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공학석사 학위논문

Effect of Humic Acid on
Arsenic(III), (V) Sorption onto
Zero-valent Iron, Hematite, and
Magnetite

영가철, 적철석, 자철석의 비소 흡착에 대한
휴믹산의 영향

2017년 2월

서울대학교 대학원

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Abstract

Effect of Humic Acid on Arsenic(III), (V) Sorption onto Zero-valent Iron, Hematite, and Magnetite

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Humic acid (HA) and iron oxides or zero-valent iron with iron oxides shell can coexist, and their interaction alters their ability to adsorb pollutant in the environment. The influence of HA on arsenic adsorption onto three types of irons (zero-valent iron, hematite and magnetite) was investigated with different contact order using batch sorption experiments. The results indicated that the presence of HA led to a decrease in the arsenic adsorption, and the order of the amounts of As adsorption were found to follow as: $As-Fe > (HA-As)+Fe > (HA-Fe)+As$. These results can have important implications to design the arsenic pollution remediation system and understand the behavior of arsenic in the natural environmental system.

Keywords: arsenic, sorption, humic acid, zero valent iron, hematite, magnetite

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Chapter 1 Introduction

1.1 General

Arsenic is a notoriously toxic element and widely distributed in the environment. Long-term exposure to arsenic may cause serious health issues such as skin cancer, lung cancer, diabetes, and other diseases of the cardiovascular and nervous systems. (Ratnaike, 2003; Karagas et al., 2004). It occurs naturally in inorganic and organic forms, such as arsenic acid (H_3AsO_4) and arsenous acid (H_3AsO_3) and their dissociation derivatives (H_2AsO_4^- , HAsO_4^{2-} , H_2AsO_3^- , and HAsO_3^{2-}), arsenites, arsenates, monomethylarsenic acid (MMAA), and dimethylarsenic acid (DMAA) (Bodek et al., 1988). Inorganic Arsenic is generally more toxic and mobile than organoarsenic species, while trivalent arsenite [As(III)] is considered to be more toxic, soluble, and mobile than pentavalent arsenate [As(V)].

High concentration of arsenic, exceeding $10\mu\text{gL}^{-1}$, the maximum concentration limit (MCL) recommended for potable waters by the World Health Organization (WHO, 1993), have been reported in groundwater from all over the world including Bangladesh, West Bengal, India, Inner Mongolia (Raman et al., 2005). The groundwater arsenic contamination of these areas has become a serious public health issue as untreated groundwater is the primary source of water for drinking, domestic and agricultural use in these regions (Simeoni et al., 2003). This contamination usually geogenic but can intensified by human activities such as mining, pesticides use, smelting of

non-ferrous metals, burning of fossil fuels and timber treatment (Moore and Ramamoorthy, 1984).

Arsenic removal technologies that are commercially available, such as aeration, prechlorination, and sedimentation, do not meet the proposed maximum contamination level for arsenic (Kim et al., 2004). Therefore, many enhanced treatment processes have been developed to effectively remove arsenic from water. Precipitation/coprecipitation process causes dissolved arsenic to form low-solubility solid minerals. Adsorption process for arsenic removal is to separate solutes from solvent, where the solute increases on the adsorbent surfaces and decreases in the solvent. Ion exchange process uses synthetic resins to remove dissolved ions from water. Membrane separation process, including microfiltration, reverse osmosis, electrodialysis, ultrafiltration, has also proved to be effective for arsenic removal from water (Feenstra et al., 2007). Among the possible treatment process, adsorption is considered to be less expensive than membrane separation, easier and safer to handle as compared with the contaminated sludge produced by precipitation, and more versatile than ion exchange (Gallegos-Garcia et al., 2012). Iron (hyd)oxides and zero-valent iron (ZVI) and has been proved as effective arsenic adsorbents (Mamindy-Pajany et al., 2011; Su et al., 2001; Couture et al., 2013 etc.). During the arsenic adsorption process, the operating conditions such as pH, DO, hardness, existence of natural organic matter may have an important role in controlling the overall effectiveness of arsenic removal. Among those factors, natural organic matter (NOM) is the breakdown products of once-living organisms as well as products they leave behind.

Humic acid (HA) typically represent a large portion of natural organic matter (NOM) distributing in soils, sediments and waters. A lot of studies show that HA in the soil or water can be adsorbed onto clay minerals or iron oxides and their surface characteristics are altered, having negative effect on arsenic removal capacity of ZVI and iron oxides (S.H et al., 2009, Ko et al., 2007, Luo et al., 2015, Rao et al., 2009 etc.). However, it is still not clear to what extent the influence of HA would be in terms of arsenic adsorption on irons with different components or surface charge. Also, ternary components (HA, arsenic and iron adsorbent) do not always react simultaneously. In natural heterogeneous systems, adsorption loading order may vary. Some recent studies show that the complexation of HA with arsenic also can occur (Fakour et al., 2014; Kim 2013), and it is presumed that contact order of the components can alter the arsenic sorption characteristics of ZVI and iron oxides. Due to the nature of reaction system mentioned above, the adsorption characteristic and mechanisms of each sequence are to be characterized and studied in detail for further understanding of arsenic adsorption.

To investigate the effects of HA in a ternary system (HA, arsenic and iron adsorbent) in detail, batch sorption experiments were performed on three types of irons with different loading orders. The result could enhance our understanding of the arsenic contamination in HA-laden water and provide theoretical bases for the arsenic contaminated water remediation system design.

1.2 Scope and Objectives

The main purpose of this study is figuring out the effects of NOM in a ternary system (NOM, arsenic and iron adsorbent) in detail. As pre-experiments, As-HA complexation experiments were performed using HPLC-ICP-MS as well as HA adsorption experiments on three types of irons (zero-valent iron, hematite and magnetite). Also, batch sorption experiments were performed on three types of irons with different loading orders.

In this study, changes in arsenic species and desorption effects are not considered in this study.

