pH 4.

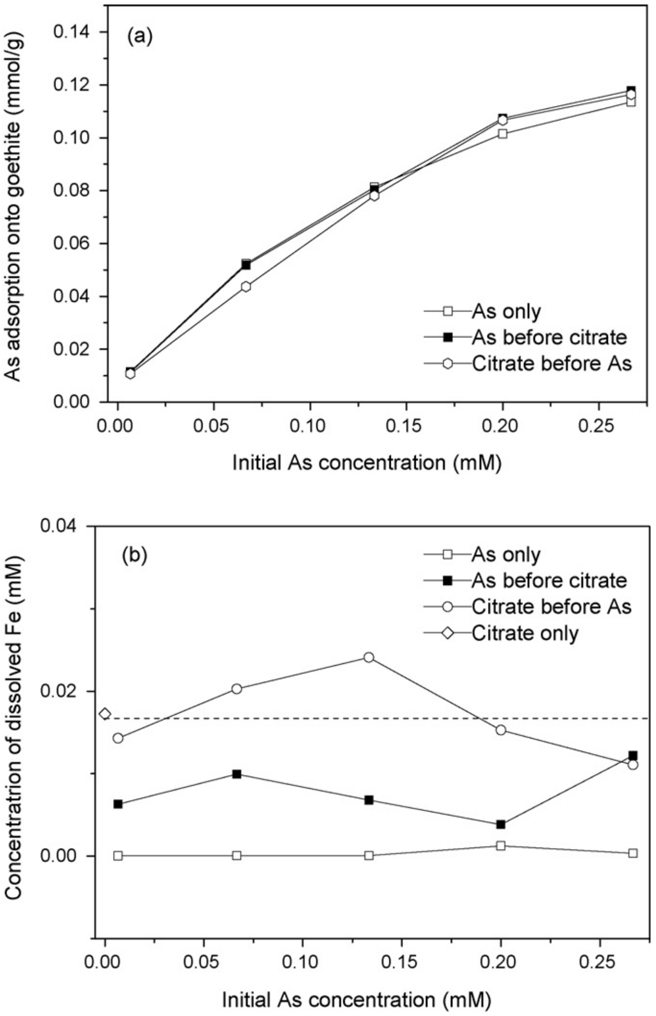

**Fig. 2.** Relationship of arsenate adsorption onto goethite (a) and dissolution of goethite (b) by different contact order of arsenate and citrate at pH 7.5.

### *2.2. Adsorption experiments*

Arsenate adsorption experiments were conducted in batch reactors with a volume of 50 ml and goethite solid concentration of 0.5 g/l at 20 °C. The concentration of acetate, oxalate and citrate was 3.0, 1.5 and 1.0 mM, respectively in view of the same amount of carboxyl groups. Arsenate concentration was 0.006 and 0.12 mM for low and high surface coverage, respectively. Goethite was pre-equilibrated in 0.01 M $NaNO_3$ solution in an end-over-end shaker at 20 °C for 24 h to fully hydrate the goethite surface. The suspensions were adjusted to the targeted pH and equilibrated for another 2 h. Arsenate and other co-occurring organic acids solutions with the same pH values were simultaneously introduced into the goethite suspensions and the pH of the system was controlled constant throughout the adsorption tests. An equilibration time of 3 days was applied for all adsorption tests based on previous kinetics studies [19].

Adsorption of arsenate in the presence of citrate was carried out using different addition order of the adsorptives. In the first case, arsenate was added to the pre-equilibrated goethite suspension and the mixture was agitated at 20 °C for 3 days. Then, citrate solution was added and the system was agitated for another 3 days. This system was designated as (arsenate–goethite)–citrate. In the second case, the same procedure was applied but citrate was first brought to contact with goethite and the system was designated as (citrate–goethite)–arsenate. In the third case, arsenate and citrate were brought to contact with goethite simultaneously.

