

Effect of contact order on the adsorption of inorganic arsenic species onto hematite in the presence of humic acid

Ilwon Ko^a, Allen P. Davis^b, Ju-Yong Kim^a, Kyoung-Woong Kim^{a,*}

^a Arsenic Geoenvironment Lab (NRL), Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), 1 Oryong-dong, Buk-gu, Gwangju 500-172, Republic of Korea

^b Department of Civil and Environmental Engineering and Maryland Water Resources Research Center, University of Maryland, College Park, MD 20742, USA

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Abstract

The speciation of aqueous and adsorbed As forms of arsenic (As) is a major environmental concern in the presence of humic acid (HA). The speciation during As adsorption process by the effect of contact order were evaluated in various equilibrated ternary systems consisting of As, HA and hematite. One ternary system was composed of the preequilibrated As(III)– or As(V)–HA complex, with the subsequent addition of hematite ((As–HA)–hematite system), and the other consisted of the preequilibrated HA–hematite, with the addition of As(III) or As(V) (As–(HA–hematite) system). The presence of HA led to a decrease in the As adsorption, opposite to cationic adsorption. The order of the amounts of As adsorption were found to follow as: As(V)–hematite > hematite–(As(V)–HA) > As(V)–(HA–hematite) > As(III)–hematite > hematite–(As(III)–HA) > As(III)–(HA–hematite). Free As(V) and As–HA complex were preferentially adsorbed onto the hematite surface. The immobilization of As can come from adsorbed HA on mineral surfaces, and formation of As–HA complex, following their slow kinetics.

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1. Introduction

Arsenic is a contaminant in metal mine wastes, industrial effluents and many groundwaters [1]. The inorganic forms are more toxic than organic forms of As, and in particular, As(III) is more toxic than As(V) [2,3]. The World Health Organization (WHO) has established a provisional guideline of 10 µg/L for As in drinking water [4].

Iron oxides and organic matter, as two important geochemical phases, play significant roles in controlling metal and metalloid interactions in the environment. Humic acid (HA) represents 50–90% of dissolved organic carbon in aquatic and terrestrial soil systems [5]. HA can complex metals and metalloids, and further may adsorb onto mineral particle surfaces. These modified surface sites often control the fate and transport of trace contaminants in both aquatic and terrestrial environments. HA can also participate in redox reactions, photochemical reactions

and the formation of coatings onto mineral surfaces [6–8]. The ability of HA to form complexes with metals and metalloids comes from its high content of oxygen-containing functional groups, which include carboxylic, phenolic, enolic and alcoholic groups [5]. The adsorption of HA onto metal oxides has been described as a ligand-exchange mechanism [9]. Initially, the humic carboxyl group forms an outer-sphere complex with a protonated hydroxyl group on the oxide surface; a subsequent ligand exchange step yields an inner-sphere complex.

Many researchers have reported that the adsorption of trace element onto iron-oxides in the presence of HA [8,10], and its thermodynamic deviation [11]. Adsorbed HA can modify the surface adsorption properties in the way like occupation of adsorption site and complexation of aqueous trace elements. Particularly, some researchers reported the effect of loading order on the adsorption in the ternary system [12–14]. The different equilibrated ternary systems were consisted in two ways: (1) the preequilibration of mineral and HA before addition of HA and (2) the preequilibration of mineral and metal before addition of HA. According to their results, the adsorption of cationic metals concerned with no noticeable difference [12] or favor-

* Corresponding author. Tel.: +82 62 970 2442; fax: +82 62 970 2434.
E-mail address: kwkim@gist.ac.kr (K.-W. Kim).

able adsorption of cationic metal before addition of HA [13,14]. Even in natural environments, it is not always general that ternary components of HA, trace metal and mineral are reacted simultaneously with the preequilibration before addition of specific one component. Specifically, the episode of contaminant spill can be a case of addition of contaminant. However, the heterogeneous systems can also have various types of adsorption loading order, and should be characterized for further understanding of adsorption.

Although As contamination has become a significant environmental problem, the As–HA–iron oxide ternary systems remain to be investigated in detail. The adsorption of As onto iron-oxides also has been examined in the presence of humic or fulvic acid [8,15–18]. These organic acids inhibited As adsorption to mineral surfaces due to oxyanionic competition and sluggish kinetic processes. HA can bind directly to the oxide surface, and if similar sites are employed in As adsorption, this competition and site blockage may decrease As adsorption. In addition, the formation of organically complexed As by bridging metals and ligand exchange have been postulated [8,18]. The formation of ternary HA–As–surface complexes, binary HA–(bridging metal)–As, and ligand exchange reactions are possible [17]. Compared with cationic metal–organic complexes, As complexation with HA is less favorable, which can prevent As from adsorbing as an organic complex onto iron-oxide surfaces [8]. The overall effect on As adsorption by the addition of HA will depend on the stability of interaction involving As speciation.

