Mechanistic Evaluation of Arsenite Oxidation in TiO_2 Assisted Photocatalysis

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We report herein a detailed assessment of the roles of O_2, H_2O_2, $^{\bullet}OH$, and $O_2^{-\bullet}$ in the TiO_2 assisted photocatalytic oxidation (PCO) of arsenite. Although both arsenite, As(III), and arsenate, As(V), adsorb extensively onto the surface of TiO_2, past studies relied primarily on the analysis of the arsenic species in solution, neglecting those adsorbed onto the surface of TiO_2. We used extraction and analyses of the arsenic species adsorbed onto the surface of the TiO_2 to illustrate that the oxidation of As(III) to As(V) occurs in an adsorbed state during TiO_2 PCO. The TiO_2 photocatalytic oxidation (PCO) of surface adsorbed As(III) in deoxygenated solutions with electron scavengers, Cu^{2+}, and polyoxometalates (POM) yields oxidation rates that are comparable to those observed under oxygen saturation, implying the primary role of oxygen is as a scavenger of the conduction band electron. Pulse radiolysis and competition kinetics were employed to determine a rate constant of 3.6×10^6 M^{-1} s^{-1} for the reaction of As(III) with $O_2^{-\bullet}$. Transient absorption studies of adsorbed hydroxyl radicals, generated by subjecting colloidal TiO_2 to radiolytic conditions, provide convincing evidence that the adsorbed hydroxyl radical (TiO_2+$^{\bullet}OH$) plays the central role in the oxidation with As(III) during TiO_2 assisted photocatalysis. Our results suggest the reaction of superoxide anion radical does not contribute in the conversion of As(III) when compared to the reaction of As(III) with $^{\bullet}OH$ radical during TiO_2 PCO.

Introduction

Arsenic is one of the most problematic water contaminants in the world, and approximately 100 million people are at health risks worldwide due to drinking arsenic contaminated water. The main source of arsenic is geological, but human activities such as mining and pesticides can also cause arsenic pollution.[1,2] The toxicity of arsenic to human health ranges from skin lesions to cancer of the brain, liver, kidney, and stomach.[3,4] Recently, the European Union and the United States government have lowered the maximum contaminant level for total arsenic to 10 μg/L (10 ppb) in drinking water.[5]

Arsenic exists mainly as the As(III) and As(V) oxyanions, arsenite (H_3AsO_3) and arsenate (H_3AsO_4). The distribution between As(III) and As(V) and their speciation in water depends on redox potential and pH. Under groundwater conditions, As(III) is the predominate form of arsenic, which is much more toxic and mobile than As(V). As(III) has low affinity with mineral surfaces while As(V) adsorbs easily to solid surfaces.[6,7] The oxidation of As(III) to As(V) is highly desirable for enhancing the immobilization of arsenic and is required for most arsenic removal technologies. The most common method of arsenic removal is coagulation with iron salts and/or alumina, followed by microfiltration.[8,9]

TiO_2 assisted photocatalysis is an advanced oxidation process for the remediation of polluted water and air.[10−12] Although the majority of TiO_2 assisted PCO studies involve organic substrates as model pollutants, photocatalytic oxidation of inorganic species has also been demonstrated.[13,14] Advanced oxidation technologies (AOTs) including TiO_2 PCO, lead to the formation of a number of reactive species, notably hydroxyl radical, hydrogen peroxide and superoxide radical anion. The considerable promise for pollutant destruction by TiO_2 PCO is mainly ascribed to the strong oxidation potential of the photogenerated valence band (VB) holes in TiO_2 ($E_{VB} = +2.7$ V vs NHE at pH 7), which yield $^{\bullet}OH$ from the oxidation of surface adsorped H_2O or OH groups.[15]

TiO_2 photocatalysis has tremendous potential for the treatment of arsenic contaminated water. The conversion of As(III) to As(V) in UV-irradiated TiO_2 suspension has been reported by a number of groups.[16−20] Most of these studies assess the conversion of As(III) during TiO_2 photocatalysis by monitoring the As(III) concentrations in solution (typically a minor fraction of the arsenic species) and do not specifically address the extent and conversion of As(III) and As(V) adsorbed (often > 90%)[21] onto the TiO_2. While it was reported that $O_2^{-\bullet}$ is the main oxidant in the conversion of As(III) to As(V) during TiO_2 PCO,[17,18] radiolysis and sonolysis studies indicate that $O_2^{-\bullet}$/$HO_2^{\bullet}$ do not appreciably convert As(III) to As(V).[22,23] A number of reports also suggest hydroxyl radical or valence band hole plays a key role in the TiO_2 PCO of As(III).[16,20] Given the conflict surrounding the role of superoxide anion radical and hydroxyl radicals during advanced oxidative treatment and TiO_2 PCO of As(III), we have conducted detailed mechanistic studies in an attempt to resolve the roles of the different reactive species formed at the surface of TiO_2 during photocatalysis. Radiolysis and competitive kinetic studies were used to access the reaction of $O_2^{-\bullet}$ with As(III). Radiolysis of TiO_2 colloids was used to generate adsorbed hydroxyl radicals (trapped holes) which decay as a function of the concentration of As(III). This study indicates