### 2.3. Potentiometric titrations

The $pH_{pznpc}$ (point of zero net proton condition) of the synthesized goethite were studied by acid–base potentiometric titrations, according to the method described previously [20]. Acid–base potentiometric titrations were performed using a cyberscan pH 510 electrode (EUTECH, America) that had been calibrated with three buffers (pH 4.01, 6.86 and 9.18). 0.01 M $HNO_3$ and NaOH solutions were used as titrants. Titrations were carried out using 0.2 g solid in 100 ml of 0.1 M $NaNO_3$ under $N_2$ at 20 °C. The effect of acetate, oxalate or citrate on $pH_{pznpc}$ of goethite was measured by titrating the pre-loaded goethite. The pre-loaded goethite was prepared by equilibrating goethite in 3.0 mM acetate, 1.5 mM oxalate and 1.0 mM citrate solution with the background electrolyte of 0.1 M $NaNO_3$ for 24 h. For each titration point, when the pH drift was <0.01 per min, the reaction was considered to reach equilibrium. Blank titrations were carried out in the same way with solutions of equivalent electrolyte composition in the absence of goethite.

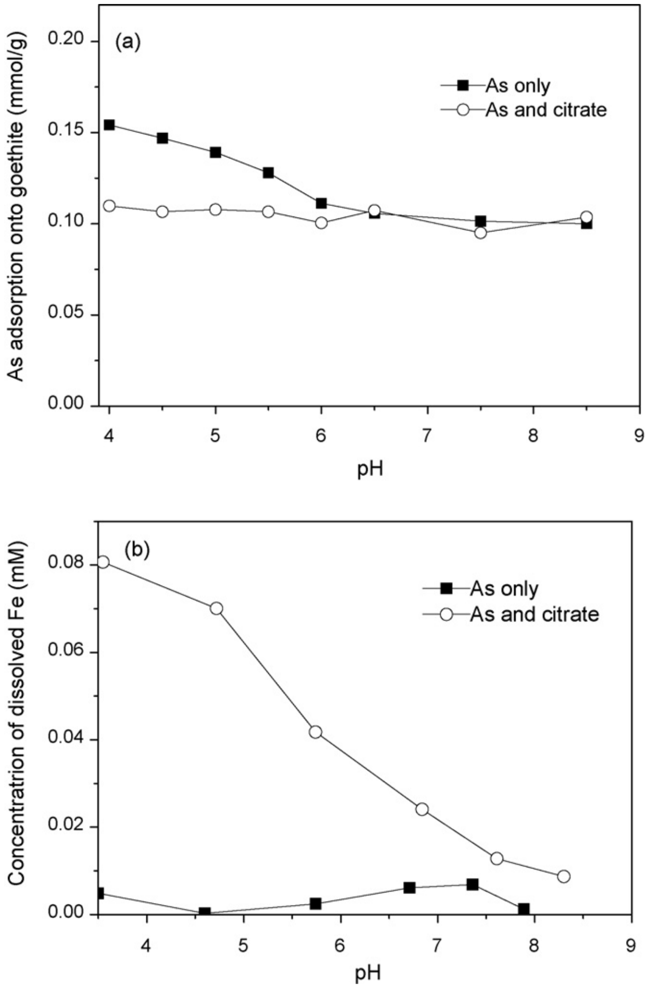

**Fig. 3.** Comparison of adsorption of arsenate onto goethite (a) and dissolution of goethite (b) in the presence and absence of citrate.