This work extends the previous studies of Ko et al. [19] in order to provide a better understanding of As adsorption onto hematite in the presence of HA extracted from soil. The specific objective was to experimentally evaluate the effect of organic and inorganic As species on the adsorption onto hematite by changing the loading order for three components of the ternary system.

2. Materials and methods

2.1. Preparation of hematite

Hematite colloids were synthesized using the modified method of Sugimoto et al. [20]. A concentrated $\text{Fe}(\text{OH})_3$ gel was prepared by mixing 100 mL of 2.0 M FeCl_3 (Sigma–Aldrich Chem Co.) with 100 mL of 6.0 M NaOH (Merck). The gel was aged in an oven ($100 \pm 1^\circ\text{C}$) for 8 days and then cooled to room temperature for 3 days. After aging and cooling, the excess salts were removed by centrifuging and redispersing the hematite colloids in deionized water, which was tested by AgCl_2 precipitation tests. The size of the hematite colloids was measured by dynamic light scattering measurements (ELS-8000, Photal, Otsuka Electronics, Japan). Potentiometric titration with a micro titrator (702SM, Metrohm, Switzerland) was performed to measure the hematite surface charge in terms of acidity at different ionic strengths (0.001, 0.01 and 0.1 M NaNO_3) with N_2 gas purging to prevent carbonate effects. The surface area of the hematite particles was measured by a multipoint BET analysis. A concentrated stock solution of hematite colloids (pH 5.7) was used for adsorption experiments.

2.2. Isolation of soil HA

Soil HA was extracted from non-contaminated forest soils (Jangsung, Jeollanamdo, Korea) following the standard procedure recommended by the International Humic Substances Society [21,22]. Electrolyte-free HA was prepared using a cation–anion-exchange resin column and stored at 4°C in the dark. The molecular size was measured by high performance size exclusion chromatography (HPSEC) using a SEC column (protein-pak 125, Waters, Milford, USA) which gave reasonable accuracy [23]. Standard solutions were made using various polystyrene sulfonates to produce a relative molecular mass (RMM) calibration curve. Spectra, used to identify functional groups were obtained with an attenuated total refractive Fourier transform infrared (ATR–FT–IR) spectrophotometer (Perkin–Elmer IR 2000 series) and a ZnSe crystal at an incident angle of 45° . Spectral scanning range was between 500 and 2000 cm^{-1} at a resolution of 2 cm^{-1} . From potentiometric titration with a micro titrator [24], carboxylic acidity and phenolic acidity were calculated using the amount of consumed NaOH over a pH range of 3–8 and 8–12, respectively. Finally, the humate salt was dissolved in deionized water and precipitated by acidification to pH 2. The precipitate was redissolved in deionized water; this precipitation and dissolution was repeated 10 times. The concentrate was freeze-dried and stored as a precipitated soil HA stock solution.

2.3. Soil HA coating experiments onto hematite

Coating experiments were conducted in 50-mL centrifuge tubes at room temperature ($25 \pm 1^\circ\text{C}$) in the dark. For the adsorption experiment, triplicate samples were prepared by adding HA (10 mg C/L) to a mixture of 100 mg hematite/L and 10 mM NaNO_3 solution. To observe the molecular size fractionation, duplicate samples were prepared by adding 10 mM NaNO_3 solution and varying amounts (0.50, 0.67, 1.00, 2.52, 5.03, 10.1, 29.2 and 50.4 g C/L) of HA stock solution to deionized water. The suspensions were shaken for 24 h in order to allow equilibration between soil HA and hematite [25]. The batch sets were then centrifuged at 6000 rpm to separate hematite from solution. The final pH was measured and the supernatants stored prior to their analyses. The total organic carbon and molecular size were determined using a PPM Lab TOC analyzer (PPM Lab Co.) and high pressure size exclusion chromatography (HPSEC), respectively. TOC represents the measurement value of HA concentration as an indicative of HA adsorption amount in adsorption system. HPSEC is suitable for the measurement of the variation in the molecular weight of HA.

