

Available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/watres

Effect of NOM on arsenic adsorption by TiO₂ in simulated As(III)-contaminated raw waters

Guojing Liu^a, Xiangru Zhang^b, Jeffrey W. Talley^{a,*}, Clive R. Neal^a, Hangyao Wang^c

^aDepartment of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556, USA

^bDepartment of Civil Engineering, Hong Kong University of Science and Technology, Hong Kong, China

^cDepartment of Chemical and Biomolecular Engineering, University of Notre Dame, IN 46556, USA

ARTICLE INFO

Article history:

Received 24 August 2007

Received in revised form

6 December 2007

Accepted 12 December 2007

Available online 17 January 2008

Keywords:

As(III)

NOM

TiO₂

Adsorption

Oxidation

Mechanism

ABSTRACT

The effect of natural organic matter (NOM) on arsenic adsorption by a commercial available TiO₂ (Degussa P25) in various simulated As(III)-contaminated raw waters was examined. Five types of NOM that represent different environmental origins were tested. Batch adsorption experiments were conducted under anaerobic conditions and in the absence of light. Either with or without the presence of NOM, the arsenic adsorption reached steady-state within 1 h. The presence of 8 mg/L NOM as C in the simulated raw water, however, significantly reduced the amount of arsenic adsorbed at the steady-state. Without NOM, the arsenic adsorption increased with increasing solution pH within the pH range of 4.0–9.4. With four of the NOMs tested, the arsenic adsorption firstly increased with increasing pH and then decreased after the adsorption reached the maximum at pH 7.4–8.7. An appreciable amount of arsenate (As(V)) was detected in the filtrate after the TiO₂ adsorption in the simulated raw waters that contained NOM. The absolute amount of As(V) in the filtrate after TiO₂ adsorption was pH dependent: more As(V) was presented at pH > 7 than that at pH < 7. The arsenic adsorption in the simulated raw waters with and without NOM were modelled by both Langmuir and Freundlich adsorption equations, with Freundlich adsorption equation giving a better fit for the water without NOM and Langmuir adsorption equation giving a better fit for the waters with NOM. The modelling implies that NOM can occupy some available binding sites for arsenic adsorption on TiO₂ surface. This study suggests that in an As(III)-contaminated raw water, NOM can hinder the uptake of arsenic by TiO₂, but can facilitate the As(III) oxidation to As(V) at TiO₂ surface under alkaline conditions and in the absence of O₂ and light. TiO₂ thus can be used *in situ* to convert As(III) to the less toxic As(V) in NOM-rich groundwaters.

Published by Elsevier Ltd.

1. Introduction

Arsenic is a common contaminant in drinking water supplies, with a contamination level ranging from <1.0 to >1000 µg/L (<0.013 to >13.3 µM) (Welch et al., 2000; Smedley et al., 2002; Mandal and Suzuki, 2002; Bissen and Frimmel, 2003). Long-

term exposure to arsenic can cause various cancers (Smith et al., 2000). The World Health Organization (WHO) recommended the maximum concentration of arsenic of 10 µg/L (1.33 µM) in drinking water in order to reduce its potential harm to human health (WHO, 1993). The WHO-recommended regulation for arsenic in drinking water has recently been

*Corresponding author. Tel.: +1 574 631 5164; fax: +1 574 631 9236.

E-mail addresses: gliu@nd.edu (G. Liu), xiangru@ust.hk (X. Zhang), jtalley1@nd.edu (J.W. Talley), neal.1@nd.edu (C.R. Neal), hwang4@nd.edu (H. Wang).
0043-1354/\$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.watres.2007.12.023

adopted by the New European Community and the U.S. Environmental Protection Agency (USEPA) (EC, 1998; USEPA, 2001a). The USEPA estimates that about 5% of the total water systems in the United States have arsenic levels in source water greater than this updated regulation (USEPA, 2001b). The discrepancy between the high arsenic concentrations in raw water and the stringent standard calls for an emergent modification of the current treatment technology and a development of new treatment technologies.

Arsenic exists in water primarily as the inorganic oxyanions of arsenite (As(III)) and arsenate (As(V)), with As(III) predominating in anaerobic waters and As(V) prevailing in oxic waters (Masscheleyn et al., 1991; Smedley et al., 2002; Katsoyiannis et al., 2007). Recent surveys about arsenic redox speciation in groundwater, which is a major source of drinking water throughout the world (Smedley et al., 2002), suggest that As(III) can represent up to 67–99% of total arsenic in groundwater (Mukherjee and Bhattacharya, 2001; Bednar et al., 2002). As a contaminant, As(III) is more problematic than As(V) because As(III) is more toxic and more difficult to remove from water. Commonly used arsenic treatment technologies including coagulation/filtration, ion exchange, adsorption on activated alumina, etc. usually require a pre-oxidation of As(III) to As(V) in order to achieve a satisfactory total arsenic removal (USEPA, 2001a). Many oxidation technologies, including the addition of conventional oxidants, solar oxidation, and biological oxidation have been developed (Katsoyiannis and Zouboulis, 2006). As an emerging oxidation technology for As(III) transformation to As(V), TiO₂ photocatalytic oxidation (TPO) have attracted substantial attentions as this method is environmentally benign (Yang et al., 1999; Bissen et al., 2001; Lee and Choi, 2002; Dutta et al., 2005; Ferguson et al., 2005; Xu et al., 2005).

During the TPO process, As(III) is oxidized by O₂ or air on the surface of the light-irradiated TiO₂. TiO₂ is a widely used photocatalyst. Upon the absorption of sufficient energetic light, TiO₂ can generate valence-band holes and conduction-band electrons. The valence-band holes are powerful oxidants that can convert the adsorbed As(III) to As(V) (Lee and Choi, 2002). On the other hand, the conduction-band electrons can react with the adsorbed O₂ or H₂O to form H₂O₂ and/or reactive radicals such as OH[•] and O₂^{•-}, which are also capable of oxidizing As(III) (Lee and Choi, 2002; Dutta et al., 2005; Xu et al., 2005). Because all reactions involved in As(III) oxidation through the TPO occur on TiO₂ surface, the adsorption of the reacting As(III) by TiO₂ plays an important role for the overall reaction. Several studies of As(III) adsorption by TiO₂ are available, with most of them considering the influence of pH, initial arsenic concentration, and the presence of common anions such as phosphate and bicarbonate (Dutta et al., 2004; Ferguson et al., 2005; Bang et al., 2005; Pena et al., 2005, 2006), and relatively few considering the effect of natural organic matter (NOM) on As(III) adsorption (Lee and Choi, 2002).

NOM is a complex mixture of acidic organic molecules that originates from a variety of natural sources (e.g., soil, sediment, water, etc.) (Letterman et al., 1999). NOM is ubiquitous in aquatic environment. A recent survey about As(III) levels in the groundwaters of the Bengal Delta Plain aquifers in Bangladesh suggests that the groundwaters with

high As(III) concentrations tend to have high concentration of NOM (Mukherjee and Bhattacharya, 2001). NOM has been reported to be an essential component controlling arsenic mobilization at aluminum or iron (hydro)oxide–water interface (Grafe et al., 2001, 2002; Redman et al., 2002; Ko et al., 2004; Bauer and Blodau, 2006). However, few studies have been conducted specifically for NOM effects on arsenic adsorption by TiO₂ (Lee and Choi, 2002). In studying the effect of a commercially available humic acid (HA) on As(III) oxidation rate through the TPO, Lee and Choi (2002) observed that the presence of HA had an insignificant effect on the As(III) adsorption by TiO₂. In their study, however, an extremely high concentration of As(III) (500 μM) was used, so the effect of NOM on As(III) adsorption could be different for real raw waters which usually contain less than 13.3 μM of As(III).