Chapter 2 Materials and Methods

2.1 Materials

All chemicals used in this study were reagent grade. As(III) and As(V) solutions were prepared by adding appropriate amounts of NaAsO₂ (sodium meta-arsenite; Sigma, USA) and Na₂HAsO₄·7H₂O (sodium arsenate heptahydrate; Wako, Japan) into deionized (DI) water from Milli-Q apparatus (Millipore, USA), respectively. To prepare a stock solution of HA, commercially available HA (Aldrich Chemicals, Switzerland) was dissolved in deionized (DI) water followed by solution filtration through 0.45 μm nylon membranes (Pall Corporation, USA). During the experiments, HNO₃ (nitric acid; Kanto, Japan) and NaOH (sodium hydroxide; Samchun, Korea) were used for adjusting solution pH to 6. Also, 0.01 M NaNO₃ used as background electrolyte for all experiments.

Sorption experiments were conducted with three commercial mineral adsorbents: zero-valent iron (Fe), hematite (Fe₂O₃), magnetite(Fe₃O₄). The main physicochemical properties of adsorbents are displayed in Table 2.1.

All adsorbents were passed through -325mesh (44 μm) and the surface area of the adsorbents was measured by the BET method using nitrogen adsorption. The point of zero charge (pH_{pzc}) of the zero-valent iron was determined by the potentiometric titrations at (Sposito, 1998) at an ionic strength of 0.001, 0.01, 0.1 M NaNO₃ by 0.1 M HCl or NaOH. The plot of

adsorbed proton charge vs. pH was made. The pH_{pzc} was obtained from the pH corresponding to the common intersection point in the plot, which was 7. The pH_{pzc} of hematite was obtained by measuring zeta potential with different pH values. The pH_{pzc} , as measured by electrophoretic techniques, can be defined as the pH where zeta potential is zero, which was 9 in the case of Hematite. Zeta potential was analyzed by Nano-ZS60 (Malvern Instruments, UK).

Table 2.1 The main physicochemical properties of adsorbents.

Mineral additives	Zero-valent iron	Hematite	Magnetite
Supplier	Acros	Alfa Aesar	Alfa Aesar
Particle size (μm)	<44	<44	<44
Specific area (m^2/g)	0.2 ^{a)}	7.0	7.2
pH_{pzc}	7	9	6.4 ^{a)}

^{a)}Mamindy-Pajany et al., 2011

2.2 Methods

2.2.1 Humic Acid–Arsenic Complexation Experiments

To study the interaction of arsenic with humic acid in water, complexation experiments were performed at various arsenic concentration (0.5, 1, 5, 10, 15mg/L), ionic strength (0, 0.01, 0.1 M NaNO_3) and initial pH (2, 4, 6, 8) conditions using 45mL glass vial at room temperature. First,

various arsenic concentration (0.5, 1, 5, 10, 15mg/L) was put in contact with a constant concentration of humic acid (20mg/L) for 24hrs at pH 6. Other sets of experiments were conducted with constant humic acid (20mg/L) and arsenic concentration (10mg/L) conditions but different pH values (2, 4, 6, 8, 10) or ionic strength conditions (0, 0.01, 0.1) for 24hrs. The humic acid – arsenic complexation concentration was calculated by the difference between total arsenic concentration and inorganic arsenic concentration using HPLC-ICP-MS (Altus A-10/NexION 350D, Perkin Elmer).

2.2.2 Humic Acid–Iron Sorption Experiments

Batch sorption experiments were performed at room temperature, where 0.04g of iron materials were added to a series of 45mL glass vial containing 40mL 0.01M NaNO₃ and humic acid (0.5, 1, 5, 10, 15, 30mg/L) under a desired initial pH and ionic strength, respectively. The solutions were shaken for 24hrs to reach adsorption equilibrium and then the supernatants were filtered through 0.45µm nylon membranes (Pall Corporation, USA). The humic acid concentration in the supernatants was measured by using TOC analyzer (Shimadzu, Japan). The humic acid adsorbed on zero-valent iron, hematite and magnetite were calculated by their humic acid concentration difference before and after adsorption. The effect of pH and ionic strength were observed by setting the initial solution pH at 2, 4, 6, 8, and 10 under a constant 0.01M NaNO₃, or by adjusting the ionic strength to 0, 0.01, and 0.1M NaNO₃ under a constant pH 6, respectively.

2.2.3 Arsenic Sorption Experiments

Arsenic adsorption was evaluated in the binary (arsenic – iron materials) system and ternary (arsenic – iron- humic acid) system. 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) - humic acid binary system, with the addition of iron materials, and the other consisted of the preequilibrated humic acid – iron materials binary system, with the addition of As(III) or As(V).

Batch sorption experiments were performed at room temperature, where 0.04g of iron materials were added to a series of 45mL glass vial under a desired initial arsenic concentration (0.5, 1, 5, 10, 15, 30mg/L) and ionic strength values (0.01, 0.1 M NaNO₃). Six experimental systems were evaluated in duplicate at pH 6. As(III)-iron, As(V)-iron, (As(III)-HA)-iron, (As(V)-HA)-iron, As(III)-(HA-iron), As(V)-(HA-iron). The parentheses enclose the preequilibration of the binary system. The solutions were shaken for 24hrs to reach adsorption equilibrium and then the supernatants were filtered through 0.45µm membranes (Adventec, Japan). The arsenic concentration in the supernatants was measured by using inductively coupled plasma-optical emission spectrometer (ICP-OES, Ultima 2000, USA).

Among the empirical models, Langmuir and Freundlich models are the most used to describe the adsorption isotherms. These representations allow calculating thermodynamics values induced by the adsorption process. Arsenic adsorption was modeled with Langmuir adsorption isotherm using the

following equation:

$$Q = \frac{Q_{max}K_Lc}{1 + K_Lc}$$

Where Q (mg/g) is the adsorption amount at an equilibrium concentration of c (mg/L), K_L is the parameter relevant to adsorption, Q_{max} is the maximum adsorption capacity.