2.4. Arsenic adsorption experiments

As adsorption chemical speciation were evaluated in the binary As–hematite system and ternary As–HA–hematite systems. In order to compare the adsorption properties of the different equilibrated ternary systems, the order of component addition was varied. One ternary system was composed of the preequilibrated As(III)– or As(V)–HA binary system, with the

Table 1
Properties of hematite and soil HA used in this study

Parameter	Unit	Values
Hematite		
Average diameter	nm	765 ± 110
PZC (point of zero charge)	pH	9.2
Surface area	m ² /g	17
Surface site density	moles/g sites/nm ²	2.30 × 10 ⁻³ 2.31
HA (humic acid)		
Elemental composition	wt.%	C (54 wt.%), H (4.78 wt.%), O (41 wt.%), N (0.52 wt.%)
Acidity	meq/g C	6.8 (carboxyl group), 2.7 (phenolic group)
Average molecular weight	Da	25,991 ± 63 (at pH 7.0)

addition of hematite, and the other consisted of the preequilibrated HA–hematite binary system, with the addition of As(III) or As(V). The preequilibration of As(III)–HA, As(V)–HA and HA–hematite was performed for 24 h, and checked to confirm the composition of each chemical species.

As(III) and As(V) solutions were prepared from NaAsO₂ (Fluka) and Na₂HAsO₄·7H₂O (Sigma–Aldrich Chem Co.), respectively, and the ionic strength was adjusted to 10 mM NaNO₃ (Merck). Adsorption experiments were carried out with bare hematite and humic-coated hematite. Batch adsorption experiments were conducted in a 2-L glass flask with an initial total volume of 2.0 L, consisting of 1.0 mg/L As(III) or As(V), 10 mg C/L HA and 100 mg/L hematite, which was maintained at an intermediate pH (5.7–6.8). Six experimental systems were evaluated in duplicate; As(III)–hematite, As(V)–hematite, As(III)–(HA–hematite), As(V)–(HA–hematite), (As(III)–HA)–hematite and (As(V)–HA)–hematite. The parentheses enclose the preequilibration of the binary system. Deionized water was used after 1-h purging with N₂ gas. The clear glass flasks with a cork cap were exposed to ambient light and were incubated on a shaking incubator at 20 °C and 200 rpm with injection of N₂ gas. Samples were periodically collected (5 min to 30 days) and centrifuged at 6000 rpm for 5 min; the supernatant was filtered through a 0.2 μm-syringe filter and then diluted with 0.1 M HNO₃. The total amount of adsorbed As was calculated from the difference between the total As and the aqueous As species (As–HA complex, As(III), and As(V)).

2.5. Arsenic speciation analysis

The cartridge method of Yalcin and Le [26] was employed to separate the inorganic As forms from HA-complexed As. Three milliliters of solution sample was passed through strong cation (SCX) and anion exchange (SAX) cartridges (Supelco) at a flow rate of 1 ± 0.1 mL/min; the columns had been preconditioned with methanol and deionized water (1:1). The cation and anion exchange cartridges retained the As–HA complex and As(V), but eluted As(III). The As(V) retained on the anion exchange cartridge was subsequently eluted with 1.0 M HCl to separate it from the As–HA complex [2]. Total aqueous As (after separation through filtration and centrifugation), As(V) (extracted using 1.0 M HCl) and As(III) (freely released) were measured

and As–HA complex and adsorbed As were calculated from differences of their respective concentrations. The concentrations of As in the aqueous phases were determined by hydride generation atomic absorption spectrophotometric analysis of the various column eluents (HG-AAS, Perkin-Elmer ZL 5100), with a detection limit of 1.0 μg/L As. Fresh sodium borohydride (Sigma–Aldrich Chem Co.) solutions supplemented with 0.1 M NaOH and 10-wt.% HCl (Merck) were prepared daily and used as the carrier.

3. Results and discussion

3.1. Properties of hematite and HA

The properties of hematite colloid used in this study are shown in Table 1. It is nanoscale, i.e., an average diameter of 765 ± 110 nm. The point of zero charge of hematite was found to be 9.2, and lies at the upper end of the values 7.2–9.5 for hematite reported previously [27,28]. The surface area of the hematite particles was found to be 17 m²/g. Despite an average molecular weight for the soil HA of 25,991 ± 63 Da, varying molecular weights existed. Elemental analysis provided an average molecular formula for the soil HA of C₁₁₄H₁₄₃O₈₁N based on the elemental composition. FT-IR scans exhibit a large peak at 1716 cm⁻¹, associated with the carbonyl of the carboxylic acid group, and a broad curve at 3420 cm⁻¹, associated with carboxylates, phenols and alcohols. From potentiometric titration with a micro titrator, carboxylic acidity and phenolic acidity were 7.3 and 3.5 meq/g C, respectively. Ten purification pretreatment procedure eliminated significant levels of metals from the HA as identified from an metal analysis (75.9 mg Al/L, 82.2 mg Fe/L, 20.2 mg Ca/L, 15.34 mg Mg/L and 0.51 mg Mn/L).