In this study, the effect of NOM on arsenic adsorption by TiO₂ in simulated As(III)-contaminated raw waters was examined. Batch adsorption experiments were performed as a function of contact time, pH, initial DOC concentration, and initial As(III) concentration. The experiments were performed under anaerobic conditions and in darkness to avoid As(III) oxidation caused by TiO₂ photocatalysis. Five types of NOM from different environmental origins were tested. Arsenic redox speciation in the filtrates after the adsorption were examined. Mechanisms behind the observed effects were discussed.

2. Materials and method

2.1. Materials and chemicals

All chemicals were of analytical grade. Milli-Q water, which was supplied by the Millipore MR3 water purifier system, was used to prepare all solutions. The Milli-Q water was passed through a 0.2-μm membrane (Gelman FP-Verical) in order to remove the existing microbes or other reacting colloidal substances that may affect the arsenic redox speciation (Liu et al., 2006).

Sodium arsenite (NaAsO₂, 99%) was obtained from Sigma. Stock As(III) solution (13.3 mM) was prepared by dissolving 0.866 g NaAsO₂ into 500 mL Milli-Q water. The As(III) stock solution was stored in a high density polyethylene bottle, and was kept in darkness at 4 °C.

The TiO₂ used in this study was a commercially available titanium dioxide, Degussa P25 (Germany). The Degussa P25 TiO₂ contains 80% of anatase and 20% of rutile (Hoffmann et al., 1995). It has a Brunauer–Emmett–Teller surface area of 55 m²/g and a pH_{pzc} (the pH at the point of zero charge) of 6.7 in 0.01 M NaCl. A stock TiO₂ suspension was prepared by mixing 1 g of Degussa P25 TiO₂ with 1 L of background electrolyte (0.01 M NaCl). The TiO₂ stock suspension was sonicated for 20 min each time before use in order to resuspend the precipitated TiO₂ particles.

Five different types of NOM were used in this study. They are Suwannee River NOM (SRNOM), Gohy-573 fulvic acid (GFA), Elliott soil humic acid (EHA), Pahokee peat humic acid (PHA), and Aldrich humic acid (AHA). SRNOM, EHA, and PHA are well-characterized NOMs. SRNOM originated from Suwannee River of

Georgia, USA; EHA was from prairie soils of Indiana, Illinois, and Iowa, USA; PHA was from peat soil of the Florida Everglades, USA. The three types of NOM were purchased from the International Humic Substances Society. GFA is a fulvic acid extracted from the Gorleben groundwater, Germany (Kim et al., 1990). AHA is a commercially available HA from Aldrich. SRNOM and GFA were used without further modification. The stock solution of SRNOM or GFA was prepared by dissolving the NOM powder standard into 0.01 M NaCl to reach a concentration of 900–1000 mg/L. For EHA, PHA, and AHA, the HA standard was dissolved in 0.01 M NaOH (pH 11–12) at 850–1000 mg/L; the solution was then acidified to pH 3.8 ± 0.1 with 2 M HCl, and filtered through a 0.45- μm pore-size membrane (Gelman Supor) to remove the undissolved part of HAs; the filtrate was collected as the HA stock solution; the HA was modified in order to ensure no NOM was precipitated during the arsenic adsorption on TiO_2 . The dissolved organic carbon (DOC) concentration in the HA stock solution was determined using a Shimadzu 5050 TOC analyzer. The modified EHA, PHA, and AHA are, respectively, denoted as MEHA, MPHA, and MAHA in the rest of the manuscript. All the NOM stock solutions were kept in glass bottles in darkness at 4 °C. Adsorption experiments were preformed within 6 weeks after the stock solutions were prepared.

2.2. Adsorption studies

Simulated As(III)-contaminated raw waters were prepared by mixing 0.01 M of NaCl with various concentrations of As(III) and NOM. Batch adsorption experiments were performed to determine the adsorption of arsenic by TiO_2 in these simulated raw waters. All adsorption experiments were performed in an anaerobic chamber in order to avoid As(III) oxidation. The anaerobic chamber was maintained with a purified makeup gas consisting of N_2 (95%) and H_2 (5%). All solutions together with the stock TiO_2 suspension were purged with high purity N_2 gas for at least 30 min and then immediately transferred into the anaerobic chamber.

The adsorption experiments were carried out in 15-mL acid washed polyethylene bottles (amber). Adsorption of arsenic onto TiO_2 was initiated by adding 0.75 mL of TiO_2 stock suspension (1 g/L) into 14.25 mL of the simulated raw water, resulting in a TiO_2 concentration of 0.05 g/L. After the addition of TiO_2 , the pH of the suspension was adjusted to a desired value using HCl and NaOH solutions (0.05–0.1 M). The suspension was then sealed and mixed on a rotator at room temperature for until the adsorption reached steady-state. At the end of mixing, the pH of the suspension was re-measured and recorded. The pH value thus measured was reported as the adsorption pH. The suspension was then filtered through a 0.22- μm PTFE syringe filter (Fisher), and the filtrate was immediately analyzed for the concentrations of total arsenic, As(III), As(V), and NOM.

2.3. Instrument analysis

The NOM concentration (expressed in UV_{254}) remaining in the filtrate after adsorption was determined using a Varian Cary 300 Bio UV-Visible spectrophotometer at the wavelength of 254 nm. Total arsenic concentration in solution was measured using a Perkin-Elmer optima 2000DV inductively coupled

plasma-optical emission spectrometry (ICP-OES). A Finnigan Element 2 sector field high resolution inductively coupled plasma-mass spectrometry (ICP-MS) was used when the arsenic concentration was lower than 0.67 μM (50 $\mu\text{g/L}$). A medium resolution mode was chosen for the ICP-MS analysis to avoid the interference from $^{40}\text{Ar}^{35}\text{Cl}^+$ dimer. The detection limits of arsenic using the ICP-OES and the ICP-MS were determined to be 25 $\mu\text{g/L}$ (0.33 μM) and 5 ng/L (6.7×10^{-5} μM), respectively. The instruments were calibrated each time before use. The concentrations of the calibration standards ranged from 0.4 to 1.07 μM for ICP-OES and from 0.067 to 0.53 μM for ICP-MS. Each sample was injected three times, and the relative standard deviation (RSD) for the triplicate analysis was within 5%. The concentrations of As(III) and As(V) remaining in solution after adsorption were simultaneously determined using ion chromatography (Dionex LC25) coupled with the ICP-MS (IC-ICP-MS). The detection limit for both As(III) and As(V) by the IC-ICP-MS was 2.7×10^{-3} μM . The IC-ICP-MS was calibrated with standards varying from 0.067 to 0.53 μM . The RSD for three injections of the sample with a concentration above 0.013 μM was usually less 7%.

3. Results and discussion

3.1. Arsenic adsorption onto TiO_2 as a function of contact time

The adsorption of arsenic by TiO_2 in the simulated raw waters containing 0 or 8 mg/L as C of NOM (i.e., SRNOM or MAHA) was examined as a function of time. The initial ratio of As(III) to TiO_2 was 53.4 $\mu\text{mol/g-TiO}_2$ for all the waters tested. No As(V) was detected in the filtrates after adsorption in the waters either with or without NOM. The experimental results are presented in Fig. 1.

Without NOM, the arsenic adsorption onto TiO_2 was rapid and reached steady-state within 1 h. The time required for the adsorption to reach steady-state is similar to the reported value that was obtained in the presence of air and light (Pena et al., 2005), although a conversion of As(III) to As(V) may occur on the TiO_2 surface with air and light present. At the steady-state, approximately 13.4 $\mu\text{mol/g-TiO}_2$ or 25% of the total arsenic was adsorbed onto the TiO_2 surface.

