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Adsorption and Photocatalyzed Oxidation of Methylated Arsenic Species in TiO₂ Suspensions

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Abstract

Monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are used as herbicides in the agriculture industry. We have demonstrated that MMA and DMA are readily degraded upon TiO₂ photocatalysis. DMA is oxidized to MMA as the primary oxidation product, which is subsequently oxidized to inorganic arsenate, As(V). The adsorption of MMA and DMA on TiO₂ surface was measured as a function of initial arsenic concentration and solution pH. The pH of the solution influences the adsorption and photocatalytic degradation to a similar degree, due to the speciation of the arsenic substrates and surface charge of TiO₂ as a function of pH. The mineralization of MMA and DMA by TiO₂ photocatalysis follows the Langmuir–Hinshelwood kinetic model. Addition of *tert*-butyl alcohol, a hydroxyl radical scavenger, during TiO₂ photocatalysis dramatically reduces the rate of degradation, indicating that [•]OH is the primary oxidant. For dilute solutions, TiO₂ may also be applicable as an absorbent for direct removal of a variety of arsenic species, namely As(III), As(V), MMA, and DMA, all of which are strongly adsorbed, thus eliminating the need for a multistep treatment process.

Introduction

Arsenic, a naturally occurring and ubiquitous element found in the Earth's crust, has been reported as a contaminant in surface and groundwater from many regions of the world, including Bangladesh, Mexico, China, India, Canada, and the U.S. (1,2). The presence of inorganic arsenite As(III) and arsenate As(V), organic monomethylarsonic acid (MMA), and dimethylarsinic acid (DMA) in groundwater are a threat to human health. While inorganic arsenic species, As(III) and As(V), typically enter ground and surface water by leaching from natural sediments and soils, organoarsenic species, notably MMA and DMA, are introduced into the environment primarily through agricultural and industrial activities. MMA and DMA are active ingredients in products commonly used for weed control and defoliation prior to cotton harvesting, and occur as problematic pollutants in groundwater at sites with a history of pesticide manufacturing and improper disposal (3). In the 1990s, over 3000 metric tons per year of MMA and DMA were estimated to be applied to cotton fields in the U.S. (3). While methylation of inorganic arsenic was proposed as a biological detoxification process, recent research indicates that methylated arsenic species cause DNA damage, chromosomal aberrations, and tumor promotion in mice and rats (4,5). The treatment of As(III) and As(V) has received extensive attention because of their threat to human health through indigestion of contaminated water (6), while reports on the remediation of organoarsenic compounds is limited to only a few examples (7–10).

TiO₂ photocatalytic oxidation, a promising technology for the treatment of wastewater and the destruction of chemical waste, has been intensively investigated for the last several decades

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(11–13). TiO_2 is the most extensively used semi-conductor photocatalyst because of its low cost, biological and chemical inertness, and stability with respect to corrosion. TiO_2 photocatalysis involves the generation of the reactive oxygen species (i.e., $\cdot\text{OH}$, $\text{O}_2^{\cdot-}/\cdot\text{O}_2\text{H}$, H_2O_2 , etc.), which subsequently degrade target pollutants. The oxidation of As(III) to As(V) by UV/ TiO_2 and subsequent adsorption of As(V) on TiO_2 have been studied by several groups as a promising method for the removal of arsenic from water (14–21). The removal of arsenic below the World Health Organization drinking water limit of $10\text{ }\mu\text{g/L}$ can be achieved by TiO_2 photocatalysis under a variety of conditions. Nakajima et al. mentioned oxidation of DMA by TiO_2 photocatalysis as a possible treatment method (22,23), but detailed studies have not been reported.

In this study, we performed detailed adsorption and kinetic studies on the TiO_2 photocatalysis of MMA and DMA. Our investigations provide clear evidence that the hydroxyl radical is the primary oxidant. Products studies demonstrate that MMA and DMA are readily mineralized to arsenate during TiO_2 photocatalysis. Our goal is to investigate the potential application of TiO_2 photocatalysis for treatment and removal of methylated arsenic species as dilute contaminants in water.

