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

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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

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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 condition 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.

Keywords: As(III), NOM, TiO₂, adsorption, oxidation, mechanism

1 Introduction

Arsenic is a common contaminant in drinking water supplies, with a contamination level ranging from <1.0 to > 1000 $\mu\text{g/L}$ (<0.013 to >13.3 μM) (Welch et al., 2000; Smedley et al., 2002; Mandal & Suzuki, 2002; Bissen & 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 $10\text{ }\mu\text{g/L}$ ($1.33\text{ }\mu\text{M}$) 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 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 & 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 & Zouboulis, 2006). As an emerging oxidation technology for As(III)

74 transformation to As(V), TiO₂ photocatalytic oxidation (TPO) have attracted
75 substantial attentions as this method is environmentally benign (Yang et al.,
76 1999; Bissen et al., 2001; Lee & Choi, 2002; Dutta et al., 2005; Ferguson et
77 al., 2005; Xu et al., 2005).

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

94 Natural organic matter (NOM) is a complex mixture of acidic organic
95 molecules that originates from a variety of natural sources (e.g., soil, sediment,
96 water, etc.) (Letterman et al., 1999). NOM is ubiquitous in aquatic environ-
97 ment. A recent survey about As(III) levels in the groundwaters of the Bengal
98 Delta Plain aquifers in Bangladesh suggests that the groundwaters with high
99 As(III) concentrations tend to have high concentration of NOM (Mukherjee

100 & Bhattacharya, 2001). NOM has been reported to be an essential component
101 controlling arsenic mobilization at aluminum or iron (hydro)oxide–water in-
102 terface (Grafe et al., 2001, 2002; Redman et al., 2002; Ko et al., 2004; Bauer
103 & Blodau, 2006). However, few studies have been conducted specifically for
104 NOM effects on arsenic adsorption by TiO_2 (Lee & Choi, 2002). In studying
105 the effect of a commercially available humic acid (HA) on As(III) oxidation
106 rate through the TPO, Lee & Choi (2002) observed that the presence of HA
107 had an insignificant effect on the As(III) adsorption by TiO_2 . In their study,
108 however, an extremely high concentration of As(III) ($500\ \mu\text{M}$) was used, so
109 the effect of NOM on As(III) adsorption could be different for **real raw waters**
110 which usually **contain** less than $13.3\ \mu\text{M}$ of As(III).

111 In this study, the effect of NOM on arsenic adsorption by TiO_2 in sim-
112 ulated As(III)-contaminated raw waters was examined. Batch adsorption ex-
113 periments were performed as a function of contact time, pH, initial DOC con-
114 centration, and initial As(III) concentration. The experiments were performed
115 under anaerobic conditions and in darkness to avoid As(III) oxidation caused
116 by TiO_2 photocatalysis. Five types of NOM from different environmental ori-
117 gins were tested. Arsenic redox speciation in the filtrates after the adsorption
118 were examined. Mechanisms behind the observed effects were discussed.

119 2 Materials and method

120 2.1 Materials and chemicals

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

126 Sodium arsenite (NaAsO_2 , 99%) was obtained from Sigma. Stock As(III)
127 solution (13.3 mM) was prepared by dissolving 0.866 g NaAsO_2 into 500 mL
128 Milli-Q water. The As(III) stock solution was stored in a high density polyethy-
129 lene bottle, and was kept in darkness at 4 °C.

130 The TiO_2 used in this study was a commercially available titanium diox-
131 ide, Degussa P25 (Germany). The Degussa P25 TiO_2 contains 80% of anatase
132 and 20% of rutile (Hoffmann et al., 1995). It has a Brunauer-Emmett-Teller
133 surface area of 55 m^2/g and a pH_{pzc} (the pH at the point of zero charge) of
134 6.7 in 0.01 M NaCl. A stock TiO_2 suspension was prepared by mixing 1 g of
135 Degussa P25 TiO_2 with 1 L of background electrolyte (0.01 M NaCl). The
136 TiO_2 stock suspension was sonicated for 20 minutes each time before use in
137 order to re-suspend the precipitated TiO_2 particles.