With the presence of 8 mg/L as C of SRNOM or MAHA, the arsenic adsorption onto TiO_2 also reached steady-state within approximately 1 h. The amounts of arsenic adsorbed by TiO_2 at steady-state were 8.12 and 7.59 $\mu\text{mol/g-TiO}_2$ for the waters containing SRNOM and MAHA, respectively. The uptake of arsenic was decreased by 39.4% or 43.3%, respectively, due to the presence of 8 mg/L as C of SRNOM or MAHA in the simulated raw water. The experimental results suggest that the tested NOMs did not change the time required for the arsenic adsorption onto TiO_2 to reach steady-state, but significantly reduced the amounts of arsenic adsorbed on TiO_2 .

3.2. Effect of initial DOC concentration on arsenic adsorption onto TiO_2

Fig. 2 presents the effect of initial DOC and As(III) concentrations on arsenic adsorption by TiO_2 in simulated raw waters

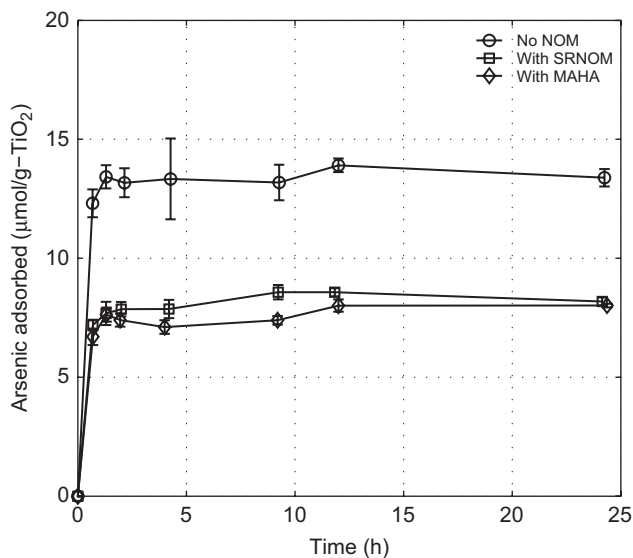


Fig. 1 – Adsorption of arsenic onto TiO_2 as a function of contact time in the simulated As(III)-contaminated raw waters with or without NOM. TiO_2 concentration, 0.05 g/L; initial As (III) concentration, 2.67 μM ; initial DOC, 0 or 8 mg/L as C; pH, 6.0 ± 0.1 ; ionic strength, 0.01 M NaCl; error bars show the range of data for duplicate samples.

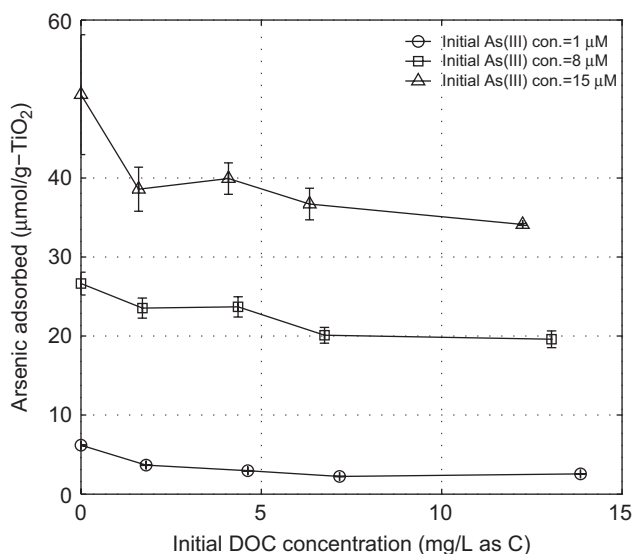


Fig. 2 – Effect of initial DOC concentration on arsenic adsorption by TiO_2 . TiO_2 concentration, 0.05 g/L; initial As(III) concentration, 1, 8, and 15 μM ; pH, 6.0 ± 0.1 ; ionic strength, 0.01 M NaCl; mixing time, 2 h; error bars show the range of data for duplicate samples.

containing 0–14 mg/L SRNOM as C and 1–15 μM As(III). The simulated raw water and TiO_2 were mixed for 2 h to ensure the arsenic adsorption to reach steady-state. Either with or without the presence of SRNOM, arsenic adsorption increased as the initial As(III) concentration increased from 1 to 15 μM , indicating that the available arsenic binding sites on TiO_2 surface have not been saturated even when the initial As(III) concentration was as high as 15 μM . The arsenic removal

efficiency, however, decreased from 31.0% to 12.2% when the initial As(III) concentration increased from 1 to 15 μM . When the initial As(III) concentration was fixed, the amount of arsenic adsorbed by TiO_2 decreased with increasing initial DOC concentration (Table 1). The decrease of arsenic adsorption with increasing DOC was more rapid at low DOC concentrations than at high DOC concentrations. When the initial DOC concentrations were below 2 mg/L as C, the reductions in arsenic adsorption were 1.4–7.5 $\mu\text{mol/g-TiO}_2$ per 1 mg/L SRNOM as C increased, while the reductions were 0.3–1.3 $\mu\text{mol/g-TiO}_2$ per 1 mg/L SRNOM as C increased when the initial DOC concentrations approached 15 mg/L as C. The experimental results suggest that NOM can be an important factor influencing As(III) adsorption on TiO_2 .

3.3. Arsenic adsorption edges/envelopes

The adsorption of arsenic on TiO_2 in the simulated raw waters with or without the presence of 8 mg/L as C of NOM was performed as a function of pH. Five types of NOM from different environmental origins were used. The initial As(III) and NOM concentrations in the simulated raw waters were 1 μM and 8 mg/L as C, respectively. The simulated raw water and TiO_2 were mixed for 2 h to ensure the adsorption to reach steady-state. The amount of arsenic adsorbed by TiO_2 in the presence and absence of NOM was plotted versus pH. The results are presented in Fig. 3.

In the absence of NOM, the amount of arsenic adsorbed by TiO_2 increased with increasing pH within the pH range of 4.0–9.4. The amount of arsenic adsorbed by TiO_2 increased by 86.7% as the solution pH varied from 4.0 to 9.4. The effect of pH on the arsenic adsorption by TiO_2 was more significant at low pH values (i.e., pH 4.0–6.7) than at high pH values (i.e., pH 6.7–9.4). In the presence of 8 mg/L as C of GFA, MEHA, MPHA, or SRNOM, the arsenic adsorption firstly increased with the increase of pH and then decreased with increasing pH, and the maximum arsenic adsorption occurred at pH 7.4–8.7, depending on the type of NOM in the simulated raw water. With MAHA, the arsenic adsorption by TiO_2 increased with increasing pH throughout the entire range of pH values tested, which was similar to the arsenic adsorption behavior without NOM. At the same pH value, the amounts of arsenic adsorbed on TiO_2 with the presence of various types of NOM were generally less than that without the presence of NOM. The observed pH effect on As(III) adsorption by TiO_2 in the absence of NOM is in good agreement with the literature (Dutta et al., 2004; Pena et al., 2005). In natural waters, both As(III) and TiO_2 can be viewed as weak acids. The proton dissociation reactions for As(III) and TiO_2 are presented in Table 2. Aqueous As(III) speciation distributions at various pH values can be calculated based on Reactions A1–A3 shown in Table 2. Within the pH range of 4.0–9.4, the primary aqueous As(III) species include the neutral H_3AsO_3^0 and the negatively charged H_2AsO_3^- . When pH is below 7.0, over 99% of As(III) exists as H_3AsO_3^0 . When pH ranges from 7.0 to 9.4, As(III) exists as a mixture of H_3AsO_3^0 (99–35%) and H_2AsO_3^- (1–65%). According to Reactions A4–A5 in Table 2, TiO_2 suspension is composed of the mixture of positively charged $\equiv\text{TiOH}_2^+$ and neutral species of $\equiv\text{TiOH}^0$ when pH is below pH_{pzc} (i.e., pH 6.7); when pH is above pH_{pzc} , the primary species of the

Table 1 – Arsenic adsorption onto TiO₂ in simulated As(III)-contaminated raw waters with various initial DOC and As(III) concentrations

