

Influence of ionic strength, electrolyte type, and NOM on As(V) adsorption onto TiO₂

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As(V) adsorption onto a commercially available TiO₂ (Degussa P25) in NaCl or NaClO₄ at various concentrations (0.001–0.1 M) was investigated. The effect of natural organic matter (NOM) on As(V) removal through the adsorption by TiO₂ was also examined. In either electrolyte, As(V) adsorption onto TiO₂ increased with the increase of ionic strength under alkaline conditions (pH 7.0–11.0). Under acidic conditions (pH 4.0–6.0), the adsorption of As(V) onto TiO₂ was insensitive to ionic strength in NaClO₄ electrolyte but decreased with increasing ionic strength in NaCl electrolyte. The presence of 2–15 mg/L NOM as C significantly decreased the fraction of As(V) adsorbed onto TiO₂ at pH 6.0 regardless of the initial As(V) concentration (1–15 μM). The measurement of zeta potential of TiO₂ with and without As(V) suggests that the presence of As(V) can shift the point of zero charge (pH_{pzc}) of TiO₂ to a lower pH value. The overall data presented in this study suggest that As(V) can form both inner-sphere and outer-sphere complexes on TiO₂ surface, and NOM is an important factor controlling As(V) adsorption onto TiO₂.

Keywords: As(V), adsorption, TiO₂, NOM, electrolyte type, ionic strength.

Introduction

Arsenic is a common contaminant in natural waters. It originates from the weathering of arsenic-containing rocks and soils, as well as from the contamination through anthropogenic activities. Arsenic is a human carcinogen that attacks multiple sites in the human body.^[1,2] Long-term exposure to arsenic can cause skin, lung, bladder, liver, and kidney cancers.^[1] In order to reduce the potential risks that arsenic may bring to human health, the World Health Organization (WHO) has recommended a maximum arsenic concentration in drinking water as 10 μg/L.^[3] It has been reported that the arsenic contamination level in source drinking water of many countries, including Argentina, Bangladesh, India, Mexico, Mongolia, Thailand, and China, can be up to 100–2000 μg/L,^[4] which is much higher than the WHO recommended guideline.

Arsenic thus has become one of the most problematic contaminants in drinking water throughout the world.^[5] Arsenic exists in water primarily as oxyanions of trivalent arsenite (As(III)) and pentavalent of arsenate (As(V)). As a water contaminant, As(III) is more problematic than As(V) since As(III) is more toxic, more mobile, and more difficult to be removed from water compared to As(V). Unfortunately, As(III) contributes to a significant proportion of total arsenic in natural waters. According to a recent survey, As(III) accounts for up to 90% of total arsenic in a groundwater in Bangladesh.^[6]

Current available technologies to remove arsenic include coagulation, adsorption, ion exchange, reverse osmosis, and electrodialysis, most of which require a pre-oxidation of As(III) to As(V) in order to achieve satisfactory arsenic removal.^[7] The oxidation of As(III) to As(V) can be efficiently achieved through a photocatalytic oxidation with the presence of TiO₂.^[8,9] Since TiO₂ has a high affinity for As(V), the TiO₂ photocatalytic oxidation of As(III) followed by As(V) adsorption by TiO₂ has been proposed to be a novel technology for removing arsenic from source water for drinking water utilities,^[10,11] with As(V) adsorption by TiO₂ determining the overall arsenic removal efficiency. The adsorption of As(V) onto TiO₂ is dependent on water pH, the type of TiO₂, and the presence of competing ions such as CO₃²⁻ and PO₄³⁻. It has been