138 Five different types of NOM were used in this study. They are Suwannee
139 River NOM (SRNOM), Gohy-573 fulvic acid (GFA), Elliott Soil humic acid
140 (EHA), Pahokee peat (PHA), and Aldrich humic acid (AHA). SRNOM, EHA,
141 and PHA are well characterized NOMs. SRNOM originated from Suwannee
142 River of Georgia, USA; EHA was from prairie soils of Indiana, Illinois, and

143 Iowa, USA; PHA was from peat soil of the Florida Everglades, USA. The three
144 types of NOM were purchased from the International Humic Substances Soci-
145 ety. GFA is a fulvic acid extracted from the Gorleben groundwater, Germany
146 (Kim et al., 1990). AHA is a commercially available humic acid from Aldrich.
147 SRNOM and GFA were used without further modification. The stock solution
148 of SRNOM or GFA was prepared by dissolving the NOM powder standard
149 into 0.01 M NaCl to reach a concentration of 900–1000 mg/L. For EHA, PHA,
150 and AHA, the humic acid standard was dissolved in 0.01 M NaOH (pH 11–12)
151 at 850–1000 mg/L; The solution was then acidified to pH 3.8 ± 0.1 with 2 M
152 HCl, and filtered through a 0.45- μ m pore-size membrane (Gelman Supor) to
153 remove the undissolved part of humic acids; The filtrate was collected as the
154 HA stock solution; The humic acid was modified in order to ensure no NOM
155 was precipitated during the arsenic adsorption on TiO₂. The dissolved organic
156 carbon (DOC) concentration in the HA stock solution was determined using a
157 Shimadzu 5050 TOC analyzer. The modified EHA, PHA, and AHA are respec-
158 tively denoted as MEHA, MPHA, and MAHA in the rest of the manuscript.
159 All the NOM stock solutions were kept in glass bottles in darkness at 4 °C. Ad-
160 sorption experiments were performed within 6 weeks after the stock solutions
161 were prepared.

162 2.2 Adsorption studies

163 Simulated As(III)-contaminated raw waters were prepared by mixing 0.01
164 M of NaCl with various concentrations of As(III) and NOM. Batch adsorption
165 experiments were performed to determine the adsorption of arsenic by TiO₂
166 in these simulated raw waters. All adsorption experiments were performed
167 in an anaerobic chamber in order to avoid As(III) oxidation. The anaerobic

168 chamber was maintained with a purified makeup gas consisting of N₂ (95%)
169 and H₂ (5%). All solutions together with the stock TiO₂ suspension were
170 purged with high purity N₂ gas for at least 30 minutes and then immediately
171 transferred into the anaerobic chamber.

172 The adsorption experiments were carried out in 15-mL acid washed polyethy-
173 lene bottles (amber). Adsorption of arsenic onto TiO₂ was initiated by adding
174 0.75 mL of TiO₂ stock suspension (1 g/L) into 14.25 mL of the simulated raw
175 water, resulting in a TiO₂ concentration of 0.05 g/L. After the addition of
176 TiO₂, the pH of the suspension was adjusted to a desired value using HCl and
177 NaOH solutions (0.05–0.1 M). The suspension was then sealed and mixed on
178 a rotator at room temperature for until the adsorption reached steady-state.
179 At the end of mixing, the pH of the suspension was re-measured and recorded.
180 The pH value thus measured was reported as the adsorption pH. The suspen-
181 sion was then filtered through a 0.22- μ m PTEF syringe filter (Fisher), and
182 the filtrate was immediately analyzed for the concentrations of total arsenic,
183 As(III), As(V), and NOM.

184 2.3 Instrument analysis

185 The NOM concentration (expressed in UV₂₅₄) remaining in the filtrate af-
186 ter adsorption was determined using a Varian Cary 300 Bio UV-Visible spec-
187 trophotometer at the wavelength of 254 nm. Total arsenic concentration in
188 solution was measured using a Perkin-Elmer optima 2000DV inductively cou-
189 pled plasma-optical emission spectrometry (ICP-OES). A Finnigan Element
190 2 sector field high resolution inductively coupled plasma-mass spectrometry
191 (ICP-MS) was used when the arsenic concentration was lower than 0.67 μ M
192 (50 μ g/L). A medium resolution mode was chosen for the ICP-MS analysis to