Initial As(III) concentration (μM)					
1		8		15	
DOC (mg/L as C)	As-adsorbed (μmol/g-TiO ₂)	DOC (mg/L as C)	As-adsorbed (μmol/g-TiO ₂)	DOC (mg/L as C)	As-adsorbed (μmol/g-TiO ₂)
0	6.18 ± 0.07	0	26.6 ± 1.4	0	50.6 ± 7.6
1.8	3.67 ± 0.04	1.7	23.5 ± 1.3	1.6	38.6 ± 2.8
4.6	2.95 ± 0.03	4.4	23.7 ± 1.3	4.1	39.9 ± 2.0
7.2	2.22 ± 0.02	6.8	20.1 ± 1.0	6.4	36.7 ± 2.0
13.9	2.55 ± 0.03	13.1	19.6 ± 1.1	12.2	34.1 ± 0.1

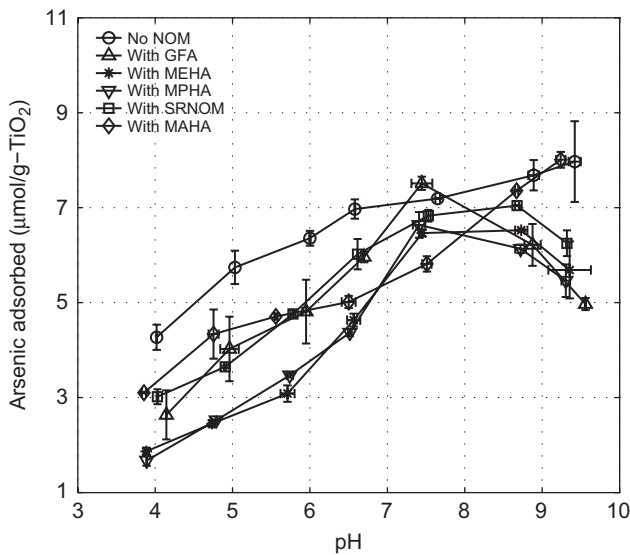
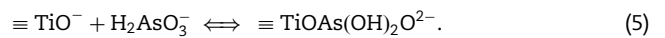
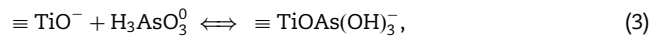


Fig. 3 – Effect of pH on arsenic adsorption by TiO₂. TiO₂ concentration, 0.05 g/L; initial As(III) concentration, 1 μM; initial NOM concentration, 8 mg/L as C; ionic strength, 0.01 M NaCl; mixing time, 2 h; error bars show the range of data for duplicate samples.

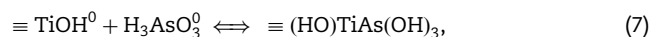
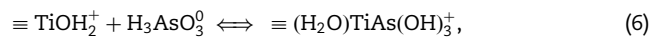
suspended TiO₂ include the neutral species of ≡TiOH⁰ and the negatively charged ≡TiO⁻. Therefore, the adsorption of As(III) on TiO₂ can be viewed as the interaction between H₃AsO₃⁰ and ≡TiOH₂⁺ / ≡TiOH⁰ when pH is below 7.0, or the interaction between H₃AsO₃⁰/H₂AsO₃⁻ and ≡TiOH⁰ / ≡TiO⁻ when pH is above 7.0. Based on the above discussion, we propose the following reactions (Reactions (1)–(15)) to explain the adsorption mechanisms of As(III) onto TiO₂ surface. Briefly, aqueous As(III) species adsorb onto TiO₂ surface through the formation of As–O–Ti, As–Ti, and hydrogen bonds. The fact that more As(III) was adsorbed onto TiO₂ at high pH values than at low pH values suggests that the formation of As–O–Ti bond (Reactions (1)–(5)) should be the major mechanism controlling the arsenic adsorption under the experimental conditions, as a proton that is originally associated with oxygen at TiO₂ surface should be released when the As–O–Ti bond forms, and the increase of solution pH favors the association between As(III) and TiO₂, leading to

an increased arsenic adsorption. The slow increasing of arsenic adsorption onto TiO₂ with the increase of pH at high pH values can be due to the formation of ≡TiO⁻ and H₂AsO₃⁻, both of which are negatively charged and their repulsion to each other may result in a compromised As(III) adsorption. In studying the vibration spectroscopic properties of adsorbed As(III) at TiO₂ surface, *Pena et al. (2006)* observed that the band position of the uncomplexed As–O shift from 795 to 780 cm⁻¹ when As(III) moved from water to TiO₂ surface, which is indicative of the formation of As–O–Ti bond. It should be noted that Reactions (1)–(15) only represent the possible bonds that may form when As(III) is adsorbed onto TiO₂. They do not necessarily reflect the actual coordination number of As(III)–TiO₂ interaction. That is, the As(III)–TiO₂ association does not necessarily be monodentate mono-nuclear.

1. Adsorption of As(III) through an As–O–Ti bond.



2. Adsorption of As(III) through an As–Ti.



3. Adsorption of As(III) through a hydrogen bond.

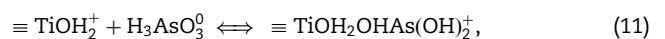


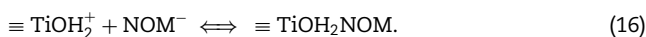
Table 2 – Deprotonation reactions for As(III) and TiO₂ in water

No.	Reaction	pK _a	Ref.
A1	H ₃ AsO ₃ ⇌ H ₂ AsO ₃ ⁻ + H ⁺	9.23	Brown and Allison (1987)
A2	H ₂ AsO ₃ ⁻ ⇌ HAsO ₃ ²⁻ + H ⁺	12.10	Brown and Allison (1987)
A3	HAsO ₃ ²⁻ ⇌ AsO ₃ ³⁻ + H ⁺	13.41	Brown and Allison (1987)
A4	TiOH ₂ ⁺ ⇌ ≡TiOH + H ⁺	pH < pH _{pzc}	Dutta et al. (2004)
A5	≡TiOH ⇌ ≡TiO ⁻ + H ⁺	pH > pH _{pzc}	Dutta et al. (2004)

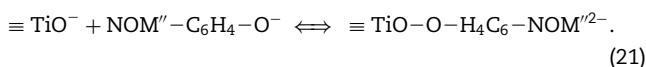
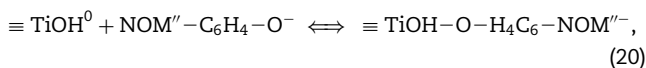
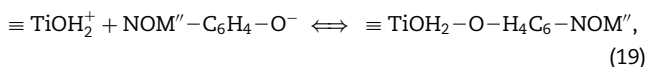
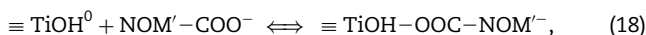
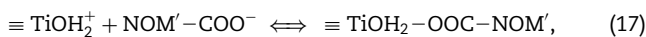


NOM is negatively charged in natural waters. It can be associated with TiO₂ through electrostatic attraction. Theoretical and experimental studies of various organic compounds adsorption by TiO₂ indicate that the carboxyl and phenolic functional groups in NOM can bind to Ti or O atom on TiO₂ surface (Persson and Lunell, 2000; Roddick-Lanzilotta and McQuillan, 2000; Langel and Menken, 2003). The following reactions ((16)–(29)) are thus proposed as the possible mechanisms for NOM adsorption onto TiO₂ surface.