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the oxidation of As(III) by hydrogen peroxide and superoxide anion radicals are relatively slow compared to oxidation by adsorbed hydroxyl radicals during TiO_2 PCO.

Experimental Section

Materials. $Na_2HAsO_4 \cdot 7H_2O$ and As_2O_3 were purchased from Aldrich and used as the source of arsenate and arsenite, respectively. Then, 668 μM solutions were prepared as stock solutions. NaOH, $NaBH_4$, phosphate, KSCN, $HClO_4$, $Cu(NO_3)_2$ and titanium(IV) isopropoxide were reagent grade and used as received from Fisher. HCl was trace metal grade from Fisher and 1-propanol was HPLC grade from Fisher. Reagent grade $SiW_{12}O_{40}^{4-}$(Aldrich) was used as the polyoxometalate (POM). 1,4-Benzoquinone was purchased from Aldrich and purified by sublimation. Titanium dioxide (Degussa P25, CAS Registry No.: 13463-67-7), with an average surface area of 50 m^2/g, was used as the photocatalyst. Ultrapure water used for the preparation of all solutions was obtained by filtration (US Filter Company) and distillation of deionized water.

Photolysis Procedure. A specific amount of TiO_2 powder was added to arsenite solutions. The TiO_2 aqueous dispersions (100 mL) were mixed on a shaker table in the dark at 300 rpm for 1 h to ensure equilibrium adsorption prior to illumination. The suspensions were transferred to Pyrex reaction vessels (12 $\times$ 1 in., 160 mL capacity, Teflon screw top) and purged with air or argon for 15 min and sealed before irradiation. Irradiation of the semiconductor suspensions was conducted in a Rayonet photochemical reactor (Southern New England Ultraviolet), model RPR-100, equipped with 16 phosphor-coated low-pressure mercury lamps ($1.5-5 \times 10^{16}$ (proton/s)/cm^3) blazed at 350 nm and a cooling fan.

Sampling and Extraction. At given time intervals, 10 mL aliquots were sampled and then centrifuged at 10 000 rpm for 20 min. The supernatant was filtered through a Millipore membrane filter (pore size 0.45 μm) and subsequently analyzed by HPLC-AFS to determine the individual arsenite and arsenate concentrations present in solution. Extraction was required to desorb the arsenic species from the catalyst for analyses. A variety chemical extraction methods have been applied for understanding arsenic bonding and speciation in soils.[7] We tested and modified a number of extraction methods, including ligand exchange, H^+-enhanced dissolution, and OH^--enhanced dissolution in the development of a method to determine the speciation and concentration of arsenic species adsorbed on the surface of TiO_2. Among the methods tested, extraction with 1 M K_2HPO_4 was the most effective procedure yielding recoveries of >85% of As(III) and As(V) from the TiO_2 surface. Because of interferences from the high concentration of phosphate, accurate HPLC-AFS detection of arsenite and arsenate individually was not possible, hence a citrate buffer (0.4 M, pH 4.4) was used to selectively measure and monitor As(III).[24] In parallel experiments, the extracts were treated with 12.5% HCl (v/v) and subsequently analyzed by direct AFS for the determination of total arsenic. The As(V) concentration is calculated from the difference in concentrations of total arsenic and As(III).