The Freundlich equation was also used to model arsenic adsorption as below.

$$Q = K_F c^{\frac{1}{n}}$$

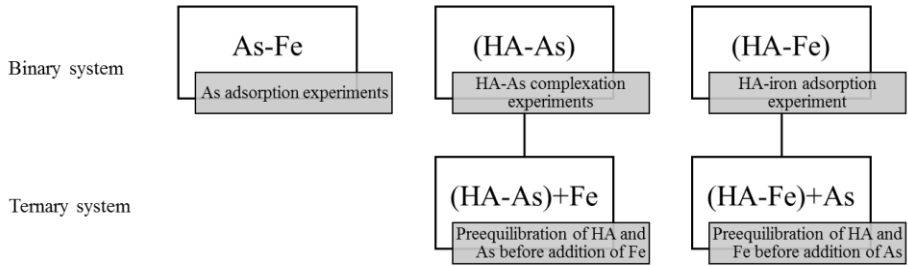
Where K_F and $1/n$ are the parameters relevant to adsorption, Q (mg/g) is the adsorption amount at an equilibrium concentration of c (mg/L).

2.2.4 Two Way Analysis of Variance (ANOVA) Test

A statistical test used to determine the effect of two nominal predictor variables on a continuous outcome variable. A two-way ANOVA test analyzes the effect of the independent variables on the expected outcome along with their relationship to the outcome itself. To determine whether each main effect and the interaction effect is statistically significant, compare the p-value for each term to a specific significance level to assess the null hypothesis. Generally, significance level (denoted α or alpha) of 0.05 is used to determine whether the effect is statistically significant or not. The statistical significance of the effect depends on the p-value, as follows:

1. If the p-value is greater than the significance level you selected, the effect is not statistically significant.
2. If the p-value is less than or equal to the significance level you selected, then the effect for the term is statistically significant.

2.2.5 Experimental Overview



Chapter 3 Results and Discussion

3.1 Arsenic Complexation with HA

Analysis of the total and inorganic arsenic revealed that a considerable portion of As(III) was complexed with HA at a different initial As(III) concentration, while As(V) relatively less bound to HA (Fig. 3.1). At 20mg/L of HA, the HA-complexed As(III) ratios increased by 2.9, 5.6, 5.9, 6.2, and 6.7% as As(III) concentration increased. The amounts of As(V) complexed with HA were 0.1-2.4% of As(V) spiked for HA 20mg/L.

The binding of As(III) to HA is related to the form of As(III) species which is stable neutral ($\text{pH} < 9$) hydroxo-complexes, such as $\text{As}(\text{OH})_3$. Since HA contains phenolates as functional entities, a ligand exchange reaction may occur (Buschmann et al., 2006). Meanwhile, some oxyanions such as inorganic As(V) species, H_2AsO_4^- and HAsO_4^{2-} , are negatively charged when pH is higher than 3. Anion binding to HA has not been fully understood so far due to generally negatively charged properties of HA in water at the neutral pH. However, these oxyanions may bind indirectly to the HA through bridging metals such as Fe, Si, Ba, Cr, Mg and Mn. The chemical composition of humic substances depends largely on its origin and treatment, but even purified HA may still have small quantities of trace elements (Gaskill et al., 1977; Ramos-Tejada et al., 2003). In addition, the presence of $-\text{NH}_2$ groups in HA could be responsible for As binding to HA through a ligand exchange (Thanabalasgam et al., 1986; Sharma et al., 2010; Wang et al., 2011).

The experiment of HA complexation with As at 20mg/L of HA and As 10mg/L revealed that ionic strength and pH of the solution has no significant effect on As binding to HA (Fig.3.2, 3.3).

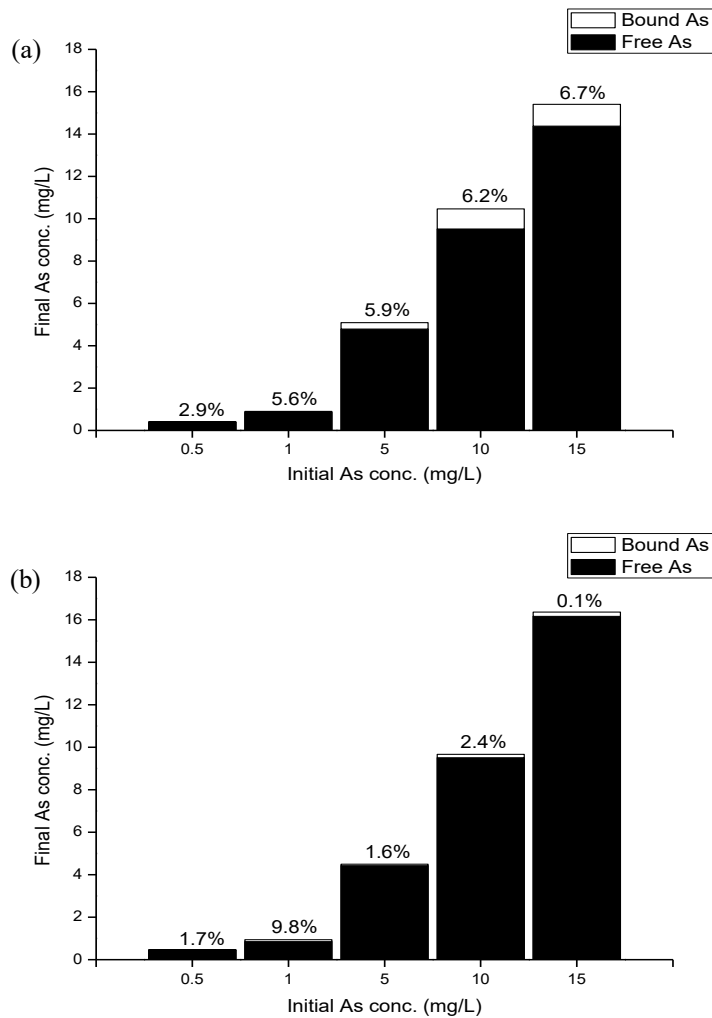


Figure 3.1 Concentration of free and bound (a) As(III) and (b) As(V) with different initial As concentration.