Experimental Section

Materials

$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, As_2O_3 , dimethylarsinic acid were purchased from Aldrich. Monosodium methane arsonate were purchased from Chem Service Inc. (West Chester, PA). Stock solutions of different arsenic species ($668\text{ }\mu\text{M}$) were prepared in volumetric glassware. All the inorganic salts are reagent grade and used as received from Fisher. HCl is trace metal grade from Fisher. Titanium dioxide (Degussa P25, CAS no. 13463-67-7), a mixture of 80% anatase and 20% rutile with an average surface area of $50\text{ m}^2/\text{g}$, was used as photocatalyst. Ultrapure water ($18\text{ M}\Omega\text{-cm}$) used for the preparation of all solutions was obtained by filtration and distillation of deionized water.

Arsenic Analysis and Speciation

Arsenic speciation analysis was performed within 6 h of sampling, using a PS Analytical Millenium Excalibur atomic fluorescence system (AFS) coupled to a high-performance liquid chromatography (HPLC). An anion exchange column, PRP X-100 ($250\text{ mm} \times 4.6\text{ mm} \times 10\text{ }\mu\text{m}$) was used for the separation of arsenic species. Details of the analytical procedures used were described elsewhere (24).

Adsorption and Photolysis Procedure

The dark adsorption experiments were conducted using 150 mL amber HDPE bottles. A specific amount of TiO_2 powder was added to MMA or DMA solutions. The TiO_2 aqueous dispersions (100 mL) were mixed on a shaker table at 300 rpm for 1 h to ensure equilibrium adsorption. To determine arsenic adsorption, 10 mL aliquots were sampled, and filtered through a Millipore membrane filter (pore size $0.45\text{ }\mu\text{m}$). HPLC-AFS was used to determine the concentration of arsenic in solution. For photocatalysis, the TiO_2 suspensions were transferred to pyrex reaction vessels ($12 \times 1\text{ in}$, 160 mL capacity, Teflon screw top). There was no detectable adsorption of arsenic species to HDPE bottles, reaction vessels, or membrane filter. The solution was purged with the appropriate gas (Argon or air) for 15 min before illumination and during irradiation. Irradiation of the suspension was conducted in a Rayonet photochemical reactor (Southern New England Ultraviolet), model RPR-100, equipped with a cooling fan and 13 phosphor-coated low-pressure mercury lamps ($1.5\text{--}5 \times 10^{16}\text{ photon/sec/cm}^2$) blazed at 350 nm. At given time intervals, 10 mL aliquots were sampled, then filtered

and subsequently the concentrations of arsenic species in solution were analyzed. In general, triplicate experiments were performed for each set and showed the reproducibility within $\pm 5\%$.

Results and Discussion

Adsorption of MMA and DMA on TiO_2

Most of the available treatment technologies for arsenic-contaminated water are based on the processes of removing inorganic arsenic, including adsorption, ion exchange, membrane separation, and chemical precipitation (25). In an attempt to better understand the adsorption process and their effect on the TiO_2 photocatalytic degradation process, we studied the adsorption of MMA and DMA and inorganic arsenic as a function of initial arsenic concentration and solution pH.

To determine the capacity of TiO_2 to absorb MMA, DMA, As(III), and As(V) (structures shown in Table 1), the concentration of TiO_2 was varied from 1.0 to 0.005 g/L at a constant initial arsenic concentration of 13.4 μM . Our absorption studies demonstrate that adsorption equilibrium can be reached by mixing at 300 rpm in dark for 60 min.

The extent of adsorption decreases with the decrease of TiO_2 concentration, as illustrated in Figure 1. Inorganic arsenic species, As(III) and As(V) exhibit the most extensive adsorption, while MMA and DMA also exhibit significant adsorption, with MMA being adsorbed to a greater extent than DMA (26,27).