Arsenic Analyses. As(III) and As(V) were determined by a PS Analytical Millenium Excalibur Atomic Fluorescence System, AFS (PSA 10.055) coupled to a HPLC (anion exchange column, PRP X-100, 250 mm $\times$ 4.6 mm $\times$ 10 μm). Details of the analytical procedures used are described elsewhere.[23]

Pulse Radioysis. Pulse radiolysis experiments were performed utilizing the Notre Dame 8-MeV Titan Beta model TBS-8/16-1S electron linear accelerator with a pulse length of 2.5−10 ns.[25] A typical experiment consisted of a series of 6−10 replicate shots, which were averaged for each determination. For dilute aqueous solutions, the irradiation energy is absorbed mainly by the solvent water, resulting in the formation of a number of reactive species, eq 1.

$$H_2O \rightsquigarrow {}^{\bullet}OH\,(2.7) + e_{aq}^{-}\,(2.7) + H^{\bullet}(0.55) + H_2\,(0.45) + H_2O_2\,(0.71) + H_{aq}^{+}\,(2.6) \quad (1)$$

The G values in the parentheses are defined as the number of species formed from 100 eV adsorbed energy. Dosimetry of the system was based on the oxidation of SCN^- to $(SCN)_2^{-\bullet}$ in N_2O saturated aqueous solutions assuming $\epsilon_{472\ nm}(SCN)_2^{-\bullet} = 7580\ M^{-1}\ cm^{-1}$ and $G = 6.13$.[26]

Preparation of Colloids. In a typical preparation, 2.5 mLs of titanium(IV) isopropoxide was dissolved in 25 mLs of 1-propanol to get 10% titanium(IV) isopropoxide in 1-propanol. A 1 μM TiO_2 colloidal solution was obtained by adding 2.97 μL of 10% titanium(IV) isopropoxide slowly in to 1.0 L of water. The solution pH was adjusted to 1.5 using 1 M $HClO_4$ to stabilize the TiO_2 colloids.[27]

Results and Discussion

Adsorption and Conversion of As(III) during TiO_2 PCO. Previous studies on the TiO_2 PCO of arsenite are based primarily on the analyses of the arsenic species in solution, with little or no monitoring of the As(III) and As(V) adsorbed on the surface of TiO_2. Since the major fraction of arsenic is adsorbed onto TiO_2 surface, we employed an extraction procedure to recover and distinguish the arsenic species bound to the catalyst surface. In a typical experiment, an arsenic containing TiO_2 aqueous suspension was irradiated at 350 nm and samples were taken at specific time intervals. The catalyst was filtered from solution and subjected to an extraction procedure to recover the adsorbed arsenic species. Excellent arsenic mass balances (≥95%) of the surface bound and dissolved arsenic species were obtained throughout our TiO_2 PCO studies. Analyses of the reaction solution and catalyst extracts were conducted to determine the levels of surface bound and dissolved As(III) and As(V).

Dark control experiments confirmed that no appreciable change occurred in the speciation of As(III) and As(V) during extraction or analysis procedures. The adsorption of As(III) onto the surface of the TiO_2 prior to irradiation is greater than 97% under our experimental conditions. The oxidation of As(III) is extremely fast, and within 1 min of irradiation of the TiO_2 suspension >90% of the As(III) has been converted to As(V), as illustrated in Figure 1. Both As(III) and As(V) are strongly adsorbed onto the catalyst with less than 5% in solution. Results from the analyses of the surface bound arsenic fractions confirm the oxidation of As(III) to As(V) occurs at the surface of the catalyst as previously suggested by a kinetic modeling study.[21]

Conversion of As(III) to As(V) by direct photolysis at 350 nm (in the absence of TiO_2) under air saturated conditions was insignificant (<5%) after 1 h of irradiation and the rates of oxidation in the absence of light or catalyst were also insignificant compared to those observed for TiO_2 PCO. While the control experiments clearly illustrate that the conversion of As(III) involves surface-mediated photocatalysis, the mechanism of the oxidation process is unclear.

The oxidation of As(III) by hydroxyl radical involves the formation of As(IV) which disproportionates to yield As(III) and As(V). As(IV) can also undergo oxidation by dissolved oxygen to form As(V).[28]

TiO_2 PCO involves a complex series of competing reaction processes. Absorption of light greater than the band gap energy