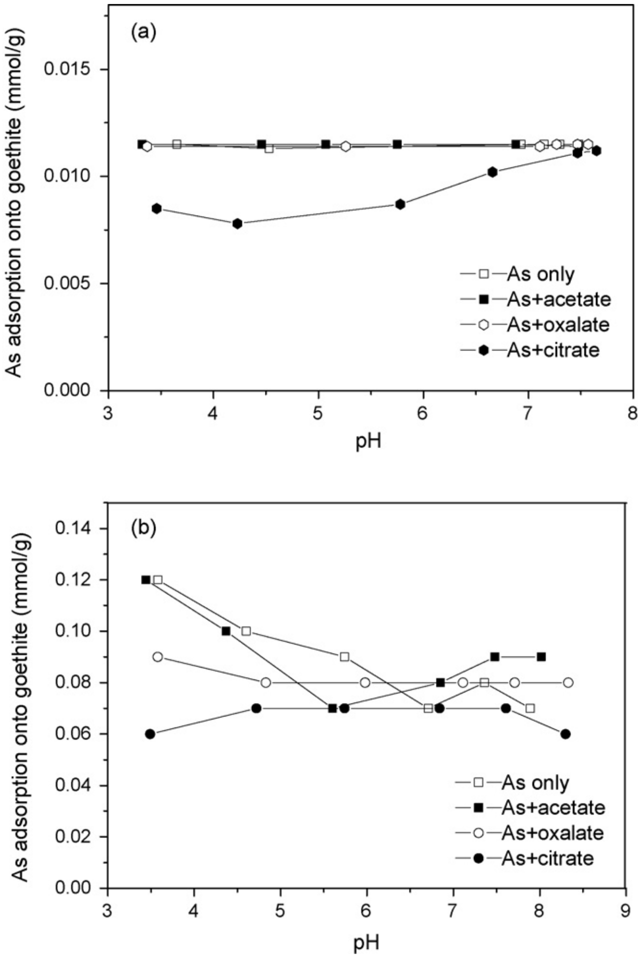

**Fig. 4.** Adsorption of arsenate at initial concentration of 0.006 mM (a) and 0.12 mM (b) in the presence of acetate (3.0 mM), oxalate (1.5 mM) or citrate (1.0 mM).

### 2.4. Determination of the concentration of arsenic and iron

Following the adsorption experiments, the samples were centrifuged at 4000 rpm for 10 min and the supernatant was decanted, filtered by 0.22 μm membrane for the analysis of the concentration of residual arsenic and iron in solution. Arsenic concentration was determined using a hydrite generator (WHA-103A2) coupled with an atomic absorption spectrophotometer (AA240, Varian) (HG-AAS) with the detection limit of 0.08 μg/l. Iron concentration was determined using an atomic absorption spectrophotometer (AA240, Varian).

## 3. Results and discussion

### 3.1. Effect of contact order on the adsorption of arsenate and goethite dissolution

The adsorption of arsenate onto goethite at pH 4.0 and 7.5 was measured by different contact order of citrate and arsenate. At pH 4.0, the presence of citrate decreased the amount of adsorbed arsenate on goethite. The inhibition of arsenate adsorption was markedly influenced by the contact order of arsenate and citrate with goethite. When citrate was added first, more inhibition was observed than the system where arsenate was introduced first.

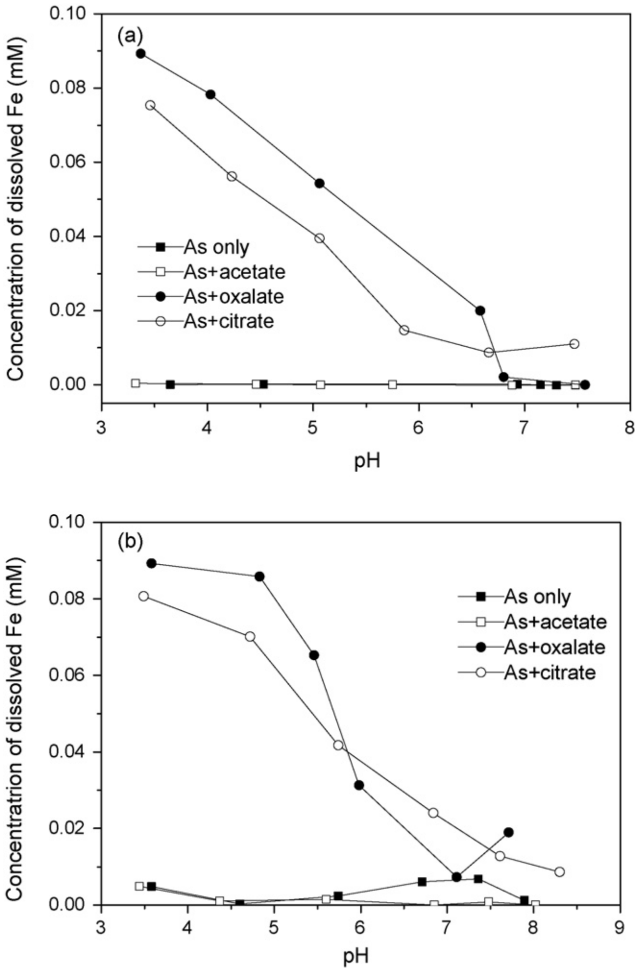

**Fig. 5.** Dissolution of goethite at initial arsenate concentration of 0.006 mM (a) and 0.12 mM (b) in the presence of acetate (3.0 mM), oxalate (1.5 mM), citrate (1.0 mM), respectively.