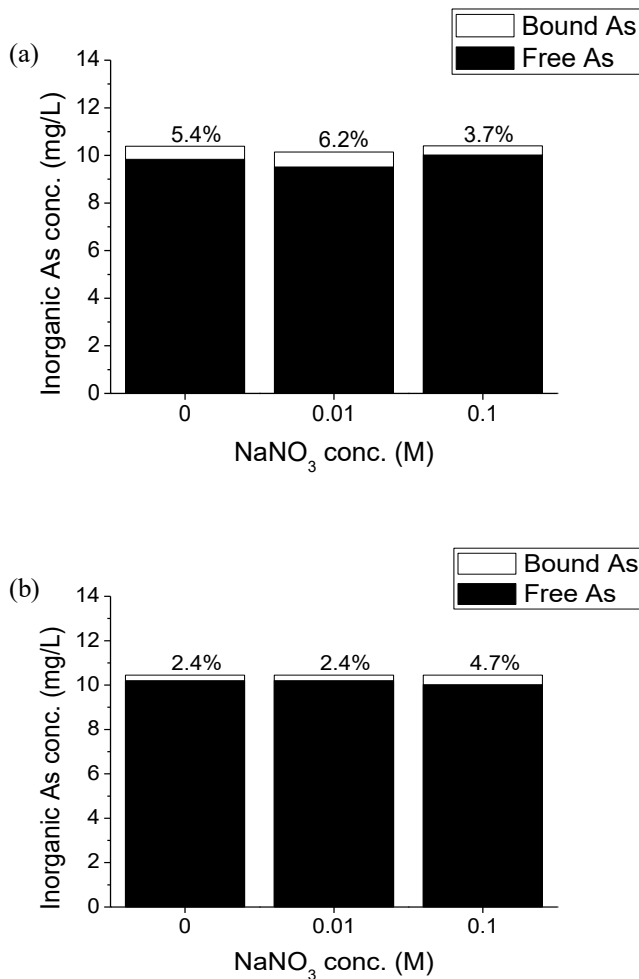


Figure 3.2 Concentration of free and bound (a) As(III) and (b) As(V) with different ionic strength condition at HA 20mg/L and As 10mg/L.

Based on the experimental results, As(III) and As(V) may form HA-As complex in water with higher affinity to As(III) than As(V). Considering that the ionic strength of most surface water and groundwater has the range of 0.001-0.02M (Aqion, 2014), the ionic strength in natural water has less impact on the complexation of HA and As in the pH which ranges from acid to neutral.

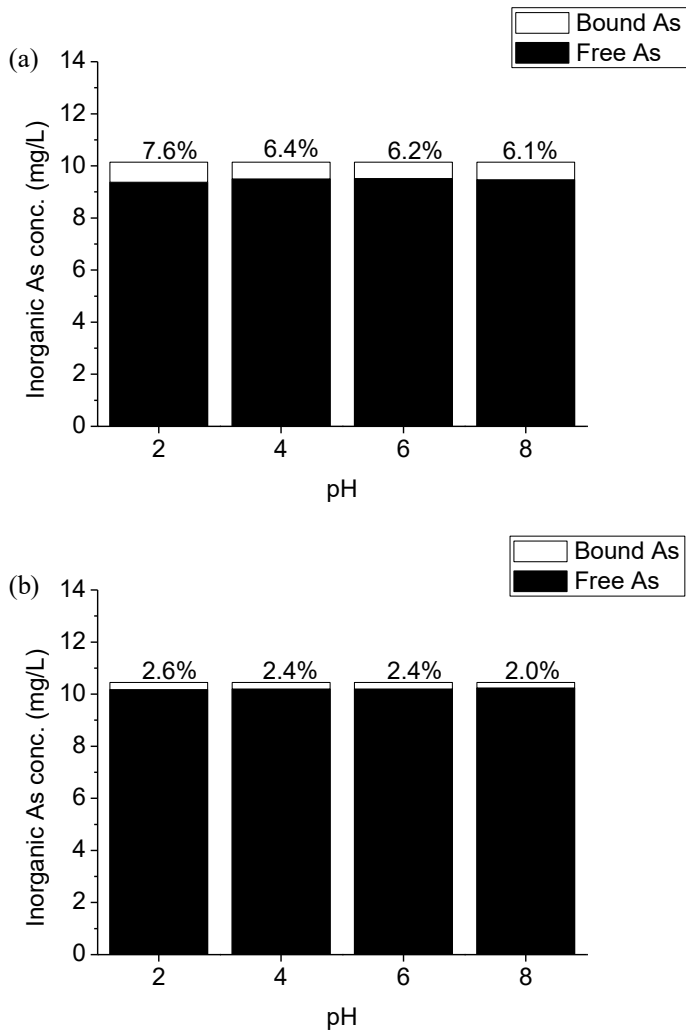


Figure 3.3 Concentration of free and bound (a) As(III) and (b) As(V) with different pH condition at HA 20mg/L and As 10mg/L.

3.2 HA Adsorption onto Iron Materials

Since the adsorption of HA on iron materials can modify the subsequent As sorption characteristics due to the coverage of binding sites on iron surfaces, HA adsorption characteristics onto iron surfaces with different initial As concentration, ionic strength conditions are tested. The HA adsorptions on zero-valent iron, hematite were better fitted with Langmuir adsorption isotherm than Freundlich equation while magnetite was better fitted with Freundlich equation as indicated by the higher determination coefficient in Table 3.1 (Fig. 3.4). The maximum adsorption capacity (Q_{\max} , mg/g) of the three iron materials followed the sequence of HM (1.0391) > ZVI (0.2605) > MG (0.2268). Also, increased in solution pH resulted in decreased HA adsorption rate (%) of HA onto iron materials, 32.81%, 52.03%, and 52.79% for ZVI, HM, and MG, respectively. The HA adsorption rate was increased 31.49% with increasing solution ionic strength in case of MG, while that of ZVI and HM was decreased 38.48%, 7.93%, respectively.