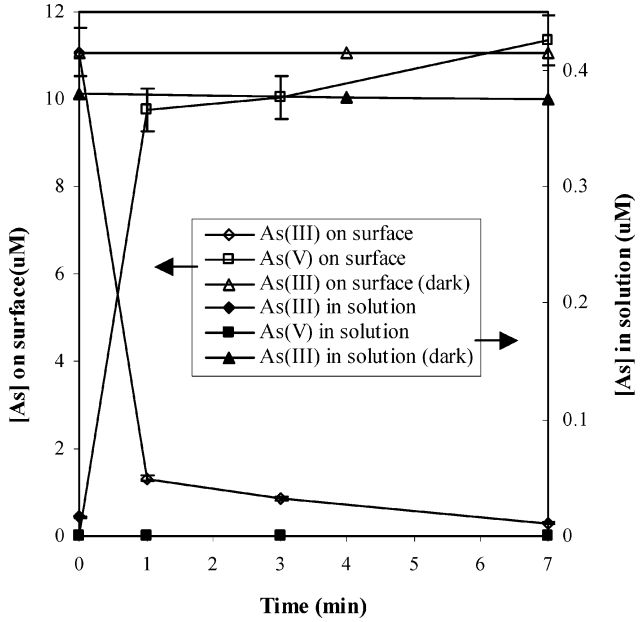

Figure 1. Concentration of As(III) and As(V) on the surface of TiO_2 and in solution during TiO_2 PCO. (air saturation, TiO_2 = 1.0 mg/mL, and $[As(III)]_0$ = 13.4 μM). The experimental error in the analytical measurements is <5% based on triplicate runs.

(wavelengths ≥ 350 nm) results in charge separation producing an electron (e^-_{CB})/hole (h^+_{VB}) pair (eq 2).

$$TiO_2 + h\nu \rightarrow h^+_{VB} + e^-_{CB} \quad (2)$$

These charge carriers can recombine, or participate in the redox processes at the interface. Oxygen is commonly used to scavenge the e^-_{CB} (eq 3), thus extending the lifetime of the h^+_{VB} and promoting oxidation processes at the interface. In aqueous media the h^+_{VB} interacts with surface hydroxyl groups and forms surface bound •OH groups, eq 4 and 5.[15] For the purposes of this paper, we will refer the trapped hole and surface adsorbed hydroxyl radical, •OH, as indistinguishable.

$$e^-_{CB} + O_2 \rightarrow \cdot O_2^{-\bullet} \quad (3)$$

$$h^+_{VB} + H_2O \rightarrow {}^\bullet OH + H^+ \quad (4)$$

$$h^+_{VB} + OH^- \rightarrow {}^\bullet OH \quad (5)$$

While superoxide anion radical and hydrogen peroxide are formed during TiO_2 PCO, •OH is generally believed to play the primary role in promoting oxidation during TiO_2 PCO. The formation of hydrogen peroxide can occur through the combination of two hydroxyl radicals or from reactions of superoxide anion radical. While hydrogen peroxide is formed during TiO_2 PCO given the short reaction time required for conversion of As(III) to As(V), we do not expect an appreciable amount of hydrogen peroxide to be formed. Under our experimental conditions the level of hydrogen peroxide in solution was below the detection limit (20 μM), as determined using the colorimetric method described by Fang et al.[29] At a much higher concentration of H_2O_2 concentration than expected during the initial stages of TiO_2 PCO, we observe relatively slow conversion of As(III), consistent with the literature.[30] Thus, we conclude the formation of H_2O_2 and its subsequent reaction leading to the oxidation As(III) were insignificant compared to the conversion of As(III) by TiO_2 PCO.

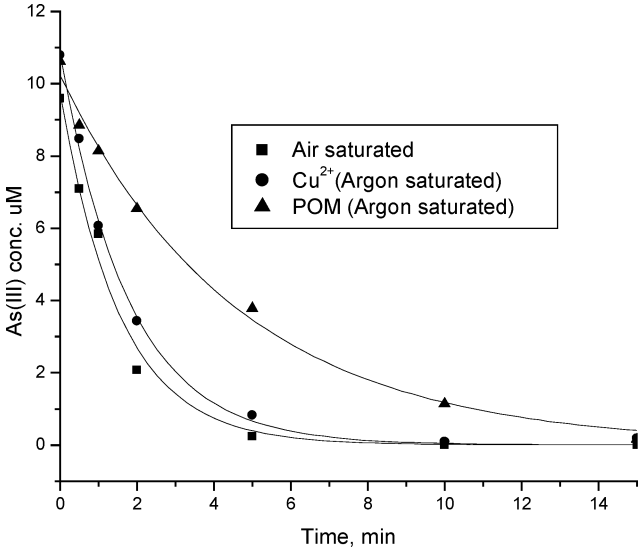

Figure 2. Effect of different scavengers on As(III) photocatalysis ([As(III) = 13.4 μM, TiO_2 = 0.1 mg/mL, $[Cu^{2+}]$ and [POM] = 1340 μM,).