1. Adsorption of NOM through electrostatic attraction.



2. Adsorption of NOM through a hydrogen bond.



3. Adsorption of NOM through a Ti–O bond.

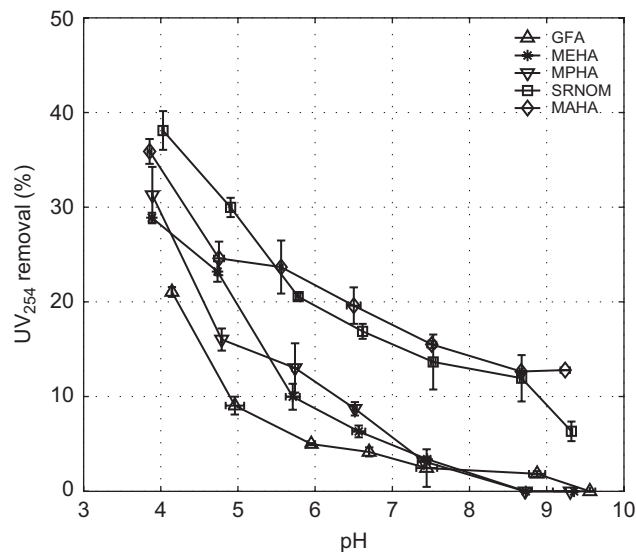
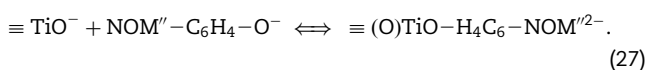
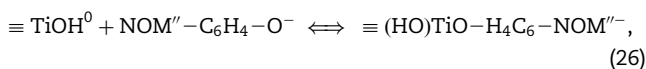
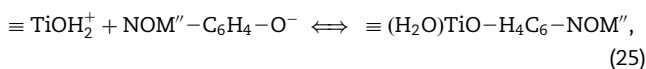
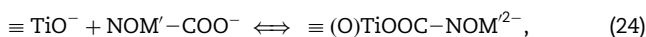
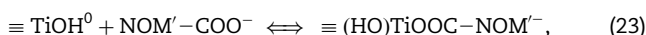
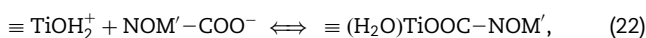
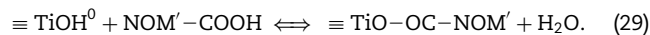
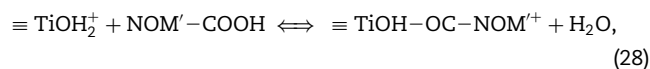


Fig. 4 – UV₂₅₄ removal during arsenic adsorption onto TiO₂ under different pH values. TiO₂ concentration, 0.05 g/L; initial As(III) concentration, 1 μM; initial NOM concentration, 8 mg/L as C; ionic strength, 0.01 M NaCl; mixing time, 2 h; error bars show the range of data for duplicate samples.

4. Adsorption of NOM through condensation.



Reactions (1)–(29) suggest that NOM can compete with As(III) for available binding sites, such as Ti or O atoms, on TiO₂ surface. Therefore, the presence of NOM in solution can reduce the arsenic adsorption through competitive adsorption. The measurement of UV₂₅₄ remaining in solution confirms that a significant amount of NOM was adsorbed on TiO₂ (Fig. 4). The adsorption of NOM onto TiO₂ decreased with increasing pH, reflecting the anionic character of NOM. If competitive adsorption is the only reason for the decreased arsenic adsorption onto TiO₂ surface, more arsenic should be adsorbed at higher pH values as more NOM is adsorbed at lower pH values. Fig. 3, however, shows that with the presence of NOM (i.e., SRNOM, GFA, MEHA, and MPHA) the arsenic adsorption decreased with increasing pH within the pH range of 7.5–9.4, implying that mechanisms other than

the competitive adsorption causing the decreased arsenic adsorption exist.

Previous studies have shown that NOM can affect As(III) adsorption onto metal (hydro)oxide through changing the speciation distribution of As(III) in water (Redman et al., 2002; Ko et al., 2004). In order to clarify this, we determined the arsenic speciation in solution before and after the addition of TiO₂ using an IC-ICP-MS. The sum concentration of As(III) and As(V) obtained from the IC-ICP-MS corresponded well with

the total arsenic concentration measured directly using the ICP-MS, indicating that NOM did not form any complexes with As(III) (Liu et al., 2006). This ruled out the possibility of aqueous NOM-As complexation that may desorb As(III) from TiO₂ surface. The measurements of arsenic redox species in the filtered solution after adsorption demonstrate that part of As(III) was oxidized into As(V) under alkaline conditions, and the presence of NOM facilitated the As(III) oxidation (Fig. 5). Without NOM, As(V) was detected only when solution pH was

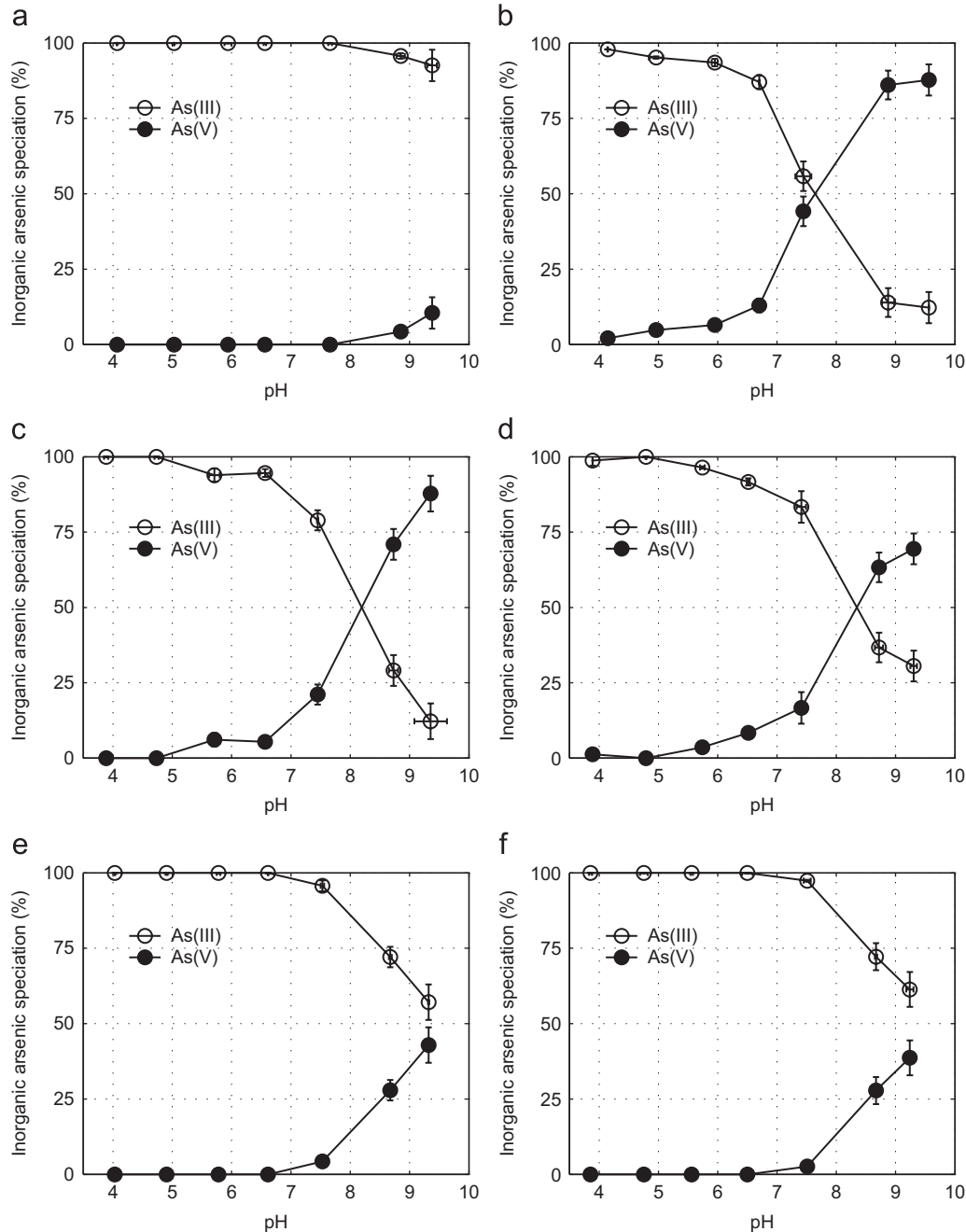


Fig. 5 – Arsenic redox speciation in the filtrates after arsenic adsorption onto TiO₂ surface in the simulated As(III)-contaminated raw waters with and without the presence of NOM. Solution contains (a) no NOM, (b) GFA, (c) MEHA, (d) MPHA, (e) SRNOM, and (f) MAHA. Initial NOM concentration, 8 mg/L as C; initial As(III) concentration, 1 μ M; TiO₂ concentration, 0.05 g/L; ionic strength is 0.01 M NaCl; mixing time, 2 h; error bars show the range of data for duplicate samples.