3.2. Adsorption of HA onto hematite

The adsorption of HA onto hematite at pH 6.0 reached a equilibrium value (93 mg C/g hematite) with 24-h equilibration, with little variation beyond this time (Fig. 1a). Wang et al. [25] also suggested that HA adsorption onto hematite equilibrated for 24 h reached adsorption equilibrium. Very strongly acidic groups are significant for the formation of strong surface complexes between organic molecules and hematite surfaces suggested by Edwards et al. [24]. Further it is observed that

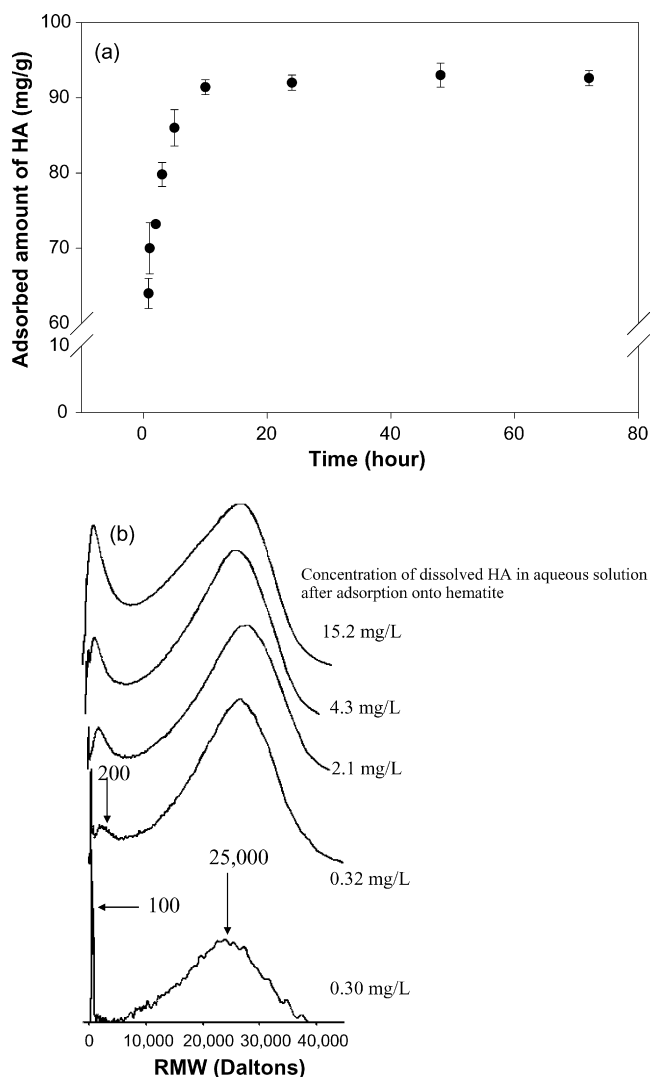


Fig. 1. (a) Adsorption of HA onto hematite in HA–hematite binary system and (b) the molecular size fractionation during HA adsorption onto hematite in the molecular size distribution profile (pH range of 6.6–7.4; $I=10$ mM NaNO_3 ; 10 mg C/L HA; 100 mg/L hematite, error bars represent the maximum and minimum value of duplicate experiments).

strongly sorbing ligand is significant for HA adsorption onto hematite, and then the affinity of HA adsorption is dependent on the molecular size and strong acidic group. Then, surface reaction between hematite surface site and organic ligand is provided with high surface affinity of the strength of acid like carboxyl and phenolic groups. For the effect of molecular size on HA adsorption, Fig. 1b characteristically shows the molecular size distribution of HA in aqueous solution after 24-h contact with hematite. The soil HA was characterized by two major peaks of ca. 200 and 25,000 Da. The peak of ca. 200 Da was not apparent at 0.30 mg/L, but appeared in higher equilibrium concentrations. The soil HA was adsorbed onto hematite as the low-weight (100–200 Da) as well as intermediate- and high-weight molecules (200–25,000 Da). Low-weight molecules can delay the total HA equilibration time due to their gradual replacement with high-weight molecules [10]. Further, the smaller HA