While hydroxyl radical induced oxidation is generally considered to be the predominant process during TiO_2 PCO, superoxide anion radical can also act as an oxidant. Our results using gamma radiolysis to selectively generate $O_2^{-\bullet}/HO_2^\bullet$ showed minimal conversion of As(III) to As(V).[22] The addition of superoxide dismutase (SOD) to solutions subjected to ultrasonic irradiation (under $O_2^{-\bullet}$ or •OH generating conditions) showed no effect on the oxidation of As(III) to As(V), while •OH scavengers had a dramatic effect, indicating •OH-mediated oxidation.[22,23] In contrast recent reports indicate that superoxide anion radical is responsible for the conversion of As(III) during TiO_2 photocatalysis.

To probe the role of oxygen, Cu^{2+} and POM (polyoxometalate) were employed as alternate electron scavengers.[31,32] It was reported that the rate of PCO of As(III) is enhanced by POM because POM acts as an electron shuttle between e^-_{cb} and O_2, but the corresponding experiments in the absence of oxygen were not reported.[18] Our control experiments confirm that in the absence of an electron scavenger and in the absence of TiO_2 with any of the employed electron scavengers no conversion of As(III) is observed.

The conversions of As(III) with oxygen as the electron scavenger (air saturated conditions) and under argon saturation with electron scavengers Cu^{2+} and POM are illustrated in Figure 2. The concentrations of Cu^{2+} and POM were comparable to typical dissolved oxygen concentrations and significantly higher than the concentrations of As(III). With Cu^{2+} as the scavenger under argon saturated conditions, the oxidation rate of As(III) is similar to the rate observed under oxygen saturated conditions without Cu^{2+}. The rate of As(III) conversion is slightly reduced when POM is the electron scavenger compared to oxygen, possibly the result of back electron transfer and/or relatively weak adsorption of anionic POM at the surface of the catalyst.

These results demonstrate a number of electron scavengers can be used during TiO_2 PCO to effectively oxidize As(III) and the primary role of oxygen appears to be as an electron scavenger. While this does not rule out the possibility that superoxide anion radical can play an important role under oxygenated conditions during PCO, superoxide anion radical is not required for effective oxidation of As(III) during TiO_2 PCO.

The Reaction of Superoxide Anion Radical with As(III). Pulse radiolysis techniques have been used to provide tremendous insight into the fundamental mechanistic aspects of TiO_2 PCO. Although pulse radiolysis involves generation of $^{\bullet}OH$ and superoxide anion radicals under homogeneous conditions and TiO_2 PCO involves a heterogeneous system, there are strong correlations of the kinetic and mechanistic aspects between the radiolytic and TiO_2 photocatalytic oxidation processes.[33−37]

We used pulse radiolysis to study the reactions of superoxide anion radical with As(III) as described below. Under radiolytic conditions, oxygen reacts with hydrated electrons to form superoxide anion radical in a diffusion-controlled reaction, eq 6, with a *G* value of 3.2.[38] An excess of *tert*-butyl alcohol 5% (v/v) was added to the solution to scavenge essentially all $^{\bullet}OH$ radicals produced during radiolysis, as illustrated by eq 7.[39]

$$e_{aq}^{-} + O_2 \rightarrow O_2^{-\bullet} \quad k_1 = 2.0 \times 10^{10}\ M^1\ s^{-1} \qquad (6)$$

$$^{\bullet}OH + t\text{-BuOH} \rightarrow H_2O + {}^{\bullet}CH_2C(CH_3)_2OH \quad k_2 = 6.0 \times 10^8\ M^{-1}\ s^{-1} \qquad (7)$$

Since superoxide anion radical, As(III) and the initial oxidation product, As(IV) possess only weak short wavelength adsorptions, we employed 1,4-benzoquinone (BQ) as competitive indicator to determine the rate constant of superoxide anion radical with As(III). The reaction of BQ with $O_2^{-\bullet}$ forms a semiquinone radical anion ($BQ^{-\bullet}$) which can be readily monitored by a characteristic peak at 430 nm using transient absorption spectroscopy.[40]

Using the reaction of BQ with superoxide anion radical as a standard reaction, represented by eq 8, and varying the concentration of As(III) in solution to compete for reaction with superoxide anion radical allows for the determination of the rate constant for eq 9.

$$BQ + O_2^{-\bullet} \rightarrow BQ^{-\bullet} + O_2 \quad k_{BQ} = 9.0 \times 10^8\ M^{-1}\ s^{-1} \qquad (8)$$

$$As(III) + O_2^{-\bullet} \rightarrow As(IV) + O_2^{2-} \quad k_{As(III)} \qquad (9)$$