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discovered that As(V) adsorption onto TiO₂ at low pH is higher than that at high pH^[10,12,13]. The TiO₂ that is porous and/or has high surface area tends to have higher adsorption capability for As(V) than the TiO₂ that is non-porous and/or has relatively low surface area, although it takes much longer for the adsorption to reach equilibrium by using the former type of TiO₂.^[10,12,14] The presence of CO₃²⁻ and PO₄³⁻ can moderately inhibit As(V) adsorption onto TiO₂.^[12] For most of previous studies, the As(V) adsorption onto TiO₂ was performed at a constant ionic strength with a single electrolyte. The variation of electrolyte type and concentration may affect As(V) adsorption onto TiO₂ because the adsorption of As(V) by TiO₂ depends largely on electrostatic attraction,^[10] which can be easily inhibited by increasing the competitive adsorption of the surface with counterions (i.e., anions) from background electrolyte. The effect of ionic strength (electrolyte concentration) on As(V) adsorption onto various types of (hydr)oxide has been presented in many articles, although it has not been specifically examined and addressed with TiO₂. It has been reported that As(V) adsorption was insensitive to ionic strength when γ -Al₂O₃, goethite or amorphous Al/Fe oxide was used as the adsorbent,^[15–17] but was sensitive to ionic strength if the adsorbent was akaganéite (β -FeO(OH)) or allophane.^[18,19] A recent study of the relationship between ion pair formation and primary charging of TiO₂ suggests that the binding affinity between TiO₂ and anions/cations from background electrolyte varies depending on the type of anion or cation.^[20] Cornu et al.^[21] reported that the variation of electrolyte type from NaNO₃ to Ca(NO₃)₂ significantly decreased the adsorption of As(V) by kaolinite within the pH range of 4.0–6.0.

Besides the possible effects that may arise from the background electrolyte, the effect of NOM on the adsorption of As(V) by TiO₂ has not been well documented in the literature either. NOM is a complex mixture of acidic organic molecules that originates from a variety of natural sources.^[22] It is ubiquitous in natural waters and is an essential element controlling the mobility of different arsenic species in aquatic environment.^[23] According to a recent survey on the chemical composition of a groundwater in Bangladesh, NOM concentration in arsenic-rich groundwaters can be up to 14.2 mg/L as C.^[24] As an anionic polyelectrolyte within the normal pH range of natural waters (pH 6.0–9.0), NOM may affect As(V) adsorption onto TiO₂ through (1) competing with As(V) for available binding sites at the surface, (2) forming complexes with As(V), and/or (3) changing the surface charge of TiO₂ through adsorption.

The purpose of this study was to investigate the adsorption of As(V) onto TiO₂ at various concentrations of 2 electrolytes (i.e., NaCl and NaClO₄). The effect of NOM on As(V) adsorption onto TiO₂ was also examined. The mechanisms behind these effects were discussed.

Materials and methods

Materials and reagents

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 an 0.2- μ m membrane (Gelman FP-Verical) before making any solution in order to remove the existing microbes or other reducing colloids that may cause As(V) reduction.^[25] Sodium arsenate (Na₂HAsO₄·7H₂O, 99%) was obtained from Sigma. Suwannee River NOM (SRNOM), which has been a well characterized NOM, was purchased from the International Humic Substances Society. Sodium chloride (NaCl, 99%) and sodium perchlorate (NaClO₄·H₂O, 99%) were from Fisher. The TiO₂ used in this study was a commercial available TiO₂ (Degussa P25). The Degussa P25 TiO₂ contains 80% of anatase and 20% of rutile, with a BET surface area of 55 m²/g.^[26]

A stock solution of As(V) (13.3 mM) was made by dissolving 2.08 g of Na₂HAsO₄·7H₂O into 500 mL of the filtered Milli-Q water. Stock TiO₂ suspensions were made by mixing 1 g of Degussa P25 TiO₂ with 1 L of NaCl or NaClO₄ background electrolyte at different concentrations (0.001, 0.01, and 0.1 M). The stock As(V) solution and the stock TiO₂ suspensions were kept in the dark in a refrigerator at 4°C for up to 6 weeks. The stock TiO₂ suspensions were sonicated for 20 min each time before use in order to resuspend the precipitated TiO₂ particles.