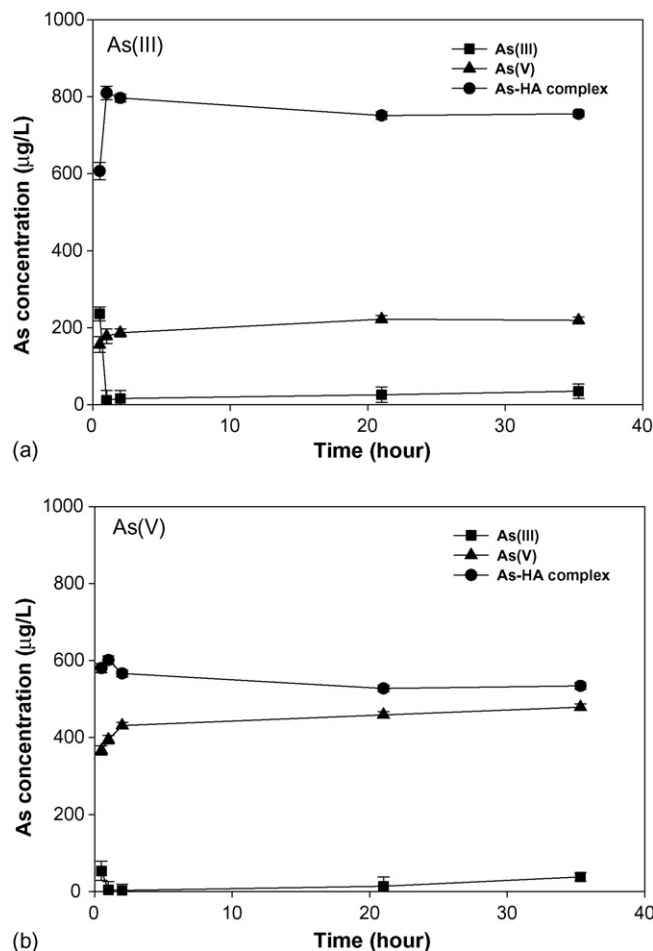


Fig. 2. Humic acid complexation and arsenic speciation in (a) binary As(III)–HA system and (b) binary As(V)–HA system (pH range of 6.2–7.1; $I=10$ mM NaNO_3 ; 10 mg C/L HA; 1.0 mg/L total arsenic, error bars represent the maximum and minimum value of duplicate experiments).

molecules can be ascribed to the more negatively charged surface [29].

3.3. Arsenic complexation with HA

Equilibration of aqueous As–HA complexation was reached within 24 h (Fig. 2), with the majority of reaction complete within 3 h. The equilibrium of As–HA complex is evidently sluggish, compared with equilibrium of binary adsorption system consisting of HA and hematite. Further As species undergoes the oxidation and reduction. Then, the kinetic influences seem to come from the change of As speciation. Complexation of As(III) with soil HA was more significant than As(V). The amounts of HA complexed with As(III) and As(V) were about 75% and 55% of the initial total As concentration (1000 $\mu\text{g/L}$). Interestingly, in the As(III)–HA system, most of As(III) formed As–HA complex, but about 200 $\mu\text{g/L}$ of As(III) was oxidized to As(V) within a few minutes (Fig. 2a). Although metal cations were present as low-level inorganic impurities in HA, the rapid oxidation can be explained by a catalytic oxidation process initiated by the inorganic impurities in soil HA. In both systems, the concentrations of free As(III) are about 50 $\mu\text{g/L}$. The weaker complexation

of As(V) compared to As(III) and the slower equilibration of the As–HA complex may be due to the electrostatic repulsion between As(V) and HA. Some oxyanions have been reported to bind indirectly to organic functional groups through bridging metals, such as Al^{3+} or Fe^{3+} [8,18]. A ternary complexation through bridging metals is considered a potential binding mechanism between HA and As [8]. Thanabalasingam and Pickering [18] proposed the hypothesis that $-\text{NH}_2$ groups were responsible for As adsorption by HA. The detailed interpretation of HA–As interaction is difficult because current understanding of the structure of HA is quite limited. Despite a pretreatment for the removal of metal ions, HA contains small amounts of bridging metals (75.9 mg Al/L, 82.2 mg Fe/L, 20.2 mg Ca/L, 15.34 mg Mg/L and 0.51 mg Mn/L after 10 times washing of HA) and a low concentration of nitrogen of total N 0.52 wt.% (Table 1). The more concentrated the humic solution, the more likely As(V) can form As–HA complex with these bridging metals and organic functional groups [19]. Although As(III) had a lower affinity for the direct formation of organic complexes with the bridging metals, the total amount of As(III)–HA was much higher than that of As(V)–HA. Since As(III) exists as a neutral species (H_3AsO_3) at intermediate pHs, it may bind directly to HA. Therefore, in this study, the soil humic colloids seem to be relevant for the complexation of As(III) rather than As(V), and As(III) prefers aqueous complexation when compared to As(V). The 24-h preequilibration of each binary system gave sufficient time to define the composition of the As species, and thereafter the preequilibrated binary systems could be used to synthesize the ternary systems.