above 8.5, and the detected As(V) concentration accounted for less than 10% of the total arsenic. With NOM, however, the percentage of As(V) over total arsenic in solution was up to 88%. With GFA, MEHA, or MPHA, an appreciable amount of As(V) was detected even when the solution pH was as low as 5.0. In the presence of NOM and at high pH values, the arsenic adsorption onto TiO₂ actually represents for the adsorption behavior of an As(III) and As(V) mixture. It appears that the different trends of arsenic adsorption versus pH should also be ascribed to the NOM-facilitated As(III) oxidation on TiO₂ surface besides the competitive adsorption. Because TiO₂ adsorbs less As(V) than As(III) at high pH values (Lee and Choi, 2002; Dutta et al., 2004), the increase of As(V) fraction in solution should lead to a decrease of the overall arsenic adsorption. The different As(III) adsorption behavior in the presence of different types of NOM should be a mixed result of (i) different NOM's capabilities in facilitating As(III) oxidation at TiO₂ surface and (ii) different NOM's capabilities in competing with As(III) and As(V) for the adsorption sites on TiO₂.

The slight oxidation of As(III) to As(V) by TiO₂ in the absence of air, light, and NOM is probably due to the vacancies of bridging oxygen atoms on TiO₂ surface, which are caused by the As(III) adsorption through the formation of Ti–O–As bonds

(Reactions (1)–(5)). The energy cost of breaking Ti–O bonds can be compensated by the adsorption of water molecules in the form of H₂O or OH⁻ (Ménétry et al., 2004). Since the adsorption of OH⁻ is more energetically favored to the oxygen vacancy than the adsorption of H₂O (Schaub et al., 2001; Tilocca and Selloni, 2003), the oxidation of As(III) is relatively more remarkable at high pH than that at low pH. Moreover, since the standard reduction potential of the As(V)/As(III) couple decreases with increasing pH (Lee and Choi, 2002), As(III) should be less difficult to oxidize under alkaline conditions. Despite the fact that NOM may desorb As(III) from TiO₂, the association of NOM with Ti atoms at the surface (Reactions (22)–(27)) may weaken the bond strength of Ti–O in Ti–O–As, boosting the bridging oxygen atom to escape from the surface. Therefore, NOM can facilitate As(III) oxidation by TiO₂ in the absence of light and O₂. Because the coordination of NOM and H can inhibit the NOM–Ti association (Langel and Menken, 2003), the effect of NOM on As(III) oxidation is more significant at high pH than at low pH. The possible mechanism for As(III) oxidation to As(V) on TiO₂ surface in the presence of NOM and in the absence of light and O₂ are illustrated in Fig. 6.

The As(III) oxidation on TiO₂ surface in the absence of O₂ could also be due to the insufficient light exclusion when

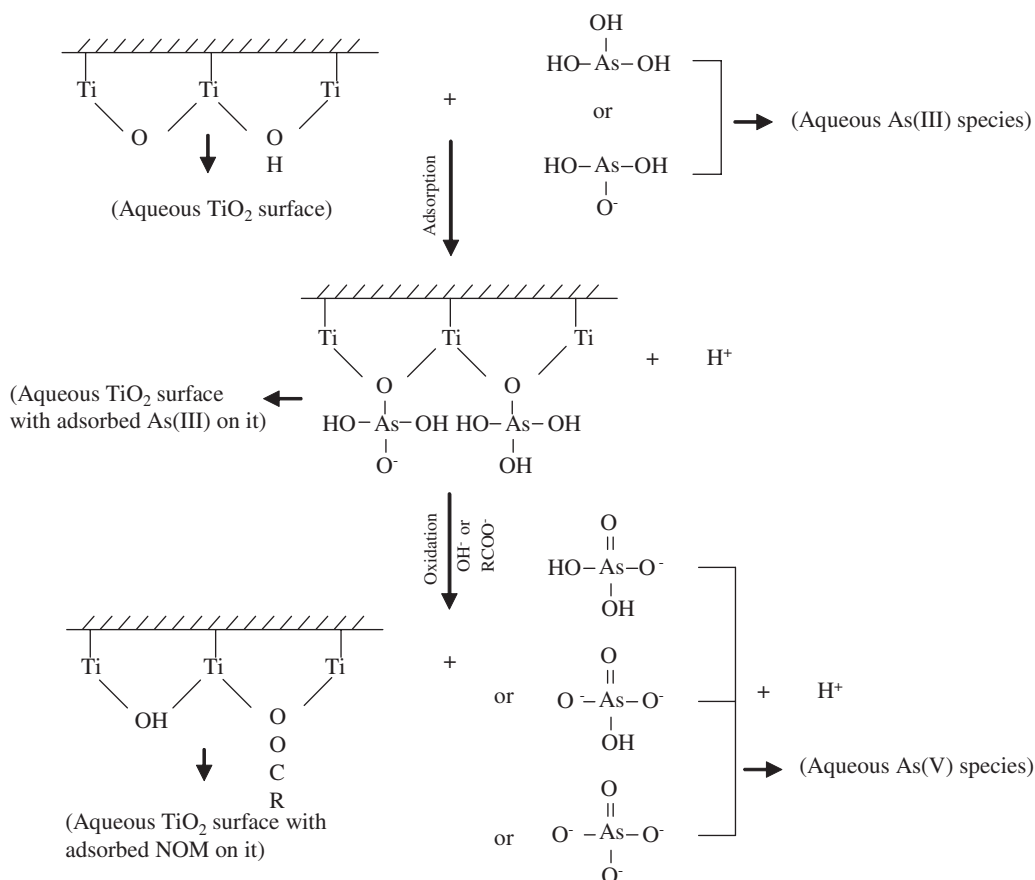


Fig. 6 – Illustration of the possible mechanism for As(III) oxidation to As(V) on TiO₂ surface in the presence of NOM and in the absence of O₂ and light.

performing the experiment (Foster et al., 1998), for the photo-generated valence-band holes in TiO_2 may oxidize the adsorbed As(III). If light had been involved in the As(III) oxidation on TiO_2 surface, NOM might have served as an electron scavenger or oxidant radical donor (e.g., O_2^-) to facilitate the oxidation of As(III) (Yang et al., 1999; Lee and Choi, 2002). The effect of NOM on As(III) oxidation would then be more significant at low pH than that at high pH because more NOM was adsorbed at low pH values (Fig. 4). This is opposite to what we have observed in our experiments (Fig. 5). Therefore, the insufficient light exclusion cannot be the major reason for the As(III) oxidation under our experimental conditions. A previous study by Lee and Choi (2002) confirms that, with the presence of light and oxygen, NOM facilitated the As(III) oxidation on TiO_2 surface more significantly at pH 3.0 than at pH 9.0.