Batch adsorption

All adsorption experiments were carried out in duplicate at 25°C in acid-washed polyethylene bottles (15 mL, amber). Adsorption of As(V) onto TiO₂ was initialized by adding 0.75 mL of TiO₂ stock suspension (1 g/L) into 14.25 mL As(V) solution (4.11 μ M) at different ionic strength levels (0.001–0.1 M). The As(V) solutions were obtained by spiking certain amount of As(V) stock solution (13.3 mM) into aliquots of NaCl or NaClO₄ solutions (0.001–0.1 M). The resulting suspensions hence had an initial As(V) concentration of 3.90 μ M. The pH values of the suspensions were adjusted to desired values using 0.1 M HCl or NaOH. The suspensions were then sealed and mixed on a rotator for 2 h to reach adsorption equilibrium. At the end of equilibrium period, the pH values of the suspensions were re-measured and recorded. The pH values measured at the end of adsorption equilibrium were reported as the adsorption pH throughout the manuscript. The suspensions were then filtered through a 0.22- μ m PTFE syringe filter (Fisher) and the filtrates were analyzed for the total concentration of arsenic.

In studying the effect of NOM on As(V) adsorption, background electrolytes that contained 2–15 mg/L SRNOM as C were used. The solutions with NOM were spiked with As(V) stock solution to reach As(V)

concentrations varying from 1.05 to 15.8 μM before they were mixed with 1 g/L of TiO_2 stock suspension at a volume ratio of 19:1. The ionic strength of the mixed suspension was fixed at 0.01 M NaCl.

The total concentration of arsenic remaining in the filtrate after adsorption was measured using a Perkin–Elmer optima 2000DV inductively coupled plasma–optical emission spectrometry (ICP–OES). A Finnigan Element 2 (Thermo Electron Corporation) sector field high-resolution 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 25 $\mu\text{g/L}$ (0.33 μM) and 5 ng/L ($6.7 \times 10^{-5} \mu\text{M}$), respectively.

The concentration of total organic carbon (TOC) remaining in the filtrate after an adsorption experiment was measured using a Shimadzu TOC-5050 analyzer. Fifty μL of 2 M HCl was added into 5-mL sample to drop the sample pH below 2.5. The sample was sparged with TOC grade air for 5 min before analysis. The TOC in each sample was analyzed in triplicate and the corresponding relative standard deviation was less than 5%.

Zeta potential measurement

The zeta potential of Degussa P25 TiO_2 was determined using a ZetaPals analyzer (Brookhaven Instrument Corporation). Samples were prepared following the same procedure as that for adsorption experiments except that the suspensions contained only TiO_2 (0.05 g/L) and were not filtered before the measurement of zeta potential. Due to electrode-blackening problem caused by high concentration of salt, only suspensions with low ionic strength (0.001–0.1 M) were used for zeta potential analysis. In order to examine the effect of As(V) adsorption on surface charging of TiO_2 , the zeta potential of TiO_2 suspension (0.05 g/L) that contained 3.90 μM As(V) was also measured at different pH values. The ionic strength of the suspensions with As(V) was controlled with 0.01 M NaCl.

Results and discussion

Zeta potential

The change of the zeta potential of Degussa P25 TiO_2 in NaCl with pH at different ionic strengths and As(V) levels is presented in Figure 1. The pH_{pzc} of TiO_2 under various conditions was derived using the method described in the Pena et al.^[27] The results suggest that the zeta potential of TiO_2 was insensitive to the variation of ionic strength from 0.001 to 0.01 M. In either 0.001 or 0.01 M NaCl solution, the pH_{pzc} of Degussa P25 TiO_2 was determined to be 6.7, which is in good agreement with the literature reported value.^[10]