The HA adsorption on iron materials involves various mechanisms including Van der Waals forces, electrostatic attraction, and specific binding (Antelo et al., 2007; Schlautman and Morgan, 1994; Grossl et al., 1997; Weng et al., 2006), which seem to the adsorption characteristics of HA on iron materials depending on the types of irons or the solution conditions (pH, ionic strength, etc). In this study, HM showed highest HA adsorption capacity due to its positively charged surfaces at pH 6 (pH < PZC). HA adsorption rate (%) decreased with increasing solution pH due to both the less positively charged

surface of iron materials and more negatively charged of HA functional groups at high pH values, which was consistent with previous studies (Luo et al., 2015; Zhou et al., 2014). The HA adsorption experiments with different ionic strength conditions showed different results with previous studies. Luo et al. (2015) suggested that the increased ionic strength might compress the thickness of electric-double-layer and hydration shells of both adsorbent and adsorbate, leading to a favorable status to the adsorption process, and this effects would approach a maximum when the ionic strength further increased. However, the HA adsorption rate (%) onto ZVI and HM decreased with increasing ionic strength in this study. Thus, the major HA adsorption onto iron materials could depend on the types of iron materials and their surface characteristics. For more specific discussion, further investigation should be performed.

Table 3.1 Adsorption isotherms of HA on iron materials fitted by Langmuir and Freundlich equations.

Adsorbents	Freundlich equation			Langmuir equation		
	K_F	n	R^2	Q_{max}	K_L	R^2
ZVI	49.5459	1.3758	0.8751	0.2605	0.2575	0.9778
HM	101.4737	2.4119	0.6834	1.0391	0.2054	0.9919
MG	46.562	1.4499	0.9377	0.2268	0.2681	0.7225

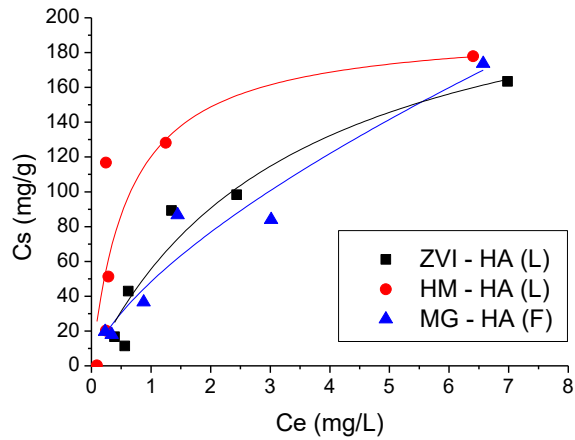


Figure 3.4 The adsorption isotherms of HA on zero-valent iron, hematite, and magnetite. ZVI, zero-valent iron; HM, hematite; MG, magnetite. L and F in parentheses mean Langmuir isotherm and Freundlich isotherm, respectively.

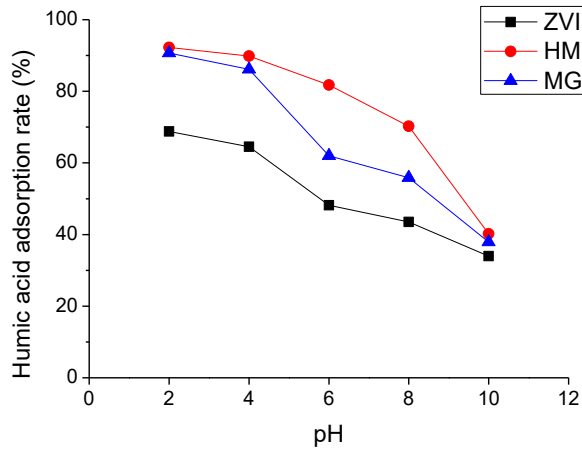


Figure 3.5 The HA adsorption rate (%) on ZVI, HM, and MG at different pH values. ZVI, zero-valent iron; HM, hematite; MG, magnetite.

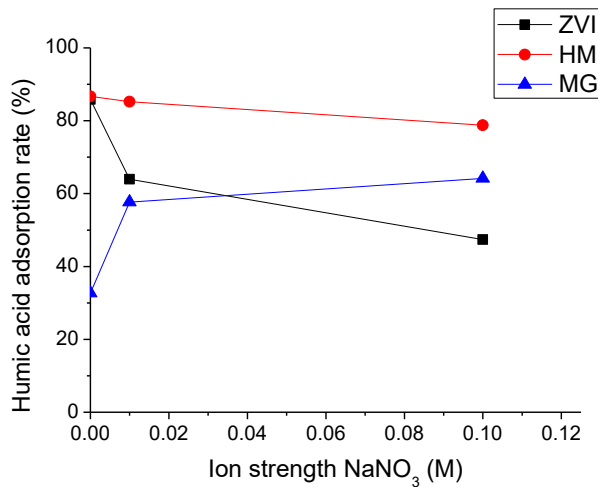


Figure 3.6 The HA adsorption rate (%) on ZVI, HM, and MG at different ionic strength values. ZVI, zero-valent iron; HM, hematite; MG, magnetite.

3.3 Arsenic Adsorption in the Ternary System

3.3.1 Arsenic Adsorption Isotherm

Batch sorption experiments were conducted with different contact order (Fig 3.7). Experimental results show that ZVI-As and (HA-As) + ZVI were better fitted with Langmuir isotherm, while (HA-ZVI) + As was better fitted with Freundlich isotherm. The adsorption equilibrium data of HM are fitted well by the Langmuir model whereas MG is better fitted to the Freundlich model. These results are consistent with several published studies (Mandiny-Pajany et al., 2011; Luo et al., 2015) and specific sorption model coefficients are listed in Table 3.2. ZVI has a maximum As(III) adsorption capacity ($Q_{\max} = 24.7863$) about four times higher than other adsorbents (Q_{\max} MG 5.2306 < Q_{\max} HM 2.5284) even the surface area is the smallest ($0.2 \text{ m}^2/\text{g}$; ZVI < $7.0 \text{ m}^2/\text{g}$; HM < $7.2 \text{ m}^2/\text{g}$; MG). Similar to the maximum adsorption capacity of As(III), a maximum As(V) adsorption capacity of ZVI ($Q_{\max} = 10.4025$) was about four times higher than other adsorbents (Q_{\max} MG 2.3359 < Q_{\max} HM 2.5284). Also, the arsenic sorption experiments with HA show similar tendency with the results.