The ability of citrate to decrease arsenate adsorption on goethite ranked in the order: (citrate–goethite)–arsenate > (arsenate–goethite)–citrate > arsenate–goethite (Fig. 1a). Fig. 1b showed the amount of dissolved goethite (as Fe concentration) by citrate in above systems. The ability of citrate to dissolve goethite was also depend on the contact order of arsenate and citrate. Dissolved iron in the solutions was in the order: citrate–goethite > (citrate–goethite)–arsenate > (arsenate–goethite)–citrate > arsenate–goethite. The ability of citrate to inhibit arsenate adsorption is in good agreement with the ability to dissolve goethite, which suggested that there is obvious interrelationship between suppression of arsenate adsorption and dissolution of goethite. When citrate was added first, more goethite was dissolved and consequently, adsorption of arsenate was suppressed more severely. Compared with the binary (citrate–goethite) system, citrate-promoted dissolution of goethite can be inhibited in the presence of arsenate, which is due to the forming of binuclear complexes between arsenate and goethite surface. Stumm (1997) indicated that arsenate is most likely to form bridging surface complexes at kink and edge sites of crystals, and essentially extend the crossing-linking of the “polymer” or solid. Energetically, simultaneous removal of two or more metal centers together with arsenate is unfavorable [15]. Hence, the adsorption of arsenate can prevent the substrate from citrate attack and inhibited goethite dissolution.

At pH 7.5, the presence of citrate had little effect on arsenate adsorption irrespective of contact order (Fig. 2a), which may be attributed to the less goethite dissolution (Fig. 2b) compared with that at pH 4. Fig. 3 shows the effect of citrate on the adsorption of arsenate and dissolution of goethite at pH 4.0–8.5. At lower pH region (pH 4.0–6.5), arsenate adsorption was significantly reduced by citrate while at higher pH region (pH 6.5–8.5), the effect of citrate on arsenate adsorption was not significant. Citrate-promoted goethite dissolution decreased sharply with increasing pH. The decreased effect of citrate on arsenate adsorption at higher pH was consistent with the decreased citrate-promoted goethite dissolution at high pH.

The pH dependence of the suppressive effect of citrate on arsenate adsorption probably related to the difference of citrate adsorption mode at different pH, i.e. via inner-sphere complex at mildly acidic pH and via the formation of outer-sphere complex at mildly alkaline [21]. Similar mechanism was also proposed for the adsorption of other organic acids (phthalate and benzene carboxylates) onto goethite [22,23]. In contrast, the adsorption of arsenate on goethite is mainly by inner-sphere complexation at both acidic and alkaline pH [3,4,24]. Hence the adsorption of arsenate was more significantly suppressed.

### 3.2. *Arsenate adsorption and goethite dissolution in the presence of acetate, oxalate or citrate*

The effects of acetate and oxalate on arsenate adsorption and goethite dissolution were also investigated. For the initial arsenate concentration of 0.006 mM, acetate and oxalate showed little effect on arsenate adsorption at pH 4.0–8.5, while citrate decreased arsenate adsorption at acidic pH (Fig. 4a). For the initial arsenate concentration of 0.12 mM, oxalate and citrate decreased arsenate adsorption, while acetate had no effect. At lower arsenate concentration, the less competitive effect was attributed to the lower surface coverage of goethite and the stronger affinity of arsenate with goethite. Compared with oxalate, citrate more significantly inhibited arsenate adsorption at pH 4.0–8.5 (Fig. 4b). Mohapatra et al. also observed that for arsenic-loaded ferrihydrite, the organic species increased arsenate extraction in the order: citrate > oxalate > acetate, indicating citrate most significantly affected the release of arsenic from the arsenic-rich ferrihydrite and Al-ferrihydrite [13]. Fig. 5 shows that except