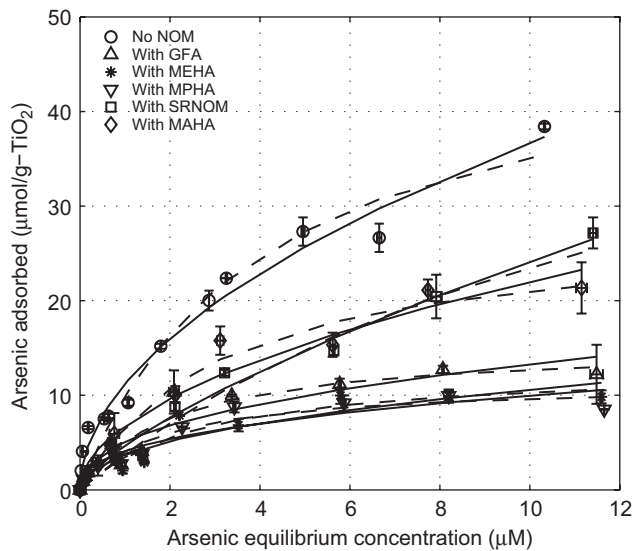


Fig. 7 – Arsenic adsorption isotherms with and without the presence of NOM. TiO_2 concentration, 0.05 g/L; initial DOC concentration, 8 mg/L as C; pH, 6.0 ± 0.1 ; ionic strength, 0.01 M NaCl; mixing time, 2 h; error bars show the range of data for duplicate samples. Solid and dashed lines represent the Freundlich and Langmuir modelling, respectively.

3.4. Arsenic adsorption isotherms

The adsorption capacities of TiO_2 for arsenic in the simulated raw waters with and without the presence of various types of NOM were examined (Fig. 7). Langmuir and Freundlich adsorption equations, which are the two most common adsorption models, are used to fit the experimental data. The parameters obtained by non-linear least-square regression for both Langmuir and Freundlich isotherms for arsenic adsorption with and without NOM are presented in Table 3.

The observed arsenic adsorption capacity of Degussa P25 TiO_2 in the absence of NOM at pH 6.0 was $49.2 \pm 12.5 \mu\text{mol/g-TiO}_2$, which is in reasonable agreement with the literature value of $32 \mu\text{mol/g-TiO}_2$ at pH 6.3 (Ferguson et al., 2005). The adsorption capacity of TiO_2 for arsenic decreased with the presence of 8 mg/L NOM as C in solution. Both Langmuir and Freundlich isotherms fit the experimental data well. For the water free of NOM, Freundlich isotherm fits the data better than Langmuir isotherm, which is indicative of a multisite adsorption of arsenic on TiO_2 surface (Dutta et al., 2004). For the waters containing NOM, Langmuir isotherm gives a better fit for the experimental data than Freundlich isotherm, implying that some available binding sites for arsenic were occupied by NOM. The examination of adsorption dependence on the two different adsorption isotherms supports the fact that NOM competes with As(III) for adsorption at the TiO_2 surface.

4. Conclusions

TiO_2 is an ideal adsorbent for arsenic removal from raw water. Compared to other commonly used adsorbents such as granular activated carbon, TiO_2 has a relatively large specific surface area and has a high affinity to both As(III) and As(V) within the pH range of natural waters (Mohan and Pittman, 2007). More importantly, light-irradiated TiO_2 can accelerate the oxidation of As(III) to As(V), which is less toxic and less difficult to remove through conventional water treatment methods (Yang et al., 1999; Bissen et al., 2001; Lee and Choi, 2002; Dutta et al., 2005; Ferguson et al., 2005; Xu et al., 2005). The As(III) oxidation efficiency and the overall arsenic

Table 3 – Isotherm parameters for arsenic adsorption in the simulated As(III)-contaminated raw waters with and without the presence of NOM

Type of NOM	Langmuir equation $([\text{As}]_{\text{ad}} = \frac{K L_t [\text{As}]_{\text{eq}}}{1 + K [\text{As}]_{\text{eq}}})$			Freundlich equation $([\text{As}]_{\text{ad}} = K_F \cdot [\text{As}]_{\text{eq}}^{1/n})$		
	K (1/ μM)	L_t ($\mu\text{mol/g-TiO}_2$)	r^2	K_F	n	r^2
No NOM	0.25 ± 0.14	49.2 ± 12.5	0.96	11.2 ± 1.44	1.94 ± 0.27	0.98
GFA	0.49 ± 0.34	15.3 ± 3.68	0.93	5.11 ± 1.45	2.41 ± 0.88	0.90
MEHA	0.37 ± 0.27	13.1 ± 3.68	0.93	3.79 ± 1.14	2.24 ± 0.79	0.90
MPHA	0.57 ± 0.32	11.3 ± 9.19	0.94	4.13 ± 1.01	2.61 ± 0.90	0.90
SRNOM	0.07 ± 0.05	57.3 ± 27.5	0.98	4.66 ± 0.98	1.40 ± 0.20	0.98
MAHA	0.32 ± 0.15	27.6 ± 4.99	0.98	6.80 ± 1.65	1.96 ± 0.48	0.96

removal through the coupled TPO-adsorption process can be affected by the adsorption of As(III)/As(V) onto TiO₂ surface (Ferguson et al., 2005).

We examined the arsenic adsorption onto a commercially available TiO₂ in simulated As(III)-contaminated raw waters in the presence and absence of five types of NOM that represent different environmental origins. The adsorption experiments were performed in the absence of light and oxygen. We found that NOM decreased the arsenic adsorption within the tested pH range of 4.0–9.4. The effects of NOM on arsenic adsorption at low to neutral pH values are due to NOM competition with As(III) for available binding sites on TiO₂. At high pH values, some As(III) was oxidized to As(V) due to the vacancies of bridging oxygen atoms on TiO₂ surface, and the presence of NOM dramatically facilitated this oxidation process. Thus the observed effect of NOM on the arsenic adsorption under alkaline conditions should be a mixed result of NOM-facilitated As(III) oxidation and As(III)/As(V) adsorption. The investigation suggests that NOM is an important element controlling arsenic speciation and adsorption on TiO₂ surface.

Many previous studies have shown that TiO₂ is an effective photocatalyst to convert As(III) to As(V) with the assistance of light and O₂ (Yang et al., 1999; Bissen et al., 2001; Lee and Choi, 2002; Dutta et al., 2005; Ferguson et al., 2005; Xu et al., 2005). The application of TiO₂ in practice can be limited due to the high energy cost for irritating the photocatalyst. Our study reveals that As(III) can be rapidly oxidized into As(V) by TiO₂ in NOM-rich waters without light and O₂, i.e., a light supplier may not be necessary for the oxidation treatment. Additionally, this finding indicates that TiO₂ may be applied as an *in situ* treatment technology to convert As(III) to the less toxic As(V) in groundwaters, as many As(III)-contaminated groundwaters are anaerobic in nature (Welch et al., 2000) and contain pronounced amounts of NOM (Mukherjee and Bhattacharya, 2001).

Acknowledgments

This study was funded by the Notre Dame Environmental Molecule Scientific Institute through the National Science Foundation (NSF EAR02-21966). The TiO₂ used in this study was provided as a gift by Degussa Company. Dr. Manfred Wolf (GSF—Institute for Groundwater Ecology, Neuherberg) provided a ground water fulvic acid sample (Gohy-573 fulvic acid). We thank the two anonymous reviewers for their helpful suggestions.