Adsorption of arsenic on mineral surfaces can be of two types: non-specific and specific. In non-specific adsorption, the electrostatic attraction lies between a charged surface and an oppositely charged ion in solution in which the adsorbed ion resided at a certain distance from the mineral surface. On the other hand, in specific adsorption a coordination complex is formed between

the ion and the mineral surface, which is stronger as compared to non-specific adsorption (Flora, 2014). Arsenic adsorption is a complex phenomenon and depends upon properties of the solid surface, hydration, solution pH, crystallinity, concentration, species of arsenic and competing ions etc. Among them, the iron content and the surface crystallinity of the adsorbents are considered to be related to the arsenic adsorption capacity of iron minerals. Trivedi et al. (2001) found from their XAS studies that the octahedral hydration shell of crystalline iron oxides such as goethite converted into a tetragonal structure upon adsorption, whereas amorphous iron oxides viewed as a mosaic of short octahedral chains resulting in a greater sorption capacity than crystalline iron oxides. In our study, ZVI surface would go through a spontaneous corrosion reaction. Water molecules are the primary oxidant of the ZVI surface, and Fe(II) is the initial oxidant product. The Fe(II) formed at the corroding ZVI surface reacts with OH⁻ to form ferrous hydroxide (Fe(OH)₂) followed by further oxidation to Fe(II), Fe(III) mixed phase which leads to form amorphous thin oxide shell on the surface of ZVI. This amorphous thin oxide shell of ZVI and their high iron content may provide more sorption sites which arsenic can be specifically bound, thus ZVI showed higher sorption capacity than HM or MG.

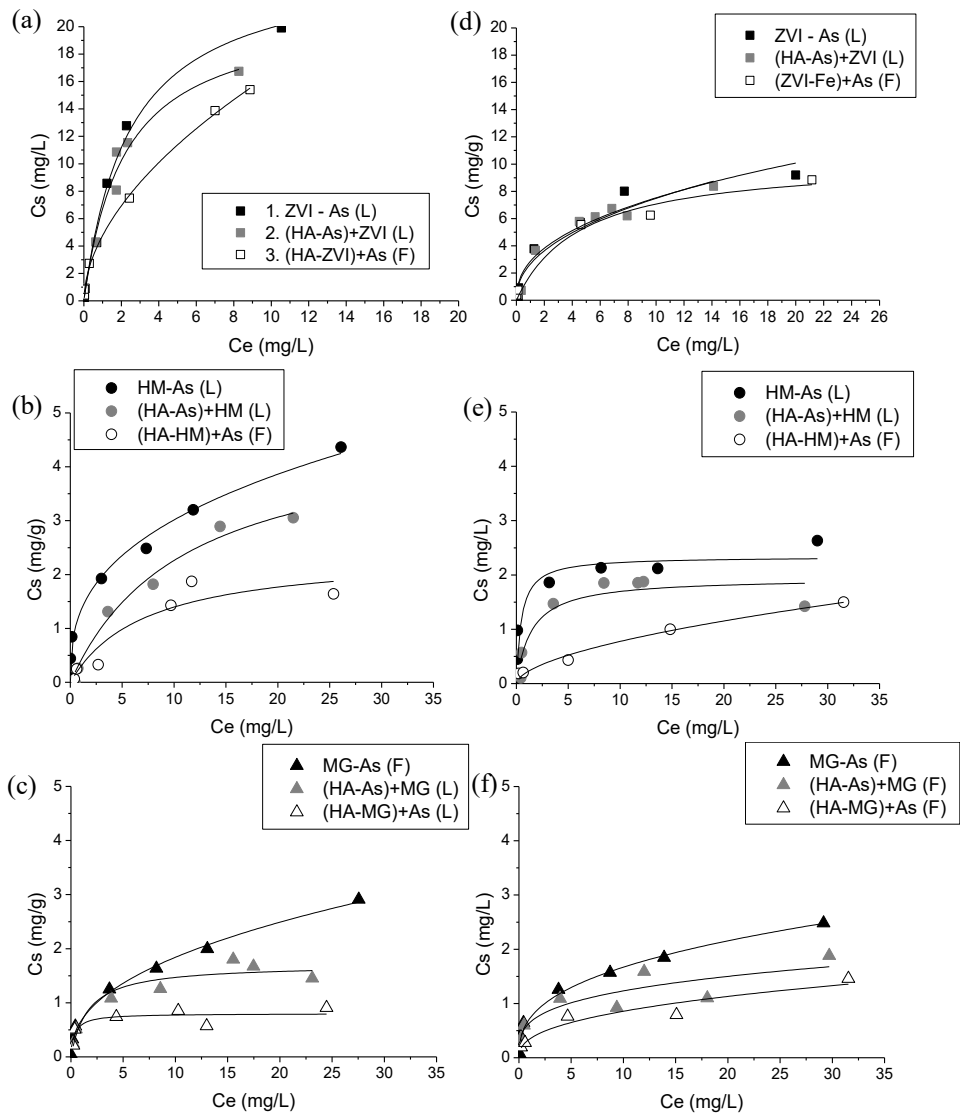


Figure 3.7 (a-c) As(III) and (d-f) As(V) adsorption isotherm with different contact order. ZVI, zero-valent iron; HM, hematite; MG, magnetite. L and F in parentheses means Langmuir isotherm and Freundlich isotherm, respectively.

Table 3.2 Arsenic adsorption isotherms with different contact order fitted by Langmuir and Freundlich equations.