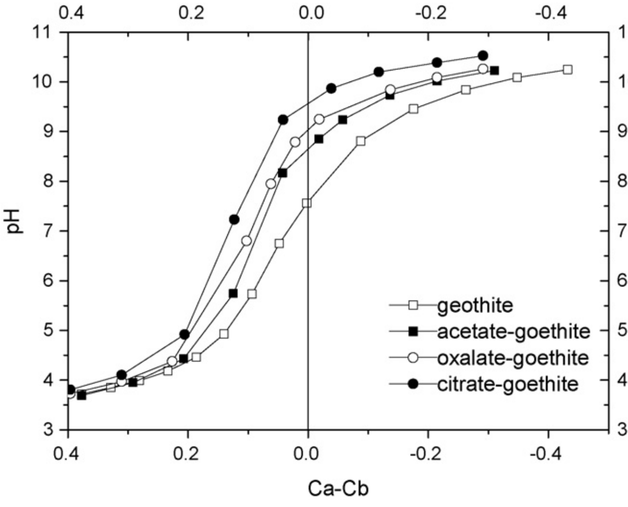

**Fig. 6.** $pH_{pznpc}$ shift of goethite with and without adsorbed acetate, oxalate or citrate.

acetate, both oxalate and citrate promoted goethite dissolution. By comparing goethite dissolution (Fig. 5) and arsenate adsorption (Fig. 4) in the presence of three organic acids, it is proposed that dissolution effect by organic acids may play an appreciable role in the reduced arsenate adsorption onto goethite, especially at high surface arsenate coverage and lower pH. It is noted that oxalate dissolved more goethite than citrate, but citrate caused more suppression of arsenate adsorption. Furrer and Stumm (1986) observed that oxalate was most effective to promote hydrous oxides dissolution by forming five-membered chelate rings at the surface [25]. Reichard et al. demonstrated that oxalate-enhanced DFO-B (desferrioxamine-B mesylate)-promoted goethite dissolution, on the contrary, citrate inhibited the dissolution process [16]. Compared with citrate, oxalate dissolved more goethite but had less effect on arsenate adsorption, which implies that arsenate inhibition cannot be attributed only to organic acid-promoted goethite dissolution.

To gain insight of the role of competition for binding sites in affecting arsenate adsorption by citrate, the pH of the zero proton condition of goethite was decided by acid–base potentiometric titration in the presence and absence of adsorptives. Generally, specifically adsorbable anions shift $pH_{pzc}$ (point of zero charge) to lower pH but $pH_{pznpc}$ (point of zero net proton condition) towards higher pH [19,26]. Fig. 6 shows the acid–base titration curves of goethite and organic acid-adsorbed goethite. The $pH_{pznpc}$ shifts are in the order: citrate > oxalate > acetate, which indicated that citrate has the highest affinity to goethite compared with acetate and oxalate. Filius et al. also found that at $pH < 7.5$, more citrate was adsorbed by goethite than other organic acid such as oxalate, phthalate, malonate and lactatethe [27]. Similar results were also reported by other researchers [28,29]. Among the three organic acids used in this work, the greatest suppression of arsenate adsorption by citrate was probably attributed to citrate's strongest affinity for goethite surface, which was consistent with previous studies [9–12]. Hence, from the above results, it can be suggested that competitive adsorption rather than organic acid-promoted goethite dissolution played a key factor for the decreased arsenate adsorption on goethite.

## 4. Conclusions

Arsenate adsorption at water–goethite interface was inhibited in the presence of citrate at low/high initial arsenate concentration. It is proposed that citrate-promoted goethite dissolution and citrate competition with arsenate are responsible for the inhibition of arsenate adsorption on goethite. Oxalate showed much less effect on arsenate adsorption than citrate although it dissolved goethite more significantly. The effect of oxalate/citrate on arsenate adsorption at water–goethite is highly pH-dependent. At lower pH, arsenate adsorption was suppressed more heavily than at higher pH, which may be due to the higher goethite dissolution and oxalate/citrate adsorption at lower pH. Acetate did not decrease arsenate adsorption because of its disability to dissolve goethite and adsorb onto goethite.

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