On the basis of the competitive reactions of BQ and As(III) with superoxide anion radical the rate constant for the reaction of As(III) with $O_2^{-\bullet}$ can be expressed mathematically,[41] by eq 10,

$$\frac{Abs_{0(BQ^{-\bullet})}}{Abs_{(BQ^{-\bullet})}} = 1 + \frac{k_{As(III)}[As(III)]}{k_{BQ}[BQ]} \qquad (10)$$

where $Abs_{0(BQ^{-\bullet})}$ is the absorbance of the benzoquinone radical anion at 430 nm in the absence of As(III) and $Abs_{(BQ^{-\bullet})}$ is the absorbance at 430 nm in the presence of specific As(III) concentrations. On the basis of this relationship, the rate constant can be determined from the change in absorbance at 430 nm as a function of [As(III)]/[BQ]. The initial As(III) concentration was varied from 0.49 to 10 mM at constant BQ concentration of 0.02 mM to maintain pseudo-first-order conditions. A plot of change in absorbance at 430 nm as a function of [As(III)]/[BQ], illustrated in Figure 3, yields a linear relationship with slope representing the ratio $k_{As(III)}/k_{BQ}$. Dividing the slope by the literature value for k_{BQ} yields a rate constant of 3.6×10^6 $M^{-1}\ s^{-1}$ for the reaction of As(III) with superoxide anion radical.

The rate constant for the reaction of $HO^{\bullet}$ with As(III) is $8.5 \times 10^9\ M^{-1}\ s^{-1}$, more than 3 orders of magnitude faster than $O_2^{-\bullet}$ under homogeneous conditions.[28] This observation contradicts Choi et al. remark that superoxide anion radical is the predominant oxidant during TiO_2 PCO.[17,18] Their conclusion is based in part on differences observed for As(III) oxidation using Pt-modified and naked TiO_2 catalysts. However such a comparison between the two catalyst cannot be taken as evidence since modification with noble metals (Pt, Au, etc.) is expected to increase the efficiency of charge separation and the yield of reductive and oxidative conversions.[42,43] Analogous explanations can be used to rationalize the faster observed rates of As(III) oxidation under humic acid and dye sensitized PCO conditions. Visible light sensitized TiO_2 PCO was employed to produce superoxide anion radical without yielding hydroxyl radicals,[18] however the oxidation of As(III) under such conditions can also occur by type I and II photooxidation processes and thus is also not conclusive to the involvement superoxide anion radical.[44]

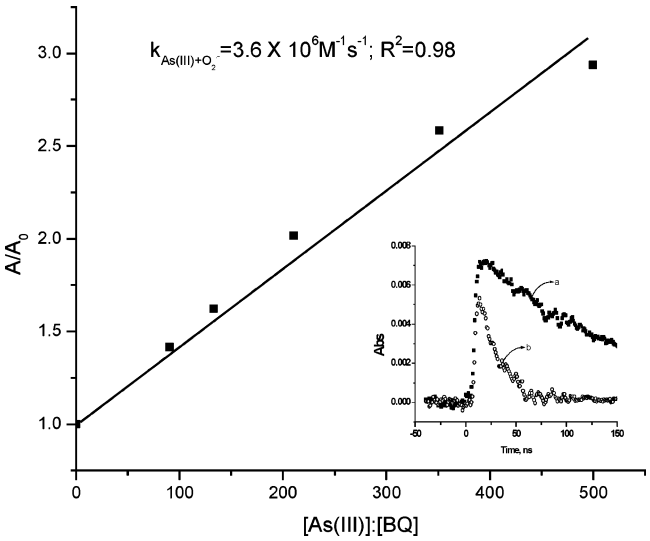

Figure 3. Change in absorbance (A_0/A) at 430 nm as a function of [As(III)]/[BQ] during pulse radiolysis generation of $O_2^{-\bullet}$ (O_2 saturated; pH 7). The inset shows the growth of the $BQ^{-\bullet}$ absorbance at 430 nm (a) without and (b) with 10 mM As(III).

Under pulse radiolysis conditions the reaction of As(III) with superoxide anion radical is slow compared to the reaction hydroxyl radical with As(III).