3.4. Arsenic adsorption in the ternary system

3.4.1. Preequilibration of As–HA complex with subsequent addition of hematite

After the binary preequilibration of the As(III)– or As(V)–HA system, the As species in the ternary system are shown in Fig. 3a and b, respectively. The amount of total adsorbed As(III) or As(V) equilibrated to 490 and 780 $\mu\text{g/L}$, respectively (Fig. 3). According to the adsorption affinity of oxyanions, As(V) adsorbs more favorably onto iron oxide than As(III) [1]. In this system, As(V) adsorbed onto hematite in the presence of HA to a greater extent than As(III).

For the As(III)–HA system, the initial amounts of As(III) and As–HA complex decreased and the concentration of As(V) progressively increased slightly, indicating the oxidation of As(III) (Fig. 3a). Characteristically, Fig. 3a shows an abnormal adsorption situation, that is, rapid adsorption followed by slight desorption of the adsorbed As species. Most of the adsorption in the As(III)–HA system resulted from As–HA complex since the concentration decreased from 735 to 200 $\mu\text{g/L}$ (near 24 h). As(III) decreased from 90 to 50 $\mu\text{g/L}$ (over 100 h). As(V) rapidly decreased from 180 to 130 $\mu\text{g/L}$ (near 24 h) and finally increased to 200 $\mu\text{g/L}$ (over 100 h) due to the oxidation of As(III).

The decrease in the As(III) concentration by oxidation, noted during the binary preequilibration (Fig. 2a), continued with more progressive oxidation of As(III) in the ternary system (Fig. 3a). Furthermore, colloidal hematite can also act as a catalyst for

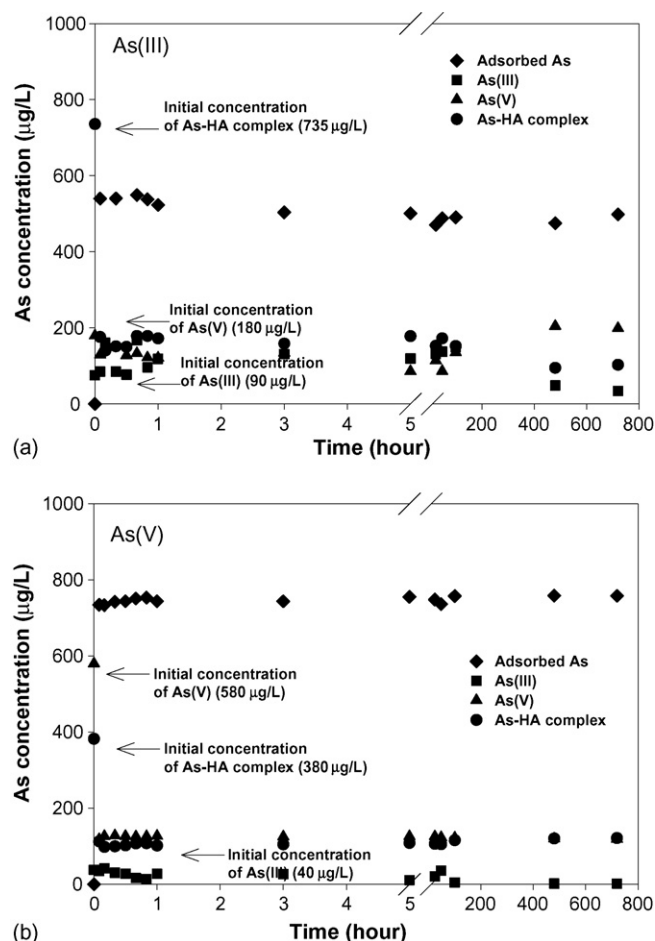


Fig. 3. Adsorption of (a) As(III) and (b) As(V) onto hematite and arsenic speciation in the ternary system after the binary pre-equilibration of As–HA (pH range of 6.2–6.8; $I = 10 \text{ mM NaNO}_3$; 10 mg C/L HA; 100 mg/L hematite; 1.0 mg/L arsenic, symbols represent the mean value of duplicate experiments).

As(III) oxidation at neutral pH [30]. The oxidation of As(III) in this study may have been catalyzed by iron, HA or an iron–HA complex.

In the As(V)–HA system, both free As(V) and As–HA complex (initial concentrations of 480 and 530 $\mu\text{g/L}$, respectively) decreased to identical concentrations (110 $\mu\text{g/L}$ over 100 h) as a result of their adsorption onto hematite (Figs. 2b and 3b). The reduction in As(V) concentration was greater than that of As–HA complex indicating that free As(V) was strongly adsorbed as compared with As–HA complex.