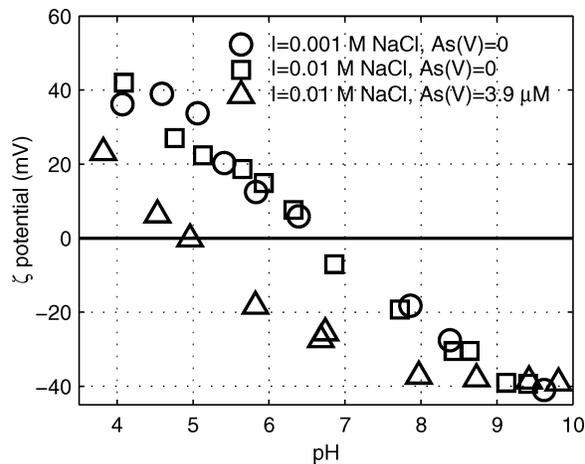


Fig. 1. Zeta potential of 0.05 g/L Degussa P25 TiO_2 as a function of pH and ionic strength in 0.001–0.01 M NaCl.

The zeta potential of TiO_2 was lower in the presence of As(V) than in the absence of As(V) when pH was below 8.0. With the presence of 3.9 μM As(V), the pH_{pzc} of TiO_2 shifted from 6.7 to 5.0.

The measurement of zeta potential is useful to distinguish inner-sphere complexes from outer-sphere complexes. According to Hunter,^[27] zeta potential measures the electrokinetic potential between the surface at the shear plane and any point in the mass of the suspending liquid. The shear plane is at the outer edge of the inner part of the double layer and near the outer Helmholtz plane or the Stern layer, depending on the models to describe the interface. In pure water, the net surface charge of TiO_2 at the interface arises from the adsorption of H^+ or OH^- on the neutral $\equiv\text{TiOH}^0$ site. When the positive charge contributed by the adsorbed H^+ is balanced by the negative charge contributed by the adsorbed OH^- , the net surface charge of the particle is zero, and the pH at this condition is termed pH_{pzc} . At the pH_{pzc} , the neutral surface is considered to interact equally with the indifferent cation and anion, which can adsorb onto the particle through the formation of outer-sphere complexes via van der Waals forces.^[20]

The non-specific ion adsorption (i.e., outer-sphere complexation) thus will not affect the zeta potential value of the particle at the pH_{pzc} , and the change of indifferent electrolyte concentration will not cause shift of the pH_{pzc} of the particle. The adsorption of cation and anion by the neutral particle at the pH_{pzc} can be asymmetric if ions that can specifically associate with the surface through the formation of inner-sphere complexes exist in the system. The specific ion adsorption (i.e., inner-sphere complexation) always occurs inside of the shear plane, and it can change the zeta potential value of the surface when the pH equals to the pH_{pzc} of the particle prior to the adsorption. The pH_{pzc} of the particle can, therefore, be changed due to the specific adsorption of ions by the surface.

Based on the theory discussed above, the significant shift of pH_{pzc} of TiO₂ to a lower value due to the presence of As(V) (Fig. 1) indicates that As(V) formed inner-sphere complexes at TiO₂ surface. The shift of pH_{pzc} of a nanocrystalline TiO₂ due to As(V) adsorption was observed by Pena et al.^[28] The researchers also provided data from spectroscopy to prove the existence of inner-sphere complexes formed between As(V) and TiO₂. The zeta potential of Degussa P25 TiO₂ in 0.001 to 0.01 M NaClO₄ was measured. The results (not shown) are not significantly different from those obtained in NaCl.

Influence of pH and ionic strength

Figure 2 shows the adsorption of As(V) onto TiO₂ as a function of pH and ionic strength in NaCl (Fig. 2a) and NaClO₄ (Fig. 2b). In either electrolyte, the adsorption of As(V) by TiO₂ decreased with increasing pH. When NaCl was used as the background electrolyte, the As(V) adsorption decreased as the ionic strength increased at low pH (4.0–6.0) and increased with increasing ionic strength at high pH (7.0–11.0) (Fig. 2a). When NaClO₄ was used as background electrolyte, the As(V) adsorption was insensitive to ionic strength at low pH (4.0–6.0) (Fig. 2b). The increase of ionic strength tended to increase As(V) adsorption onto TiO₂ when pH was from 7.0 to 11.0, which was similar to the observed ionic strength effects on As(V) adsorption in NaCl at high pH values. At low ionic strength (0.001–0.01 M), the adsorption of As(V) by TiO₂ was almost the same in NaClO₄ as that in NaCl at the same pH. When the ionic strength was high (0.1 M), the As(V) adsorption onto TiO₂ was generally higher in NaClO₄ than in NaCl at the same pH values.