To further explore the adsorption behavior of inorganic arsenic, MMA and DMA, isotherm parameters were determined which may be relevant for treatment applications. Dark adsorption experiments were conducted at a constant TiO_2 concentration of 0.1 mg/mL and varying arsenic concentrations from 0.13 to 26.7 μM at natural pH (after mixing but without adjustment). The natural pH of the individual solutions were between 6.5 and 7.2. Langmuir adsorption isotherms were used to assess the adsorption capacities of TiO_2 for the different arsenic species. The Langmuir adsorption isotherm is often used to describe the heterogeneous adsorption process, according to the following equation (28):

$$Q_{\text{ad}} = Q_{\text{sat}} \frac{K_{\text{ad}} C_{\text{eq}}}{1 + K_{\text{ad}} C_{\text{eq}}} \quad (1)$$

where Q_{ad} is the specific adsorbed quantity of a substrate and C_{eq} is the substrate concentration; K_{ad} is the adsorption constant and Q_{sat} is the saturation (maximum) adsorption, designated here as adsorption capacity. Unique adsorption sites, monolayer adsorption, and no interaction between the adsorption sites are the assumptions used in deriving the Langmuir isotherm.

The adsorption of arsenic species is nicely described by Langmuir isotherm with correlation coefficients (R^2) from 0.969 to 0.999. The adsorption parameters Q_{sat} and K_{ad} are listed in Table 2. The adsorption capacity, Q_{sat} , of the inorganic species is 1.5–2.0 times greater than MMA and 3–4 times greater than DMA. The presence of the two methyl groups and only one hydroxyl group on DMA compared to MMA with one methyl group and two hydroxyl groups has direct influence on the adsorption behavior. While the methyl groups have different electronic, spatial, and geometric influences on the adsorption compared to hydroxyl groups, the hydroxyl groups are known chelating groups to the TiO_2 surface (27). Our results are consistent with a recent paper which gives an excellent account of the possible effects of the substituents on the adsorption of MMA and DMA versus As(V) on iron oxides (10).

Based on an estimated density of TiO_2 surface hydroxyl groups, ranging from 3.3 to 5.4 nm^{-2} (29,30), the maximum absorbed concentration corresponds to between $10 \pm 2\%$ monolayer coverage for DMA, $25 \pm 6\%$ for MMA, and $38 \pm 9\%$ for As(V). The adsorption

capacity ratio of DMA:MMA: As(V) is approximately 1:2:3, which parallels the ratio of hydroxyl groups (chelating groups) in the three arsenic species. The coverage of As(V) > MMA > DMA is also consistent with the explanation that hydroxyl groups increase the adsorption capacity.

Effect of pH on Adsorption

The solution pH can have a pronounced effect on the speciation of arsenic species and the surface charge of TiO₂, and therefore plays a key role in the TiO₂ adsorption and photocatalysis of arsenic species. At constant arsenic and TiO₂ concentrations, the solution pH was adjusted from 3 to 11 using 0.04 M HCl and 0.04 M NaOH. To maintain constant ionic strength, NaCl (0.04 M) was employed. The adsorptions of MMA and DMA were determined from the difference between the initial concentration and the concentration that remained in solution following addition and equilibration with TiO₂. The adsorptions of MMA and DMA as a function of pH are shown in Figure 2. MMA and DMA exhibit higher adsorptions at lower pH. DMA displays a maximum adsorption (~80%) at pH 5, which decreases gradually as the pH increases. The adsorption of MMA is >95% from pH 3 to 8 and drops gradually above pH 9. The adsorption behavior is dependent on the charges of MMA and DMA and the TiO₂ surface. TiO₂ has a point of zero charge (pzc) of 6.8; therefore, under acidic conditions, the positive charge of the TiO₂ surface increases as the pH decreases; above pH 6.8, the negative charge at the surface of TiO₂ increases with the increasing pH. MMA is neutral at pH < 4.1, and exists predominantly as a monoanion between pH 4.1 and 8.7, and as dianion at pH > 8.7 (8), where electrostatic repulsion between the double negatively charged MMA and the negatively charged TiO₂ surface leads to significant decrease in adsorption. At alkaline conditions, hydroxide ion may also compete with arsenic species for surface adsorption. The solution pH could also have an effect on the co-aggregation of TiO₂ and reduce the effective surface area. The observation that adsorption generally decreased with increasing pH, where the expectation is that co-aggregation of TiO₂ would be minimized because of electrostatic repulsion indicates co-aggregation alone cannot account for the observed results. Co-aggregation and surface area may be important but must be further investigated to access their roles.