Reaction of (TiO_2 + $^{\bullet}OH$) with As(III). Following the work of Lawless et al, pulse radiolysis and TiO_2 colloids were used to directly monitor the lifetimes of absorbed hydroxyl radicals at the surface of TiO_2.[15] Radiolysis of N_2O-saturated aqueous solutions with high-energy electrons generates primarily $^{\bullet}OH$ radicals as N_2O scavenges hydrated electrons, as shown in Eq 11, to selectively produce hydroxyl radical as the primary radical.[45]

$$N_2O + e_{aq}^{-} + H_2O \rightarrow {}^{\bullet}OH + N_2 + OH^{-} \quad k = 8.7 \times 10^9\ M^{-1}\ s^{-1} \qquad (11)$$

A system consisting of 90% $^{\bullet}OH$ radicals was achieved under these conditions with G($^{\bullet}OH$) = 5.4. Under such conditions in the presence of TiO_2 colloids, $^{\bullet}OH$ is trapped at the surface of TiO_2 to form a transient, the same species that is observed during photoexcitation of TiO_2.[15] The transient is assigned to adsorbed hydroxyl radical/ trapped hole, which will be referred to as (TiO_2 + $^{\bullet}OH$) for the purposes of this paper. Figure 4 illustrates the absorption spectrum of the transient taken immediately after the pulse to generate (TiO_2 + $^{\bullet}OH$) in the presence and absence of As(III). The spectrum shows an onset of absorption at wavelengths <470 nm with a maximum at ~360 nm, and is

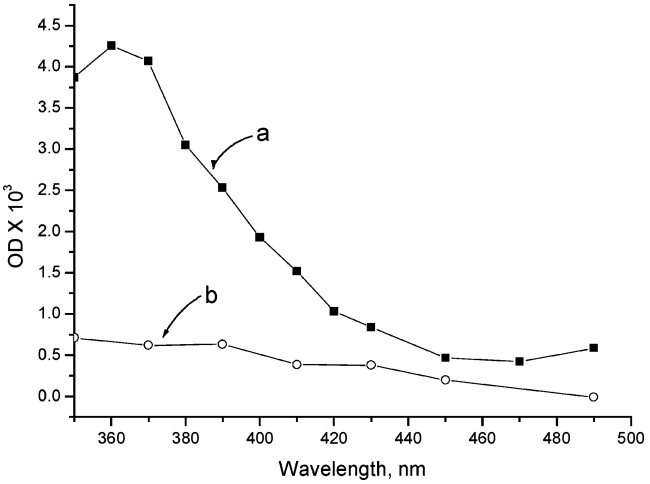

Figure 4. Absorbance of (TiO_2+•OH) reaction a without As(III) and (b) with 10 mM As(III). (TiO_2 1.0 μM; pH 1.5; N_2O saturated; 10 mM As(III)).

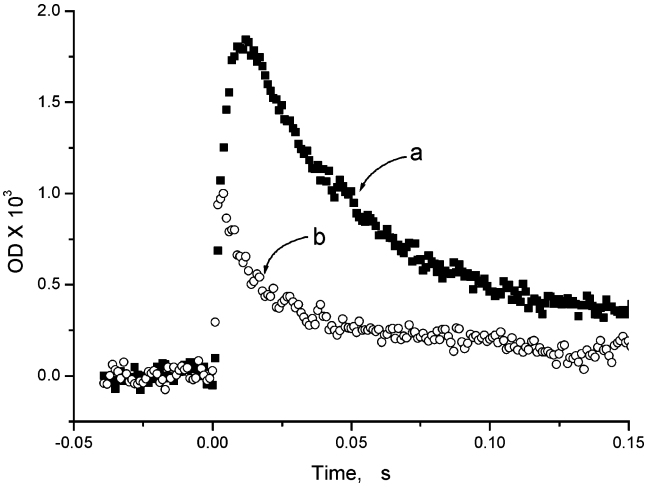

Figure 5. Absorption time profile at 370 nm recorded following pulse radiolysis of TiO_2 colloids (a) in the absence and (b) in the presence of 1.0 mM As(III). (TiO_2 1.0 μM; pH 1.5; N_2O saturated).

attributed to the trapped hole (absorbed hydroxyl radical), eq 12.

$$\{\text{Ti(IV)}-\text{O}^{2-}-\text{Ti(IV)}\} + {}^{\bullet}\text{OH} \rightarrow \{\text{Ti(IV)}-\text{O}^{2-}-\text{Ti(IV)}\}-\text{OH}^{\bullet} \leftrightarrow \{\text{Ti(IV)}-\text{O}^{\bullet-}-\text{Ti(IV)}\}-\text{OH}^{-} \quad (12)$$

The absorbance of As(III, IV, V) does not overlap with the (TiO_2 + •OH) absorbance at 370 nm. The rate of decay of the absorption at 370 nm increases with increasing concentration of As(III), as illustrated in Figures 4 and 6. The dependence of the (TiO_2 + •OH) decay rate on As(III) concentration is reminiscent of a Langmuir-type adsorption/desorption quasi-equilibrium reported for SCN^-.[15] Our proposed mechanism for the oxidation of As(III) is given by the sequence of reactions 13−16.