Adsorbents	Freundlich equation			Langmuir equation		
	K_F	n	R^2	Q_{max}	K_L	R^2
ZVI-As(III)	6.9088	2.1366	0.9464	24.7863	0.4103	0.9917
(HA-As(III))+ZVI	6.9427	2.2741	0.9401	21.3126	0.4618	0.9746
(HA-ZVI)+As(III)	4.7676	1.8498	0.9980	23.2744	0.2132	0.9847
HM-As(III)	1.3235	2.7971	0.9908	5.2306	0.1525	0.9231
(HA-As(III))+HM	0.5227	1.6669	0.9522	4.7511	0.0908	0.9798
(HA-HM)+As(III)	0.4036	2.0367	0.8769	2.4066	0.1381	0.9761
MG-As(III)	0.6760	2.2979	0.9906	2.5284	0.2670	0.9204
(HA-As(III))+MG	0.6408	3.5449	0.9155	1.4454	0.9819	0.9846
(HA-MG)+As(III)	0.5008	4.8572	0.9098	0.8841	2.2643	0.9836
ZVI-As(V)	2.8511	2.3732	0.9243	10.4025	0.3595	0.9805
(HA-As(V))+ZVI	2.6604	2.2250	0.9460	9.3616	0.3601	0.9737
(HA-ZVI)+As(V)	2.6498	2.5119	0.9808	10.3385	0.2161	0.9717
HM-As(V)	1.1223	3.7664	0.9557	2.3359	2.0827	0.9571
(HA-As(V))+HM	0.6833	2.3376	0.8816	2.2609	0.4521	0.9541
(HA-HM)+As(V)	0.2088	1.7535	0.9795	2.5759	0.0435	0.9547
MG-As(V)	0.7155	2.7164	0.9735	2.5284	0.2670	0.9024
(HA-As(V))+MG	0.6422	3.5329	0.8406	1.4505	1.1454	0.9131
(HA-MG)+As(V)	0.3412	2.5009	0.9020	1.4503	0.2006	0.8801

3.3.2 Effect of Contact Order

Changing the component loading order in the ternary system led to different characteristics of adsorption. The order of the amounts of As adsorption were found to follow as: As-Fe > (HA-As)+Fe > (HA-Fe)+As. To determine whether the effect of contact order of three components (HA, Fe, As) on arsenic adsorption is statistically significant, a two-way analysis of variance (ANOVA) analysis was conducted, and the results are listed in Table 3.3-3.5. All p-value from the results was less than a significant level of 0.05 (0.0004 and 0.0123 for ZVI; 0.0442 and 0.0376 for HM; 1.0E-07 and 4.8E-06 for MG), which indicates that there are statistically significant differences between each sequence of contact for every adsorbent.

Table 3.3 A two-way ANOVA analysis results for ZVI

Adsorbates	Source	DF	Adj SS	Adj MS	F-Value	P-Value
As(III)	Contact order	5	0.1793	0.0358	12.9422	0.0004
	Adsorption rate (%) of each sequence	2	0.0072	0.0036	1.3082	0.3128
As(V)	Contact order	4	0.3365	0.0841	6.5240	0.0123
	Adsorption rate (%) of each sequence	2	0.0146	0.0073	0.5674	0.5882

Table 3.4 A two-way ANOVA analysis results for HM

Adsorbates	Source	DF	Adj SS	Adj MS	F-Value	P-Value
As(III)	Contact order	5	0.7529	0.1505	3.4777	0.0442
	Adsorption rate (%) of each sequence	2	0.3219	0.1609	3.7170	0.0620
As(V)	Contact order	4	0.4945	0.1236	4.3101	0.0376
	Adsorption rate (%)	2	0.2559	0.1279	4.4619	0.0499

Table 3.5 A two-way ANOVA analysis results for MG

Adsorbates	Source	DF	Adj SS	Adj MS	F-Value	P-Value
As(III)	Contact order	5	0.8237	0.1647	78.3893	1.0E-07
	Adsorption rate (%) of each sequence	2	0.0283	0.0141	6.7458	0.0139
As(V)	Contact order	4	0.6904	0.1726	61.4814	4.8E-06
	Adsorption rate (%) of each sequence	2	0.0716	0.0358	12.7606	0.0032

3.3.3 Ionic Strength Experiments

Increasing ion strength caused higher sorption, which was consistent with previous studies (Luo et al., 2015; Tombacz et al., 2000). In this study, the ionic strength results were showed using a compare factor which is defined as below, and the calculated compare factor values of three adsorbents are listed in Table 3.6. In case of ZVI, increasing in ionic strength has no significant effect on arsenic adsorption with different contact order. However, ionic strength affected the arsenic adsorption with different contact order for HM and MG.

$$\text{Compare factor} = \frac{(HA - As) + Fe \text{ Arsenic removal rate (\%)}}{(HA - Fe) + As \text{ Arsenic removal rate (\%)}}$$

Luo et al. (2015) assume that the increased ionic strength might compress the thickness of the electric double layer and hydration shell of both adsorbents and adsorbates, leading to a favorable status to the adsorption process. Also, it is assumed that there would be effects of ionic strength with different contact order on arsenic adsorption onto irons. For more specific discussion, further investigation should be performed.

Table 3.6 Compare factor from ionic strength experiments

	ZVI		HM		MG	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
0.01 M NaNO ₃	1.03	1.04	1.01	1.03	1.10	1.07
0.1 M NaNO ₃	1.00	1.02	1.37	0.84	2.13	0.99