Effects of ionic strength on ion adsorption edges can also be used to distinguish inner-sphere from outer-sphere complexes. According to Hayer et al.,^[29] adsorption through outer-sphere complexation can be sensitive to the variation of ionic strength because (i) the background electrolyte

ion can compete with the non-specific adsorption ion for available binding sites at the surface, and (ii) the activity of the adsorbing species can be influenced by the variation of the interfacial potential due to the changing of ionic strength as the outer-sphere complexes are located at the same plane in the generalized triple layer model with the adsorbed background electrolyte ions. Inner-sphere complexation, which occurs in a plane that is closer to the surface compared to that where the background electrolyte ions stay, is generally not affected by ionic strength. Based on this theory, our data shown in Figure 2 suggest that As(V) formed outer-sphere complex throughout the pH range tested.

The observed ionic strength effects on As(V) adsorption reflect a cooperative effect from both Na⁺ and Cl⁻/ClO₄⁻. As shown in Figure 1, the surface charge of TiO₂ was positive when pH is below pH_{pzc} , and the positively charged surface would favor ion pair formation between Cl⁻/ClO₄⁻ and TiO₂. The adsorption of As(V) by TiO₂ would thus be lowered by elevating the concentration of competitive anions (i.e., Cl⁻/ClO₄⁻). The fact that the ionic strength effect on As(V) adsorption in NaClO₄ was not as significant as that in NaCl is probably due to the different binding affinities of Cl⁻ and ClO₄⁻ onto TiO₂ surface, i.e., Cl⁻ may be more competitive in being adsorbed by TiO₂ than ClO₄⁻. By summarizing 22 references for pair formation constants of various monovalent cations and anions binding with TiO₂, Bourikas et al.^[20] concluded that Cl⁻ has a stronger binding with TiO₂ than ClO₄⁻. Their conclusion supports our observation that Cl⁻ exhibited more inhibition effect on As(V) adsorption than ClO₄⁻. When pH is above pH_{pzc} , the TiO₂ surface was negatively charged. The adsorption of Na⁺ by TiO₂ would help the surface to maintain a relatively positive charge environment at high pH values, which would slow the change of surface interfacial potential with pH resulting in a favored As(V) adsorption. The effect of Na⁺ seemed to have over-competed the competition effects from Cl⁻/ClO₄⁻, resulting in an enhanced As(V) adsorption with