193 avoid the interference from $^{40}\text{Ar}^{35}\text{Cl}^+$ dimer. The detection limits of arsenic
 194 using the ICP-OES and the ICP-MS were determined to be $25\text{ }\mu\text{g/L}$ ($0.33\text{ }\mu\text{M}$)
 195 and 5 ng/L ($6.7\times 10^{-5}\text{ }\mu\text{M}$), respectively. The instruments were calibrated each
 196 time before use. The concentrations of the calibration standards ranged from
 197 0.4 to $1.07\text{ }\mu\text{M}$ for ICP-OES and from 0.067 to $0.53\text{ }\mu\text{M}$ for ICP-MS. Each
 198 sample was injected three times, and the relative standard deviation (RSD)
 199 for the triplicate analysis was within 5% . The total concentrations of As(III)
 200 and As(V) remaining in solution after adsorption were simultaneously deter-
 201 mined using ion chromatography (Dionex LC25) coupled with the ICP-MS
 202 (IC-ICP-MS). The detection limit for both As(III) and As(V) by the IC-
 203 ICP-MS was $2.7\times 10^{-3}\text{ }\mu\text{M}$. The IC-ICP-MS was calibrated with standards
 204 varying from 0.067 to $0.53\text{ }\mu\text{M}$. The RSD for three injections of the sample
 205 with a concentration above $0.013\text{ }\mu\text{M}$ was usually less 7% .

206 **3 Results and discussion**

207 *3.1 Arsenic adsorption onto TiO_2 as a function of contact time*

208 The adsorption of arsenic by TiO_2 in the simulated raw waters containing
 209 0 or 8 mg/L as C of NOM (i.e., SRNOM or MAHA) was examined as a function
 210 of time. The initial ratio of As(III) to TiO_2 was $53.4\text{ }\mu\text{mol/g-TiO}_2$ for all the
 211 waters tested. No As(V) was detected in the filtrates after adsorption in the
 212 waters either with or without NOM. The experimental results are presented
 213 in Figure 1.

214 Without NOM, the arsenic adsorption onto TiO_2 was rapid and reached
 215 steady-state within 1 h . The time required for the adsorption to reach steady-
 216 state is similar to the reported value that was obtained in the presence of

217 air and light (Pena et al., 2005), although a conversion of As(III) to As(V)
218 may occur on the TiO₂ surface with air and light present. At the steady-state,
219 approximately 13.4 $\mu\text{mol/g-TiO}_2$ or 25% of the total arsenic was adsorbed
220 onto the TiO₂ surface.

221 With the presence of 8 mg/L as C of SRNOM or MAHA, the arsenic
222 adsorption onto TiO₂ also reached steady-state within approximately 1 h.
223 The amounts of arsenic adsorbed by TiO₂ at steady state were 8.12 and 7.59
224 $\mu\text{mol/g-TiO}_2$ for the waters containing SRNOM and MAHA respectively. The
225 uptake of arsenic was decreased by 39.4% or 43.3% respectively due to the
226 presence of 8 mg/L as C of SRNOM or MAHA in the simulated raw water.
227 The experimental results suggest that the tested NOMs did not change the
228 time required for the arsenic adsorption onto TiO₂ to reach steady-state, but
229 significantly reduced the amounts of arsenic adsorbed on TiO₂.

230 3.2 *Effect of initial DOC concentration on arsenic adsorption onto TiO₂*

231 Figure 2 presents the effect of initial DOC and As(III) concentrations on
232 arsenic adsorption by TiO₂ in simulated raw waters containing 0–14 mg/L
233 SRNOM as C and 1–15 μM As(III). The simulated raw water and TiO₂ were
234 mixed for 2 h to ensure the arsenic adsorption to reach steady-state. Either
235 with or without the presence of SRNOM, arsenic adsorption increased as the
236 initial As(III) concentration increased from 1 to 15 μM , indicating that the
237 available arsenic binding sites on TiO₂ surface have not been saturated even
238 when the initial As(III) concentration was as high as 15 μM . The arsenic
239 removal efficiency, however, decreased from 31.0% to 12.2% when the initial
240 As(III) concentration increased from 1 to 15 μM . When the initial As(III)
241 concentration was fixed, the amount of arsenic adsorbed by TiO₂ 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 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 Figure 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 to 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,