DMA exists predominately as a monoanion at pH > 6.1 and as neutral at pH < 6.1 (8). Adsorption of DMA increased slightly from pH 3 to 5, and then decreases with increasing pH. The adsorption data for neutral DMA indicated that the fully protonated species was adsorbed in the presence of a nonspecifically adsorbed ion (ionic strength buffer, 0.04 M NaCl), which was present in concentration much greater than DMA. There was little electrostatic attraction between the neutral DMA and TiO₂ below pH 5. DMA is absorbed to a less extent than MMA throughout the pH range from 3 to 11, which is consistent based on the number of hydroxyl groups (chelating groups) and the differences of their pK_a. The observed MMA and DMA adsorption behavior on Degussa P25 TiO₂ is consistent with the hydroxyl chelation reported by Jing et al. (27) for nanocrystalline titanium oxide and those by Lafferty and Loeppert for iron oxides, goethite, and ferrihydrite (10). We propose similar adsorption mechanisms for MMA and DMA onto P25 TiO₂, where DMA forms monodentate inner sphere complex, and MMA forms bi-dentate inner sphere complex (27).

TiO₂ Photocatalytic Oxidation

We subjected MMA and DMA to TiO₂ photocatalysis using 350 nm light. The photocatalytic oxidation of MMA and DMA was highly efficient in the air-saturated suspensions as illustrated in Figure 3. In the absence of dissolved oxygen (under argon saturation), the degradation of both MMA and DMA was negligible. The degradations of MMA and DMA in the dark or by direct photolysis in the absence of TiO₂ were also insignificant. These control experiments clearly illustrate that the conversion of MMA and DMA involves TiO₂ surface mediated photocatalysis. Modest decreases in the concentrations of dissolved MMA and DMA were

observed for the dark controls in the presence of TiO_2 , due to the surface adsorption. The degradation of MMA and DMA under TiO_2 photocatalytic oxidation occurred with half-lives of approximately 4 and 7 min for MMA and DMA, respectively.

While these results clearly demonstrated that MMA and DMA are readily degraded by TiO_2 photocatalysis, it is important to identify the reaction byproducts of the treated solutions. TiO_2 photocatalytic oxidation of As(III) is extremely fast, involving oxidation of the arsenic atom to pentavalent oxidation state (14–20). The arsenic atom of MMA and DMA is in the pentavalent (fifth) oxidation state and is not expected to be further oxidized. The TiO_2 photocatalysis of MMA and DMA was monitored at specific irradiation times, as illustrated in Figure 4. Arsenate is the final product for both MMA and DMA oxidation. The TiO_2 photocatalysis of DMA leads to MMA, which is subsequently mineralized to As(V). The modest decrease (10–20%) in total arsenic mass balance at longer reaction times was attributed to the stronger adsorption of the oxidation product, As(V).

Effect of Initial pH on Photocatalysis

Since the adsorption of MMA and DMA on the surface of TiO_2 depends on solution pH, we investigated its role during TiO_2 photocatalysis. The photocatalysis of MMA and DMA was monitored at solution pH 3, 7, and 10. The pH of the initial solution was adjusted to the desired value. The pH was not adjusted during irradiation since we were determining the initial rates (first 10–20%). At such low conversion we do not expect significant changes in the solution pH and the products are present in relatively low concentrations. The fastest degradation of MMA was observed at pH 3 and 7, while the degradation of DMA was fastest at pH 3, and slightly slower at pH 7. Both MMA and DMA are degraded relatively slowly at pH 10. These trends are consistent with the pH effect of the adsorption as described earlier. The degradation of MMA and DMA correlates to their adsorption as reported for other substrates (31).

Influence of the Initial Concentrations

The Langmuir–Hinshelwood model has been extensively applied to describe TiO_2 photocatalytic degradation for a variety of substrates (32). Its kinetic parameters can be valuable for modeling and predicting specific treatment objectives. The initial degradation rate (r_0), under air saturated condition (constant oxygen concentration), was described by this well-known kinetic model, applied to a batch reactor:

$$\frac{1}{r_0} = \frac{1}{k_r K C_0} + \frac{1}{k_r} \quad (2)$$

where C_0 is the initial MMA or DMA concentration, k_r is often interpreted as a pseudo-first-order Langmuir–Hinshelwood-type rate coefficient relating to TiO_2 -sensitized primary oxidation events in a monolayer surface, and K is a pseudo-equilibrium constant related to monolayer adsorption. The photocatalytic experiments were performed at different initial concentrations of MMA and DMA from 0.67 to 26.7 μM and a constant TiO_2 concentration of 0.1 mg/mL. The Langmuir–Hinshelwood kinetic parameters were determined from the slope and intercept of the linear fit of $1/r_0$ vs $1/C_0$ (coefficient of determination $R^2 = 0.993$ for MMA and 0.998 for DMA). Under our experimental conditions, the rate constant k_r of MMA (1.78 $\mu\text{mol L}^{-1} \text{min}^{-1}$) is higher than DMA (1.04 $\mu\text{mol L}^{-1} \text{min}^{-1}$), which is consistent with the observation that the initial TiO_2 photocatalytic degradation of MMA is faster than DMA (Figure 1). The apparent equilibrium constants (K) for MMA and DMA are 0.033 and 0.108 L/ μmol , respectively, which is contrary to expectation. The Langmuir–Hinshelwood (L–H) kinetic model assumes noncompetitive adsorption between products and starting material. The initial product of MMA is arsenate and the initial product of DMA appears to be MMA. These products adsorb more strongly than the starting compounds DMA and MMA, and thus the pseudo-equilibrium constants (K) may be adversely influenced as observed under our

experimental conditions. Multilayer adsorption by MMA or DMA could also have an adverse effect on the apparent kinetic parameters obtained from the L–H model, which assumes monolayer coverage.

The pseudo-equilibrium constant (K) measured under irradiation for MMA and DMA and the adsorption constant K_{ad} measured in the dark (listed in Table 2) for the same compound are not in agreement. Others have reported similar observations, i.e., 13- and 220-fold differences have been reported for benzyl alcohol (33) and 4-chlorophenol (34), respectively. The apparent variability in the adsorption constants may be related to the changes in the adsorptive sites of the TiO_2 surface upon irradiation and competitive adsorption among reaction products. The possibilities of significant photoadsorption and/or involvement of reaction steps occurring in the double layer may also contribute to such observations. Furthermore, it has been demonstrated that the adsorption constant is a function of the light intensity and the electronic properties of the TiO_2 surface can undergo dramatic changes upon illumination by altering the adsorption sites (35).

Mechanistic Implications

As(III) oxidation in the UV/ TiO_2 system has been examined by several groups (15–20). Although the oxidation reaction has been shown to be robust over a wide pH range, details of the degradation pathway have been controversial.

The pollutant destruction during TiO_2 photocatalytic oxidation is mainly ascribed to the strong oxidation potential of the photogenerated valence band (VB) holes in TiO_2 ($E_{VB} = +2.7$ V as NHE at pH 7). Photoexcitation of TiO_2 leads to the formation of electron (conduction band) and hole (valence band) pair (eq 3). In the absence of an electron or hole trap, recombination of the e^-/h^+ pair occurs via thermal decay. In aerated aqueous suspensions, oxygen acts as an electron trap leading to superoxide anion radical (eq 4), prolonging the lifetime of hole, which subsequently leads to the formation of the surface associated hydroxyl radicals (eq 5). Hydroxyl radical, $\bullet\text{OH}$, is a strong oxidant and follows typical radical oxidation pathways.

In general, $\bullet\text{OH}$ is the dominant oxidant in most TiO_2 photocatalytic reactions (12,13). To investigate the role of $\bullet\text{OH}$ in MMA and DMA oxidation, $t\text{-BuOH}$, a commonly used $\bullet\text{OH}$ radical scavenger (eq 6), was added in the system (36).

As shown in Figure 6, adding excess $t\text{-BuOH}$ (100 times) inhibited the oxidation of both MMA and DMA by >80%, which provides convincing evidence for the participation of $\bullet\text{OH}$ in the oxidation of these two methylated arsenic species.

The oxidation appears to be a hydroxyl mediated process in which the methyl groups are cleaved from the arsenic atom. An analogous transformation has been reported for methyl phosphonates (37,38). From these previous studies, we expect the methyl groups in MMA and DMA to be oxidized ultimately leading to the cleavage of the arsenic–carbon bond. The detailed mechanism is still under investigation.