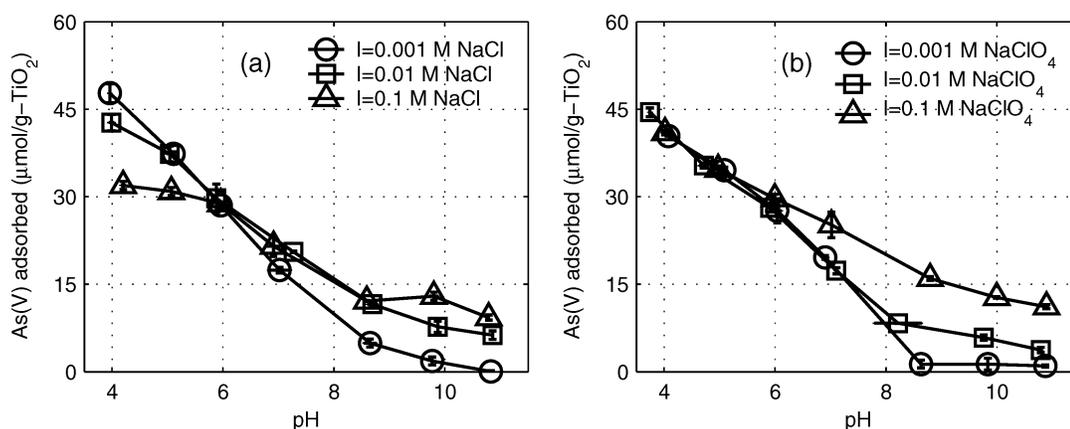


Fig. 2. As(V) adsorption onto TiO₂ as a function of pH and ionic strength in 0.001–0.1 M (a) NaCl and (b) NaClO₄. Initial As(V) concentration, 3.90 μM; Initial TiO₂ concentration, 0.05 g/L; Error bar represents the relative error for duplicate samples.

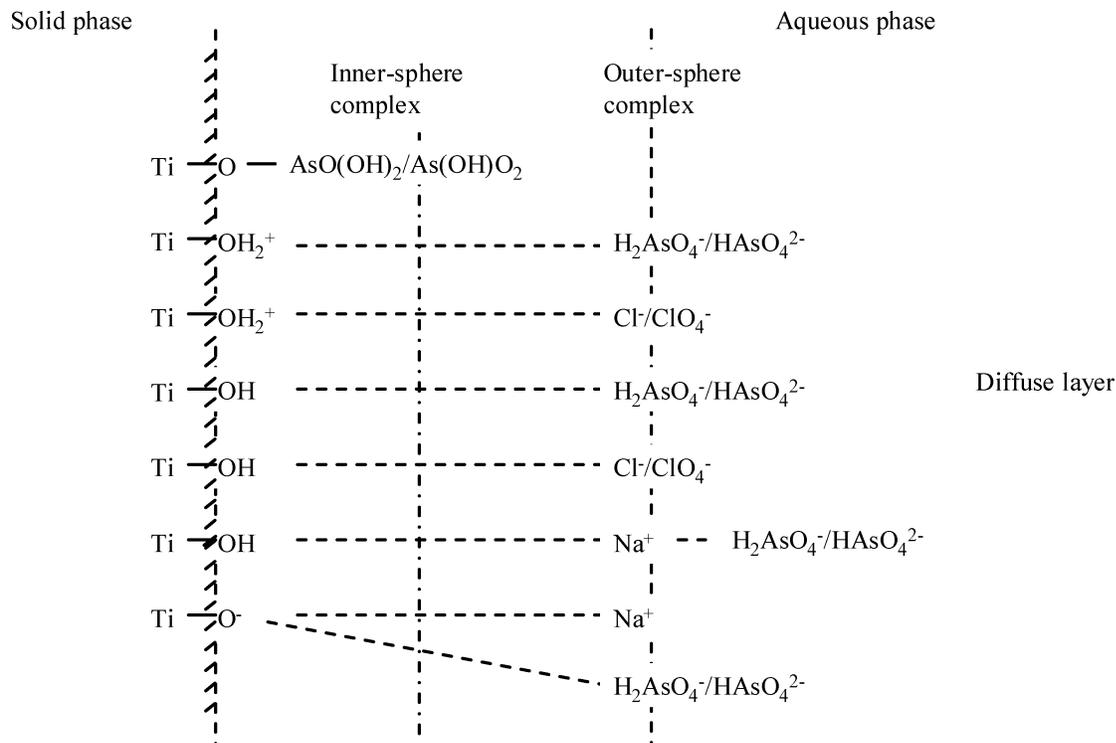


Fig. 3. Scheme of possible mechanisms for As(V) adsorption onto TiO_2 .

increasing the ionic strength. Deliyanni et al.^[18] ascribed the increased As(V) adsorption onto akaganeite with increasing ionic strength at pH 7.0–12.5 to the increased K^+ adsorption.