267 depending on the type of NOM in the simulated raw water. With MAHA, the
 268 arsenic adsorption by TiO_2 increased with increasing pH throughout the entire
 269 range of pH values tested, which was similar to the arsenic adsorption behav-
 270 ior without NOM. At the same pH value, the amounts of arsenic adsorbed on
 271 TiO_2 with the presence of various types of NOM were generally less than that
 272 without the presence of NOM. The observed pH effect on As(III) adsorption by
 273 TiO_2 in the absence of NOM is in good agreement with the literature (Dutta
 274 et al., 2004; Pena et al., 2005). In natural waters, both As(III) and TiO_2 can
 275 be viewed as weak acids. The proton dissociation reactions for As(III) and
 276 TiO_2 are presented in Table 2. Aqueous As(III) speciation distributions at
 277 various pH values can be calculated based on Reactions A1–A3 shown in Ta-
 278 ble 2. Within the pH range of 4.0–9.4, the primary aqueous As(III) species
 279 include the neutral H_3AsO_3^0 and the negatively charged H_2AsO_3^- . When pH is
 280 below 7.0, over 99% of As(III) exists as H_3AsO_3^0 . When pH ranges from 7.0 to
 281 9.4, As(III) exists as a mixture of H_3AsO_3^0 (99–35%) and H_2AsO_3^- (1–65%).
 282 According to Reactions A4–A5 in Table 2, TiO_2 suspension is composed of the
 283 mixture of positively charged $\equiv\text{TiOH}_2^+$ and neutral species of $\equiv\text{TiOH}^0$ when
 284 pH is below pH_{pzc} (i.e., pH 6.7); When pH is above pH_{pzc} , the primary species
 285 of the suspended TiO_2 include the neutral species of $\equiv\text{TiOH}^0$ and the nega-
 286 tively charged $\equiv\text{TiO}^-$. Therefore, the adsorption of As(III) on TiO_2 can be
 287 viewed as the interaction between H_3AsO_3^0 and $\equiv\text{TiOH}_2^+/\equiv\text{TiOH}^0$ when pH is
 288 below 7.0, or the interaction between $\text{H}_3\text{AsO}_3^0/\text{H}_2\text{AsO}_3^-$ and $\equiv\text{TiOH}^0/\equiv\text{TiO}^-$
 289 when pH is above 7.0. Based on the above discussion, we propose the following
 290 reactions (Reactions 1–15) to explain the adsorption mechanisms of As(III)
 291 onto TiO_2 surface. Briefly, aqueous As(III) species adsorb onto TiO_2 surface
 292 through the formation of As–O–Ti, As–Ti, and hydrogen bonds. The fact that
 293 more As(III) was adsorbed onto TiO_2 at high pH value than at low pH values

294 suggests that the formation of As–O–Ti bond (Reactions 1–5) should be the
 295 major mechanism controlling the arsenic adsorption under the experimental
 296 conditions, as a proton that is originally associated with oxygen at TiO₂ sur-
 297 face should be released when the As–O–Ti bond forms, and the increase of
 298 solution pH favors the association between As(III) and TiO₂, leading to an
 299 increased arsenic adsorption. The slow increasing of arsenic adsorption onto
 300 TiO₂ with the increase of pH at high pH values can be due to the formation of
 301 $\equiv\text{TiO}^-$ and H_2AsO_3^- , both of which are negatively charged and their repulsion
 302 to each other may result in a compromised As(III) adsorption. In studying the
 303 vibration spectroscopic properties of adsorbed As(III) at TiO₂ surface, Pena
 304 et al. (2006) observed that the band position of the uncomplexed As–O shift
 305 from 795 cm⁻¹ to 780 cm⁻¹ when As(III) moved from water to TiO₂ surface,
 306 which is indicative of the formation of As–O–Ti bond. It should be noted that
 307 Reactions 1–15 only represent the possible bonds that may form when As(III)
 308 is adsorbed onto TiO₂. They do not necessarily reflect the actual coordination
 309 number of As(III)–TiO₂ interaction. That is, the As(III)–TiO₂ association
 310 does not necessarily to be monodentate mononuclear.

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

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

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

329 NOM is negatively charged in natural waters. It can be associated with
 330 TiO_2 through electrostatic attraction. Theoretical and experimental studies of
 331 various organic compounds adsorption by TiO_2 indicate that the carboxyl and
 332 phenolic functional groups in NOM can bind to Ti or O atom on TiO_2 surface
 333 (Persson & Lunell, 2000; Roddick-Lanzilotta & McQuillan, 2000; Langel &
 334 Menken, 2003). The following reactions (Reactions 16–29) are thus proposed
 335 as the possible mechanisms for NOM adsorption onto TiO_2 surface.

336 1. Adsorption of NOM through electrostatic attraction.

338 2. Adsorption of NOM through a hydrogen bond.

344 3. Adsorption of NOM through a Ti-O bond.

351 4. Adsorption of NOM through condensation.