3.4.2. Preequilibration of HA–hematite with subsequent addition of As

The reactions proceeded in a different manner in the case of preequilibration of HA–hematite (Fig. 4), followed by As addition. In the As(III) system (Fig. 4a), the amount of adsorbed As (46% of total As(III) input) gradually increased concurrent with an increase in the amount of dissolved As–HA complex (135 $\mu\text{g/L}$ over 100 h) and free As(V) (150 $\mu\text{g/L}$ over 100 h) because of organic complexation and oxidation of As(III), respectively. Accordingly, As(III) first rapidly decreased, and then slowly continued to decrease. As shown for As(V) in

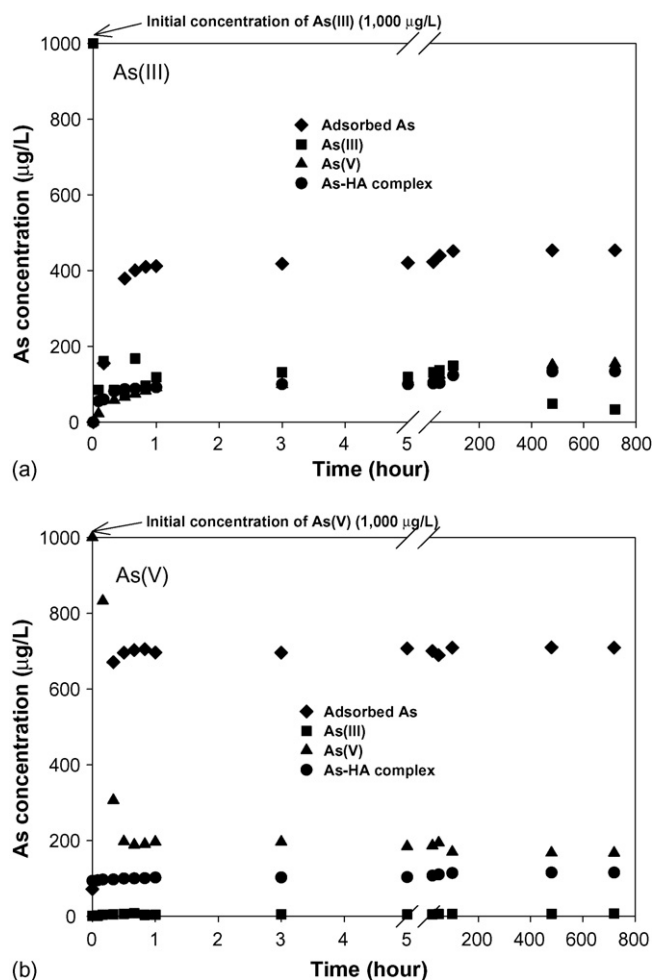


Fig. 4. Adsorption of (a) As(III) and (b) As(V) onto hematite and its speciation in the ternary system after the binary pre-equilibration of HA–hematite (pH range of 5.7–6.4; $I = 10$ mM NaNO_3 ; 10 mg C/L HA; 100 mg/L hematite; 1.0 mg/L arsenic, symbols represent the mean value of duplicate experiments).

Fig. 4b, the amount of adsorbed As (70% of total As(V) input) also increased with a decrease in As(V) (830–170 $\mu\text{g/L}$ over 100 h) and an increase in dissolved As–HA complex (115 $\mu\text{g/L}$ over 100 h).

Distinct differences are noted between the two ternary systems of (As–HA)–hematite and As–(HA–hematite), both for the adsorption processes of As(III) (Figs. 3a and 4a) and As(V) (Figs. 3b and 4b). As(III) and As(V) adsorption in the binary pre-equilibration of the HA–hematite system were both slightly less than those after the binary pre-equilibration of the As(III)– or As(V)–HA. In the (As–HA)–hematite system, free As, As–HA complex and HA simultaneously became adsorbed onto hematite. In the As–(HA–hematite) system, As was adsorbed onto humic-coated hematite directly or formed As–HA aqueous complex, requiring some HA desorption. The initial input of HA (10 mg C/L = 100 mg C/g as an adsorption loading) exceeded the maximum amount of HA adsorption (93 mg C/L) at this pH, similarly that of As(III) or As(V) (1000 $\mu\text{g/L}$ = 10 mg/g as an adsorption density) was greater than the capacity for inorganic As(III) and As(V) (6.2 and 9.5 mg/g). Consequently, in both