The effect of ionic strength on As(V) adsorption onto TiO_2 , however, did not exclude the possible formation of inner-sphere complexes between As(V) and TiO_2 . The overall data presented in Figures 1 and 2 are indicative of the coexistence of inner-sphere complex and outer-sphere complex. Possible adsorption mechanisms of As(V) onto TiO_2 are illustrated in Figure 3. Within the pH range of 4.0 to 10.0, As(V) exists primarily as H_2AsO_4^- and HAsO_4^{2-} . TiO_2 exhibits as the mixture of $\equiv\text{TiOH}_2^+$ and $\equiv\text{TiOH}^0$ at low pH and the mixture of $\equiv\text{TiOH}^0$ and $\equiv\text{TiO}^-$ at high pH.^[10] The adsorption of As(V) onto TiO_2 surface can be viewed as the interaction between $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$ and $\equiv\text{TiOH}_2^+/\equiv\text{TiOH}^0$ under acidic condition and the interaction between $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$ and $\equiv\text{TiOH}^0/\equiv\text{TiO}^-$ under alkaline condition.

Influence of NOM

The effect of NOM on As(V) removal by the adsorption onto TiO_2 at pH 6.0 is shown in Figure 4. The As(V) removal efficiency decreased with the increase of initial TOC concentration regardless of the variation of initial As(V) concentration from 1 to 15 μM . When initial As(V) concentration was 1 μM , the fraction of As(V) adsorbed onto

TiO_2 was decreased by 30.7–42.2% due to the presence of 2 to 15 mg/L SRNOM as C.

The observed NOM effects on As(V) adsorption is not surprising since NOM is also negatively charged and may compete with As(V) for available binding sites on the surface of TiO_2 . Recent studies of NOM effects on As(V) aqueous speciation distribution suggest that NOM can form complex with As(V) decreasing As(V) adsorption onto mineral surfaces.^[30] The preliminary study regarding As–NOM interaction in simulated fresh waters suggests that the complexation between As(V) and the specific NOM did not occur under the experimental conditions in this study.^[25]

Besides the competition effects, NOM can, through adsorption onto TiO_2 surface, reverse the surface charge of TiO_2 at low pH values, resulting in the decreased As(V) adsorption in presence of NOM.^[31] In another study of As(V) adsorption onto TiO_2 in the presence of NOM at various pH values, we have observed that the As(V) adsorption is less pH-dependent with NOM than without NOM, which is due to the surface charge modification of TiO_2 by NOM adsorption.^[31] It should be noted that the effect of NOM on As(V) adsorption onto TiO_2 was performed in the dark. If TiO_2 is used as a photocatalyst instead of a pure adsorbent, the NOM effects on As(V) adsorption may vary due to the photocatalytic degradation of NOM.^[32]

The measurement of TOC concentration remaining in the filtrate after As(V) adsorption suggests that there was no significant decrease of the TOC concentration after adsorption. The initial TOC concentration used in this study

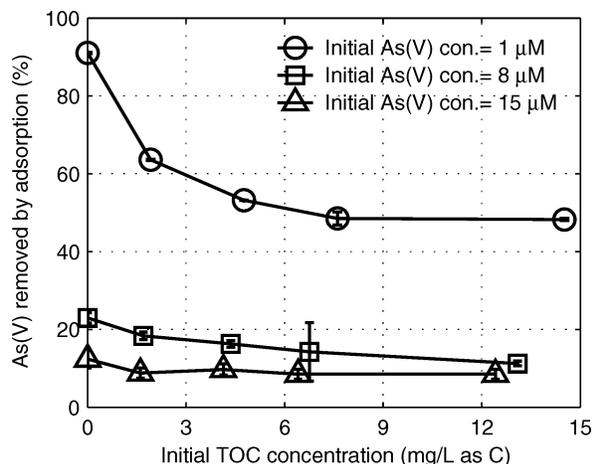


Fig. 4. As(V) removal efficiency by TiO₂ adsorption as a function of initial TOC and As(V) concentrations. I, 0.01 M NaCl; pH, 6.0 ± 0.1; Initial TiO₂ concentration, 0.05 g/L; Error bar represents the relative error for duplicate samples.