354 Reactions 1–29 suggest that NOM can compete with As(III) for available
 355 binding sites, such as Ti or O atoms, on TiO_2 surface. Therefore, the presence
 356 of NOM in solution can **reduce the arsenic** adsorption through competitive

adsorption. The measurement of UV_{254} remaining in solution confirms that a significant amount of NOM was adsorbed on TiO_2 (Fig. 4). The adsorption of NOM onto TiO_2 decreased with increasing pH, reflecting the anionic character of NOM. If competitive adsorption is the only reason for the decreased arsenic adsorption onto TiO_2 surface, more arsenic should be desorbed at lower pH values as more NOM is adsorbed at higher pH values. Figure 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 TiO_2 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 TiO_2 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 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

383 appreciable amount of As(V) was detected even when the solution pH was as
384 low as 5.0. In the presence of NOM and at high pH values, the arsenic adsorp-
385 tion onto TiO₂ actually represents for the adsorption behavior of an As(III)
386 and As(V) mixture. It appears that the different trends of arsenic adsorption
387 versus pH should also be ascribed to the NOM-facilitated As(III) oxidation on
388 TiO₂ surface besides the competitive adsorption. Because TiO₂ adsorbs less
389 As(V) than As(III) at high pH values (Lee & Choi, 2002; Dutta et al., 2004),
390 the increase of As(V) fraction in solution should lead to a decrease of the over-
391 all arsenic adsorption. The different As(III) adsorption behavior in presence
392 of different types of NOM should be a mixed result of (i) different NOM's
393 capabilities in facilitating As(III) oxidation at TiO₂ surface, and (ii) different
394 NOM's capabilities in competing with As(III) and As(V) for the adsorption
395 sites on TiO₂.

396 The slight oxidation of As(III) to As(V) by TiO₂ in the absence of air,
397 light, and NOM is probably due to the vacancies of bridging oxygen atoms
398 on TiO₂ surface, which are caused by the As(III) adsorption through the for-
399 mation of Ti–O–As bonds (Reactions 1–5). The energy cost of breaking Ti–O
400 bonds can be compensated by the adsorption of water molecules in form of
401 H₂O or OH[−] (Ménétry et al., 2004). Since the adsorption of OH[−] is more ener-
402 getically favored to the oxygen vacancy than the adsorption of H₂O (Schaub et
403 al., 2001; Tilocca & Selloni, 2003), the oxidation of As(III) is relatively more
404 remarkable at high pH than that at low pH. Moreover, since the standard
405 reduction potential of the As(V)/As(III) couple decreases with increasing pH
406 (Lee & Choi, 2002), As(III) should be less difficult to oxidize under alkaline
407 conditions. Despite the fact that NOM may desorb As(III) from TiO₂, the as-
408 sociation of NOM with Ti atoms at the surface (Reactions 22–27) may weaken

409 the bond strength of Ti–O in Ti–O–As, boosting the bridging oxygen atom to
410 escape from the surface. Therefore, NOM can facilitate As(III) oxidation by
411 TiO₂ in the absence of light and O₂. Because the coordination of NOM and
412 H can inhibit the NOM–Ti association (Langel & Menken, 2003), the effect
413 of NOM on As(III) oxidation is more significant at high pH than at low pH.
414 The possible mechanism for As(III) oxidation to As(V) on TiO₂ surface in
415 the presence of NOM and in the absence of light and O₂ are illustrated in
416 Figure 6.

417 The As(III) oxidation on TiO₂ surface in the absence of O₂ could also be
418 due to the insufficient light exclusion when performing the experiment (Foster
419 et al., 1998), for the photo-generated valence-band holes in TiO₂ may oxidize
420 the adsorbed As(III). If light had been involved in the As(III) oxidation on
421 TiO₂ surface, NOM might have served as an electron scavenger or oxidant
422 radical donor (e.g., O₂^{•−}) to facilitate the oxidation of As(III) (Yang et al.,
423 1999; Lee & Choi, 2002). The effect of NOM on As(III) oxidation would then
424 be more significant at low pH than that at high pH, because more NOM
425 was adsorbed at low pH values (Fig. 4). This is opposite to what we have
426 observed in our experiments (Fig. 5). Therefore, the insufficient light exclusion
427 cannot be the major reason for the As(III) oxidation under our experimental
428 conditions. A previous study by Lee & Choi (2002) confirms that, with the
429 presence of light and oxygen, NOM facilitated the As(III) oxidation on TiO₂
430 surface more significantly at pH 3.0 than at pH 9.0.