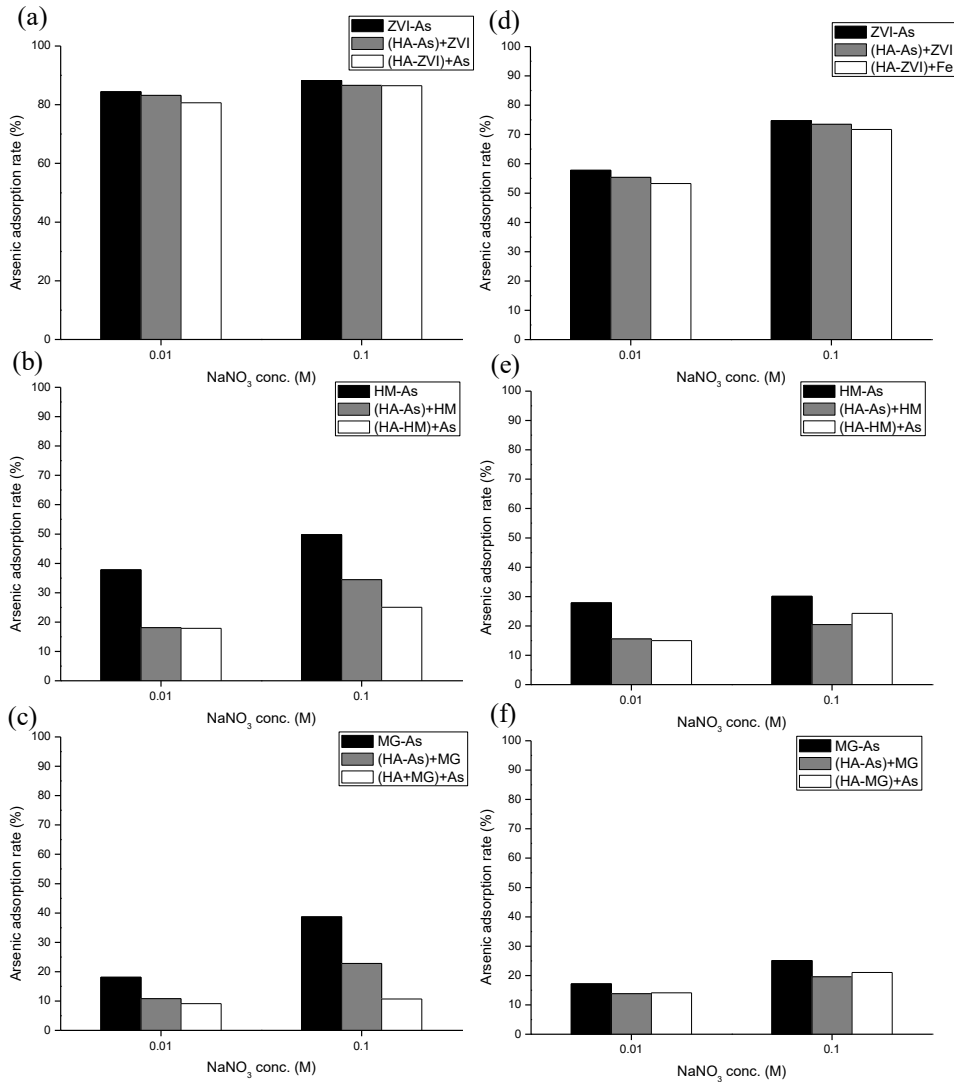


Figure 3.8 Effect of ionic strength on (a-c) As(III) and (d-f) As(V) adsorption onto ZVI, HM, and MG. ZVI, zero-valent iron; HM, hematite; MG, magnetite

Chapter 4 Conclusions

Three types of iron (zero-valent Iron, hematite and magnetite) were prepared, and their arsenic sorption characteristics are investigated in three types of equilibrium systems under same condition: i) Fe – As system, ii) Pre-equilibration of HA and As before addition of Fe, iii) Pre-equilibration of HA and Fe before addition of As.

1. In arsenic complexation with humic acid experiments, a considerable portion of As(III) was complexed with HA at a different initial As(III) concentration, while As(V) relatively less bound to HA. Also, pH and ionic strength have no significant effect on the complexation between arsenic and humic acid.

2. When HA adsorbs onto the iron surface, pH and ionic strength could be key variables of HA adsorption onto iron materials. HA was adsorbed more on HM than other two types of irons (ZVI and MG), and these characteristics can affect further arsenic adsorption onto the iron materials.

3. Changing the component loading order in the ternary system led to different characteristics of adsorption. The order of the amounts of As adsorption were found to follow as: $As-Fe > (HA-As)+Fe > (HA-Fe)+As$.

4. Increasing ion strength caused higher arsenic adsorption onto three types of irons (ZVI, HM and MG). It is assumed that there would be effects of ionic strength with different contact order in arsenic adsorption. For more specific discussion, further investigation should be performed.

These results can have important implications to design the arsenic pollution remediation system and understand the behavior of arsenic in the natural environmental system.

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초 록

토양과 지하수의 비소 오염을 처리하기 위한 흡착소재 중 철(수)산화물과 영가철 같은 철 물질은 비소 제어에 효과적인 흡착소재로 알려져 있다. 하지만, 자연 수계의 천연유기물질은 철 물질에 의한 비소 흡착을 방해하는 요인으로 작용하는 것으로 알려져 있으나 아직까지 그 메커니즘이 불분명할뿐더러 천연유기물질이 철 물질의 비소 흡착특성에 미치는 영향이 명확하게 밝혀지지 않았다. 이에 본 연구에서는 선행 실험으로 비소-휴믹산 복합체 형성 실험과 영가철, 적철석, 자철석의 휴믹산 흡착 실험을 수행하였고, 그 후 휴믹산이 영가철, 적철석 그리고 자철석의 비소 흡착 특성에 미치는 영향을 접촉 순서를 달리하여 조사하였다. 그 결과 3가 비소의 경우 최대 6.7%가 휴믹산과 복합체를 형성함을 알 수 있었고 5가 비소의 경우 최대 2.4%의 복합체 형성률을 보였다. 휴믹산은 적철석에 가장 많이 흡착되었으며($Q_{\max} = 1.0391$) 그다음으로 영가철($Q_{\max} = 0.2605$)과 자철석($Q_{\max} = 0.2268$)에 많이 흡착되었다. 접촉 순서를 달리하여 비소 흡착에 휴믹산이 미치는 영향을 알아본 실험의 비소 흡착량 순서는 다음과 같다: $As-Fe > (HA-As)+Fe > (HA-Fe)+As$. 본 연구 결과는 추후 자연 상태에서 비소의 거동을 이해하거나 비소 오염

정화 시설을 설계하는데 도움이 될 것으로 사료된다.

주요어 : 비소, 흙착, 천연유기물질, 휴믹산, 영가철, 적철석, 자철석

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