ranged from 2 to 15 mg/L as C. The load of TiO₂ was 0.05 g/L. As suggested in a previous study, about 61% of 7 mg/L as C of a lake NOM could be adsorbed onto 0.5 g/L TiO₂ at pH 5.0^[32], which is equivalent to 8.54 mg C/g-TiO₂. The surface coverage of NOM on TiO₂ could be lower given a lower initial TOC concentration or a higher pH value. Thus the decrease of TOC concentration would be lower than 0.427 mg/L as C when the load of TiO₂ was 0.05 g/L and the initial TOC concentration was below 7 mg/L as C. The difference in TOC concentration before and after TiO₂ adsorption (close to 5% of the initial) would be too low for the TOC analyzer to detect. In order to confirm this, the adsorption of NOM onto TiO₂ was examined at a higher load of TiO₂ (0.25 g/L) with an initial TOC concentration

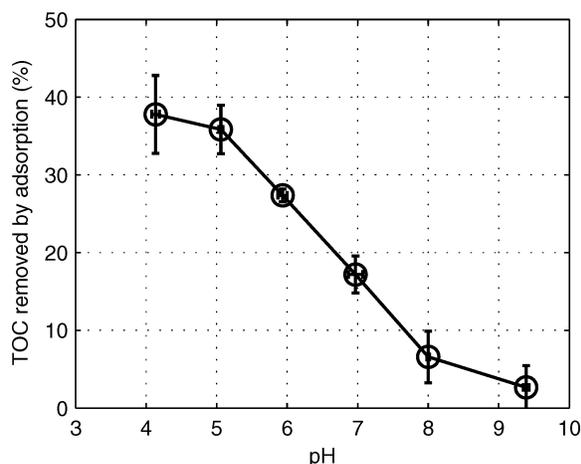


Fig. 5. NOM removal efficiency by TiO₂ adsorption as a function of pH. Initial TiO₂ concentration, 0.25 g/L; Initial NOM concentration, 8 mg/L as C, I, 0.01 M NaCl; Error bar represents the relative error for duplicate samples.

of 8 mg/L as C. The fraction of NOM adsorbed onto TiO₂ at various pH levels is presented in Figure 5. When pH of the suspension varied from 4.0 to 9.5, about 37.8–2.67% of NOM added was adsorbed onto TiO₂ surface. The surface coverage of NOM on TiO₂ at pH 6.0 was 8.77 mg C/g TiO₂, which is equivalent to 0.439 mg C/0.05 g TiO₂. This result is in reasonable agreement with the estimated value based on the data in the literature. Therefore, the relatively small proportion of NOM that was adsorbed onto TiO₂ should be responsible for the slight decrease of the TOC concentration after As(V) adsorption.

Figure 5 also suggests that the NOM adsorption onto TiO₂ decreased with the increase of pH, indicating the anionic character of NOM. The pH-dependence of NOM adsorption onto TiO₂ suggests that electrostatic interaction between NOM and TiO₂ surface is a major reason responsible for NOM adsorption onto TiO₂.

Conclusion

The influence of ionic strength, electrolyte type, and NOM on As(V) adsorption onto TiO₂ was examined. The results show that the As(V) adsorption was affected by the variation of ionic strength from 0.001 to 0.1 M. The effects of ionic strength on As(V) adsorption were more significant in NaCl than in NaClO₄ when pH was from 4.0–6.0, indicating that Cl⁻ had stronger binding with TiO₂ than ClO₄⁻. The examination of ionic strength effects on As(V) adsorption together with the measurement of zeta potential of TiO₂ with and without As(V) suggests that a mixture of inner- and outer-sphere As(V) complexes exist on the surface of TiO₂. The presence of 2–15 mg/L SRNOM decreased the adsorption of As(V) onto TiO₂, especially when the initial As(V) was low. The influence of SRNOM on As(V) adsorption onto TiO₂ is probably due to the competition of NOM with As(V) for the available binding sites on TiO₂ surface and/or the modification of surface charge of TiO₂ by NOM adsorption.

Acknowledgments

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