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, 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

455 has a relatively large specific surface area and has a high affinity to both As(III)
456 and As(V) within the pH range of natural waters (Mohan & Pittman, 2007).
457 More importantly, light-irradiated TiO_2 can accelerate the oxidation of As(III)
458 to As(V), which is less toxic and less difficult to remove through conventional
459 water treatment methods (Yang et al., 1999; Bissen et al., 2001; Lee & Choi,
460 2002; Dutta et al., 2005; Ferguson et al., 2005; Xu et al., 2005). The As(III)
461 oxidation efficiency and the overall arsenic removal through the coupled TPO-
462 adsorption process can be affected by the adsorption of As(III)/As(V) onto
463 TiO_2 surface (Ferguson et al., 2005).

464 We examined the arsenic adsorption onto a commercially available TiO_2
465 in simulated As(III)-contaminated raw waters in the presence and absence of 5
466 types of NOM that represent different environmental origins. The adsorption
467 experiments were performed in the absence of light and oxygen. We found
468 that NOM decreased the arsenic adsorption within the tested pH range of
469 4.0–9.4. The effects of NOM on arsenic adsorption at low to neutral pH values
470 are due to NOM competition with As(III) for available binding sites on TiO_2 .
471 At high pH values, some As(III) was oxidized to As(V) due to the vacancies of
472 bridging oxygen atoms on TiO_2 surface, and the presence of NOM dramatically
473 facilitated this oxidation process. Thus the observed effect of NOM on the
474 arsenic adsorption under alkaline conditions should be a mixed result of NOM-
475 facilitated As(III) oxidation and As(III)/As(V) adsorption. The investigation
476 suggests that NOM is an important element controlling arsenic speciation and
477 adsorption on TiO_2 surface.

478 Many previous studies have shown that TiO_2 is an effective photocatalyst
479 to convert As(III) to As(V) with the assistance of light and O_2 (Yang et al.,
480 1999; Bissen et al., 2001; Lee & Choi, 2002; Dutta et al., 2005; Ferguson

et al., 2005; Xu et al., 2005). The application of TiO_2 in practice can be limited due to the high energy cost for irradiating the photocatalyst. Our study reveals that As(III) can be rapidly oxidized into As(V) by TiO_2 in NOM-rich waters without light and O_2 , *i.e.*, a light supplier may not be necessary for the oxidation treatment. *Additionally, this finding* indicates that TiO_2 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 & Bhattacharya, 2001).

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Table 1

Arsenic adsorption onto TiO_2 in simulated As(III)-contaminated raw waters with various initial DOC and As(III) concentrations

Initial As(III) concentration (μM)					
1		8		15	
DOC	As adsorbed	DOC	As adsorbed	DOC	As adsorbed
(mg/L as C)	($\mu\text{mol/g-TiO}_2$)	(mg/L as C)	($\mu\text{mol/g-TiO}_2$)	(mg/L as C)	($\mu\text{mol/g-TiO}_2$)
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

Table 2

Deprotonation reactions for As(III) and TiO_2 in water

No.	Reaction	pK_a	Ref.
A1	$\text{H}_3\text{AsO}_3 \rightleftharpoons \text{H}_2\text{AsO}_3^- + \text{H}^+$	9.23	Brown & Allison (1987)
A2	$\text{H}_2\text{AsO}_3^- \rightleftharpoons \text{HAsO}_3^{2-} + \text{H}^+$	12.10	Brown & Allison (1987)
A3	$\text{HAsO}_3^{2-} \rightleftharpoons \text{AsO}_3^{3-} + \text{H}^+$	13.41	Brown & Allison (1987)
A4	$\text{TiOH}_2^+ \rightleftharpoons \equiv \text{TiOH} + \text{H}^+$	$pH < pH_{pzc}$	Dutta et al. (2004)
A5	$\equiv \text{TiOH} \rightleftharpoons \equiv \text{TiO}^- + \text{H}^+$	$pH > pH_{pzc}$	Dutta et al. (2004)

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

Fig. 1. Adsorption of arsenic onto TiO₂ as a function of contact time in the simulated As(III)-contaminated raw waters with or without NOM. TiO₂ 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.

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.

Fig. 4. UV_{254} removal during arsenic adsorption onto TiO_2 under different pH values. TiO_2 concentration, 0.05 g/L; Initial As(III) concentration, 1 μ M; 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.

Fig. 5. Arsenic redox speciation in the filtrates after arsenic adsorption onto TiO_2 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 μM ; TiO_2 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.

Fig. 6. Illustration of the possible mechanism for As(III) oxidation to As(V) on TiO_2 surface in the presence of NOM and in the absence of O_2 and light.

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.