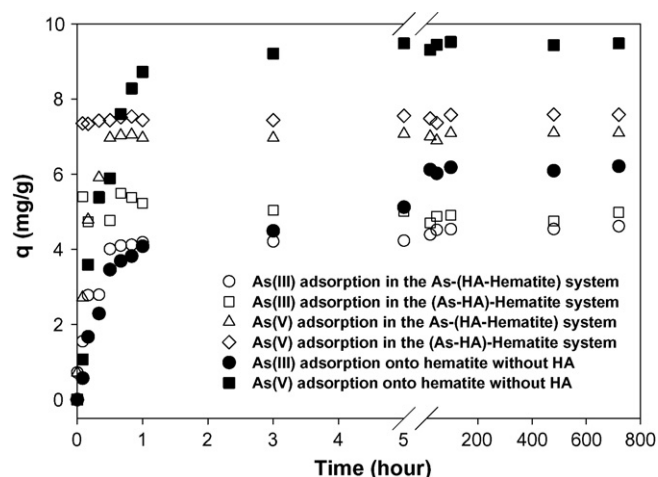


Fig. 5. Amount of arsenic adsorption as a function of time in the differently equilibrated ternary systems, compared with bare hematite.

ternary systems both free As and HA can exist in aqueous solution and may also form As–HA complex during As adsorption in the As–(HA–hematite) systems.

For comparisons of the adsorption amount in the two ternary systems, the time profile of As adsorption for all systems was plotted (Fig. 5). This figure indicates the progressive accumulation on the hematite surface with little variation of concentrations of adsorbed As beyond a 24-h equilibration time. The order of the amounts of As adsorption including the bare hematite system was As(V)–hematite > hematite–(As(V)–HA) > As(V)–(HA–hematite) > As(III)–hematite > hematite–(As(III)–HA) > As(III)–(HA–hematite) (Fig. 5). Specifically, the humic-coated hematite via the pre-equilibration of HA–hematite distinctly reduced the amount of adsorption for both As(III) and As(V) compared with (As–HA)–hematite and a simple As–hematite system. Adsorbed macromolecular HA occupies more hematite surface sites, particularly in the As–(HA–hematite) system. HA complexation and oxyanionic adsorption competition are dominant on the hematite surface. Although As(V) can strongly bind to the hematite surface, the desorption of HA by As(V) is likely to be slow and restricted to some extent by the maximum adsorption amount. The organic ligands of HA sequester surface sites and block the diffusion of As to the oxide surface [31]. Additionally, the limited adsorption sites, that is, the system exceeding the maximum adsorption of HA and greater than the maximum adsorption of inorganic As led to pronounced decrease of the overall amount of adsorption [32].

Davis and Bhatnagar [13] showed that the sequential order of adsorption of dissolved and adsorbed HA significantly altered the adsorption characteristics of cadmium onto hematite. Despite the enhanced amount of cadmium adsorption in the presence of HA, cadmium adsorption before the addition of HA was more favorable. Contrary to the cationic metal adsorption, As adsorption decreased in the presence of HA. The soil HA had low complexation affinity with As and overall reduced amounts of adsorption. In addition, HA can competitively occupy the hematite surface sites against oxyanionic As.

4. Summary and conclusions

Aqueous speciation and adsorbed form of As were evaluated in two types of equilibrated ternary systems consisting of As, HA and hematite. One ternary system was composed of the preequilibrated As–HA complex with subsequent addition of hematite ((As–HA)–hematite system), and the other consisted of the preequilibrated HA–hematite with the subsequent addition of As (As–(HA–hematite) system). Changing the component loading order in the ternary systems led to different characteristics of adsorption. In the (As–HA)–hematite system, free As, As–HA complex and HA simultaneously were adsorbed onto hematite. In the As–(HA–hematite) system, As was adsorbed onto humic-coated hematite by binding to open sites, desorbing the HA and/or forming As–HA complex. In both ternary systems As and HA can form As–HA complex in aqueous solution. Impurities-catalyzed oxidation of As(III) enhanced the concentration of As(V) in line with a decrease of As(III). Free As(V) and As–HA complex were preferentially adsorbed onto hematite surface. Arsenic adsorption degree was found to follow the order: As(V)–hematite > hematite–(As(V)–HA) > As(V)–(HA–hematite) > As(III)–hematite > hematite–(As(III)–HA) > As(III)–(HA–hematite). Overall, As adsorption decreased in the presence of the soil HA, opposite to that noted for cationic metal adsorption. The HA had low affinity of complexation with As, thereby resulting in reduced amounts of adsorption. The amount of adsorption in all As(V) systems were higher than for As(III) systems. Correspondingly, adsorption of (As(III)–HA)–hematite and As(III)–(HA–hematite) were also lower than those for As(III). Therefore, As speciation directly affects the amount of adsorption onto bare hematite and humic-coated hematite. The variation in the As species led to the different adsorption behaviors.

In natural environments, dissolved and adsorbed forms of natural organic matter affect the speciation of trace metal(oid) and adsorbed HA can alter the mineral particle surfaces. Humic acid can reduce As(III) and As(V) adsorption onto hematite, and further HA complexation can accordingly inhibit the immobilization of As in natural geoenvironments and remedial engineering actions.

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