REFERENCES

- Bang, S., Patel, M., Lippincott, L., Meng, X.G., 2005. Removal of arsenic from groundwater by granular titanium dioxide adsorbent. *Chemosphere* 60, 389–397.
- Bauer, M., Blodau, C., 2006. Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. *Sci. Total Environ.* 354, 179–190.
- Bednar, A., Garbarino, J., Ranville, J., Wildeman, T., 2002. Preserving the distribution of inorganic arsenic species in ground-
- water and acid minedrainage samples. *Environ. Sci. Technol.* 36, 2213–2218.
- Bissen, M., Frimmel, F.H., 2003. Arsenic—a review. Part I: Occurrence, toxicity, speciation mobility. *Acta Hydrochim. Hydrobiol.* 31, 9–18.
- Bissen, M., Vieillard-Baron, M.-M., Schindelin, A.J., Frimmel, F.H., 2001. TiO₂-catalyzed photooxidation of arsenite to arsenate in aqueous samples. *Chemosphere* 44, 751–757.
- Brown, D.S., Allison, J.D., 1987. An equilibrium metal speciation model: Users Manual. Environmental Research Laboratory, Office of Research and Development U.S. Environmental Protection Agency, Report No. EPA/600/3-87/012.
- Dutta, P.K., Ray, A.K., Sharma, V.K., Millero, F.J., 2004. Adsorption of arsenate and arsenite on titanium dioxide suspensions. *J. Colloid Interface Sci.* 278, 270–275.
- Dutta, P.K., Pehkonen, S.O., Sharma, V.K., Ray, A.K., 2005. Photocatalytic oxidation of arsenic (III): evidence of hydroxyl radicals. *Environ. Sci. Technol.* 39, 1827–1834.
- EC, 1998. European Commission Directive, 98/83/EC, related with drinking water quality intended for human consumption. EC, Brussel, Belgium.
- Ferguson, M.A., Hoffmann, M.R., Hering, J.G., 2005. TiO₂-photo-catalyzed As(III) oxidation in aqueous suspensions: reaction kinetics and effect of adsorption. *Environ. Sci. Technol.* 39, 1880–1886.
- Foster, A.L., Brown, G.E., Parks, G.A., 1998. X-ray absorption fine-structure spectroscopy study of photocatalyzed, heterogeneous As(III) oxidation on kaolin and anatase. *Environ. Sci. Technol.* 32, 1444–1452.
- Grafe, M., Eick, M.J., Grossl, P.R., 2001. Adsorption of arsenate (V) and arsenite (III) on goethite in the presence and absence of dissolved organic carbon. *Soil. Sci. Soc. Am. J.* 65, 1680–1687.
- Grafe, M., Eick, M.J., Grossl, P.R., Saunders, A.M., 2002. Adsorption of arsenate and arsenite on ferrihydrite in the presence and absence of dissolved organic carbon. *J. Environ. Qual.* 31, 1115–1123.
- Hoffmann, M.R., Martin, S.T., Choi, W.Y., Bahnemann, D.W., 1995. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* 95, 69–96.
- Katsoyiannis, I.A., Zouboulis, A.L., 2006. Comparative evaluation of conventional and alternative methods for the removal of arsenic from contaminated groundwaters. *Rev. Environ. Health* 21 (1), 25–41.
- Katsoyiannis, I.A., Hug, S.J., Ammann, A., Zikoudi, A., Hatziliontos, C., 2007. Arsenic speciation and uranium concentrations in drinking water supply wells in Northern Greece: correlations with redox indicative parameters and implications for groundwater treatment. *Sci. Total Environ.* 383, 128–140.
- Kim, J.I., Buckau, G., Li, G.H., Duschner, H., Psarros, N., 1990. Characterization of humic and fulvic acids from Gorleben groundwater. *Fresenius J. Anal. Chem.* 338, 245–252.
- Ko, I., Kim, J.Y., Kim, K.W., 2004. Arsenic speciation and sorption kinetics in the As-hematite-humic acid system. *Colloids Surf. A* 234, 43–50.
- Langel, W., Menken, L., 2003. Simulation of the interface between titanium oxide and amino acids in solution by first principles MD. *Surf. Sci.* 538, 1–9.
- Lee, H., Choi, W., 2002. Photocatalytic oxidation of arsenite in TiO₂ suspension: kinetics and mechanisms. *Environ. Sci. Technol.* 36, 3872–3878.
- Letterman, R., Amirtharajah, A., O'Melia, C., 1999. Coagulation and flocculation. In: Letterman, R. (Ed.), *Water Quality & Treatment*. McGraw-Hill Inc., New York, 6.1–6.61.
- Liu, G.J., Zhang, X.R., Jain, J., Talley, J.W., Neal, C.R., 2006. Stability of inorganic arsenic species in simulated raw waters with the presence of NOM. *Water Sci. Technol.: Water Supply* 6, 175–182.

- Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. *Talanta* 58, 201–235.
- Masscheleyn, P.H., Delaune, R.D., Patrick, W.H., 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environ. Sci. Technol.* 25, 1414–1419.
- Ménétry, M., Markovits, A., Minot, C., Pacchioni, G., 2004. Formation of Schottky defects at the surface of MgO, TiO₂, and SnO₂: a comparative density functional theoretical study. *J. Phys. Chem. B* 108, 12858–12864.
- Mohan, D., Pittman Jr., C.U., 2007. Arsenic removal from water/wastewater using adsorbents—a critical review. *J. Hazard. Waste Mater.* 142, 1–53.
- Mukherjee, A.B., Bhattacharya, P., 2001. Arsenic in groundwater in the Bengal delta plain: slow poisoning in Bangladesh. *Environ. Rev.* 9, 189–220.
- Pena, M., Meng, X.G., Korfiatis, G.P., Jing, C.Y., 2006. Adsorption mechanism of arsenic on nanocrystalline titanium dioxide. *Environ. Sci. Technol.* 40, 1257–1262.
- Pena, M.E., Korfiatis, G.P., Patel, M., Lippincott, L., Ment, X., 2005. Adsorption of As(V) and As(III) by nanocrystalline titanium dioxide. *Water Res.* 39, 2327–2337.
- Persson, P., Lunell, S., 2000. Binding of bi-isonicotinic acid to anatase TiO₂ (1 0 1). *Sol. Energy Mater. Sol. Cells* 63, 139–148.
- Redman, A.D., Macalady, D.L., Ahmann, D., 2002. Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ. Sci. Technol.* 36, 2889–2896.
- Roddick-Lanzilotta, A.D., McQuillan, A.J., 2000. An in situ infrared spectroscopic study of glutamic acid and of aspartic acid adsorbed on TiO₂: implications for the biocompatibility of titanium. *J. Colloid Interface Sci.* 227, 48–54.
- Schaub, R., Thostrup, P., Lopez, N., Lægsgaard, E., Stensgaard, I., Nørskov, J.K., Besenbacher, F., 2001. Oxygen vacancies as active sites for water dissociation on rutile TiO₂(1 1 0). *Phys. Rev. Lett.* 87, 2661041–2661044.
- Smedley, P., Nicolli, H.B., Macdonald, D.M.J., Barros, A.J., Tullio, J.O., 2002. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. *Appl. Geochem.* 17, 259–284.
- Smith, A., Lingas, E., Rahman, M., 2000. Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. *Bull. WHO* 78, 1093–1103.
- Tilocca, A., Selloni, A., 2003. Reaction pathway and free energy barrier for defect-induced water dissociation on the (1 0 1) surface of TiO₂-anatase. *J. Chem. Phys.* 119, 7445–7450.
- USEPA, 2001a. National primary drinking water regulations: arsenic and clarifications to compliance and new source contaminants monitoring. Fed. Regist. 66(14), 6975–7066.
- USEPA, 2001b. Fact sheet: drinking water standard for arsenic. U.S. Environmental Protection Agency, Report No. EPA 815-f-00-015.
- Welch, A.H., Westjohn, D.B., Helsel, D.R., Wanty, R.B., 2000. Arsenic in ground water of the United States: occurrence and geochemistry. *Ground Water* 38, 589–604.
- WHO, 1993. Guidelines for Drinking-water Quality, second ed. WHO, Geneva, Switzerland.
- Xu, T., Kamat, P.V., O'Shea, K.E., 2005. Mechanistic evaluation of arsenite oxidation in TiO₂ assisted photocatalysis. *J. Phys. Chem. A* 109, 9070–9075.
- Yang, H., Lin, W.-Y., Rajeshwar, K., 1999. Homogeneous and heterogeneous photocatalytic reactions involving As(III) and As(V) species in aqueous media. *J. Photochem. Photobiol. A* 123, 137–143.