$$\{\text{TiO}_2\} + \text{As(III)} \underset{k_{\text{des}}}{\overset{k_{\text{abs}}}{\rightleftharpoons}} \text{As(III)}_{\text{ads}} \quad (13)$$

$$(\text{TiO}_2+{}^{\bullet}\text{OH}) + \text{As(III)}_{\text{ads}} \xrightarrow{k_1} \text{As(IV)}_{\text{ads}} \quad (14)$$

$$\text{As(IV)}_{\text{ads}} \rightarrow \text{As(III)}_{\text{ads}} + \text{As(V)}_{\text{ads}} \quad (15)$$

$$\text{As(IV)}_{\text{ads}} + \text{O}_2 \rightarrow \text{As(V)}_{\text{ads}} + \text{O}_2^{-\bullet}/\text{HO}_2^{\bullet} \quad (16)$$

The rate of decay of the (TiO_2 + •OH) transient in the presence of the absorbed fraction of As(III), may be expressed as

$$\text{rate} = k_{\text{decay}}[(\text{TiO}_2 + {}^{\bullet}\text{OH})] = \left(k_1{}^0 + \frac{k_1 K[\text{As(III)}]}{1 + K[\text{As(III)}]}\right)[(\text{TiO}_2+{}^{\bullet}\text{OH})] \quad (17)$$

where $k_1°$ is the intrinsic decay of the (TiO_2 + •OH) species, 2.2×10^5 s^{-1}, under our experimental conditions and k_1 is the As(III)-dependent first-order decay of (TiO_2 + •OH) identified in eq 14. The adsorption−desorption coefficient, K, is defined by eq 13. The electron-transfer reaction 14 is understood to occur between As(III) and (TiO_2 + •OH), at the surface of the same particle. Figure 6 illustrates the rate of decay as a function of

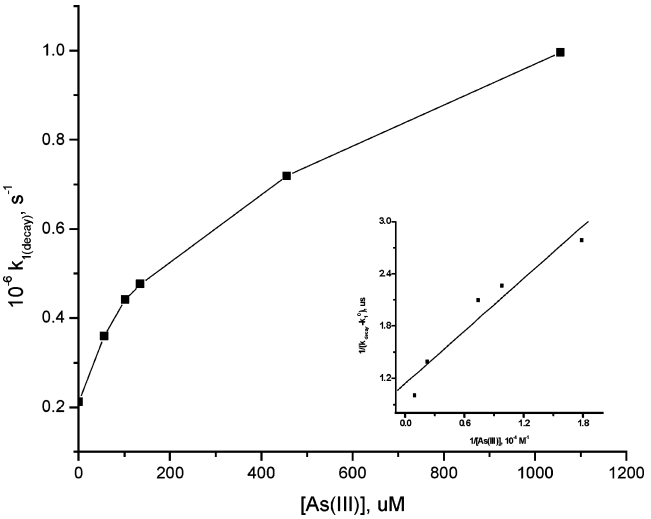

Figure 6. Dependence of pseudo-first-order rate constant of TiO_2+•-OH adduct decay at 370 nm as a function of [As(III)]. Inset: Langmuir−Hinshelwood analysis of the same result.

[As(III)] which exhibits a linear dependence as expressed by eq 18.

$$\frac{1}{k_{\text{decay}} - k_1{}^0} = \frac{1}{k_1} + \frac{1}{k_1 K[\text{As(III)}]} \quad (18)$$

The intercept and slope of the line yield $k_1 = 8.2 \times 10^5$ s^{-1} and $K = 3.8 \times 10^3$ M^{-1} ($r^2 = 0.9926$). The value of K is consistent with previous observation that As(III) strongly adsorbs to the surface of TiO_2.[17]

To summarize, our studies indicate that hydroxyl radical plays a key role in the oxidation of As(III) to As(V) during TiO_2 PCO. It is clear the oxidation of As(III) by TiO_2 PCO occurs quickly and extensively at the surface of the catalyst. We propose that adsorbed hydroxyl radical oxidizes As(III) to As(IV). The As(VI) can disproportionate at the surface TiO_2 or be readily oxidized to As(V) by molecular oxygen, •OH, etc. Our results indicate that a number of the AOTs, which employ hydroxyl radicals, may be applicable for the oxidation of arsenic in a multistep remediation processes. TiO_2 PCO can be effectively employed to treat and immobilize arsenic from contaminated drinking water.

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