In summary, TiO₂ photocatalytic oxidation of MMA and DMA leads to mineralization to As (V). Hydroxyl radical appears to be the main oxidant during TiO₂ photocatalysis of MMA and DMA. Both MMA and DMA exhibit a strong affinity to TiO₂, which is advantageous for treating dilute solutions. The adsorption capacity on TiO₂ is As(V) > MMA > DMA, which is consistent with the number of hydroxyl (chelating) groups. The adsorption and oxidation of MMA and DMA during TiO₂ photocatalysis also parallel the electrostatic interactions between the TiO₂ surface and the arsenic species as a function of solution pH. The photocatalytic oxidation of MMA and DMA leads to cleavage of the arsenic carbon bond, ultimately yielding As(V). Ferguson and Hering have demonstrated the use of a fixed-bed, flow-through reactor is effective for the removal of inorganic arsenic based on TiO₂ photocatalytic oxidation (13). Since MMA and DMA are strongly adsorbed and readily oxidized to As(V) during TiO₂ photocatalysis, such a fixed-bed reactor should also be effective for treatment and removal of MMA and DMA from aqueous solution. The influence of humic materials and related substances present in natural water on the efficiency of TiO₂ for the removal of arsenic species must be carefully evaluated, but our results suggest that TiO₂ photocatalysis has tremendous potential for the removal of organoarsenic species, MMA and DMA, as well as inorganic arsenic species, from water.

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FIGURE 1. Percentage of adsorbed arsenic species as a function of TiO₂ concentration. [As(III)]₀ = [As(V)]₀ = [MMA]₀ = [DMA]₀ = 13.4 μ M, pH around 6.8. Error bars represent one standard deviation based on triplicate experiments.

FIGURE 2. pH effect of MMA and DMA adsorption on TiO₂. [MMA]₀ = [DMA]₀ = 13.4 μM. TiO₂ = 1.0 g/L, 0.04 M NaCl. Error bars represent one standard deviation based on triplicate experiments.

FIGURE 3.

Time profiles of (a) MMA and (b) DMA oxidation in the TiO_2 suspension under various reaction conditions. $[\text{MMA}]_0 = [\text{DMA}]_0 = 13.4 \mu\text{M}$, $\text{TiO}_2 = 0.1 \text{ g/L}$, pH around 6.8, $\lambda = 350 \text{ nm}$.

FIGURE 4.

Relative concentrations of arsenic species in the solutions during TiO_2 photocatalytic oxidation of (a) MMA and (b) DMA as a function of irradiation time. $[\text{MMA}]_0 = [\text{DMA}]_0 = 13.4 \mu\text{M}$, $\text{TiO}_2 = 0.1 \text{ g/L}$, air-saturated.

FIGURE 5. pH effect on TiO_2 photocatalysis of MMA and DMA. $[\text{MMA}]_0 = [\text{DMA}]_0 = 13.4 \mu\text{M}$. $\text{TiO}_2 = 0.1 \text{ g/L}$.

FIGURE 6.

Effect of *t*-BuOH addition on the photocatalytic oxidation of MMA and DMA. $[MMA]_0 = [DMA]_0 = 13.4 \mu\text{M}$, $\text{TiO}_2 = 0.1 \text{ g/L}$, $[t\text{-BuOH}] = 1.34 \text{ mM}$, air-saturated.

TABLE 1Structure and pK_a Values of Four Arsenic Species

Arsenic Species	Structure	pK_a (8)
As(III)		9.23, 12.1, 12.7
As(V)		2.22, 6.98, 11.53
MMA		4.1, 8.7
DMA		6.2

TABLE 2Langmuir Parameters for MMA and DMA Adsorption on Degussa P25 TiO₂ at pH around 6.8

arsenic species	Q_{sat} ($\mu\text{mol/g}$)	$K_{\text{ad}} \times 10^2$ ($\text{L}/\mu\text{mol}$)	R^{2a}
As(III)	172	2.4	0.969
As(V)	159	6.8	0.999
MMA	86	11.8	0.999
DMA	37	14.1	0.995

^a R^2 is the coefficient of determination for the linear fit of $1/Q_{\text{ad}}$ vs $1/C_{\text{eq}}$.