

## Adsorption of As(V)/As(III) on TiO<sub>2</sub> and the Photocatalytic Oxidation of As(III)

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### INTRODUCTION

A great deal of attention has been given in the last two decades to the oxidative photocatalytic degradation of organic contaminants using TiO<sub>2</sub> [1-7]. The photo-oxidation of As(III) to As(V) in aqueous solution and the influence of light intensity has not yet been extensively studied in spite of the fact that this reaction might be useful to enhance removal of arsenic from drinking water.

This study focuses on surface-catalyzed As(III) oxidation by TiO<sub>2</sub> and the influence of light intensity, pH, and TiO<sub>2</sub> mineralogy (anatase and rutile) on reaction kinetics. In addition, the comparative adsorption behaviors of As(III) and As(V) on rutile and anatase, including the effect of solution pH, was investigated.

### MATERIAL AND METHODS

The first experiments were carried out by adding As(III) to the TiO<sub>2</sub> suspension; pH was pre-adjusted to 1 to 11. The experiments were carried out in the dark and under laboratory light and growth chamber light at 23 °C. Samples were collected at specified reaction times ranging from 5 minutes to 24 hours. The second experiments were conducted by adding As(III) to the TiO<sub>2</sub> suspension in the presence of calcium or sodium nitrate or phosphate as NaH<sub>2</sub>PO<sub>4</sub> with the pH initially adjusted to 4 and 8. Adsorption envelopes were obtained for both As(III) and As(V) with the pH of the TiO<sub>2</sub> suspension and As solution mixtures adjusted to obtain a range between 1 and 11. After a 24-hour reaction in the dark, the suspension was filtered; the pH of the filtrate was measured, and the filtrate was stored at 5 °C until analysis. Adsorption isotherms were obtained at pH 4. After 24 hours reaction the suspension was filtered and stored at 5 °C until analysis. As(III) and As(V) were determined by a pH-selective hydride-generation atomic-absorption procedure.

### RESULTS AND DISCUSSION

The rate of oxidation of As(III) in the presence of TiO<sub>2</sub> under laboratory light was influenced by pH. Lower suspension pH values resulted in relatively more rapid oxidation of As(III). Complete oxidation of As(III) took place within 4 hours at low pH values (1 to 3). At pH 7 to 10, 8 hours were required to oxidize 500 µg L<sup>-1</sup> of As(III) to As(V). Only 85 % of the As(III) was oxidized to As(V) after 24 hours when the suspension pH was 11. In the case of oxidation under growth chamber light, there was no significant influence of pH on rate of oxidation. The rate of oxidation was faster than oxidation under laboratory light and 2 hours were sufficient to oxidize 1000 µg L<sup>-1</sup> As(III) to As(V) at all pH values. In the dark there was no oxidation. This study, therefore, demonstrated that light intensity plays an important role in enhancing As(III) oxidation. The oxidation of As(III) by TiO<sub>2</sub> was slightly slower when Ca<sup>+2</sup> or Na<sup>+</sup> was added to the reaction vessels at both pH 4 and 8. Also, a slower As(III) oxidation rate was observed in presence of phosphate.

The point of zero charge (pzc) for rutile was approximately pH 5.8. As(V) adsorption was faster at low pH. At low pH the surface has a net positive charge that would attract H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> ions. But at high pH, the surface has a net negative charge and would tend to repel the HAsO<sub>4</sub><sup>-</sup> ions in solution. These electrostatic factors could influence both the kinetics and equilibrium of As(V) adsorption. The experimental results indicated that As(V) adsorption was higher at lower pH. At the lower equilibrium As(III) concentrations, adsorption at pH 9.2 was generally higher than at pH 4.6; however, at the higher equilibrium concentrations approximately equivalent amounts of As(III) were

adsorbed at pH 4.6 and 9.2. In the pH range of 4.6 – 9.2,  $\text{H}_3\text{AsO}_3^\circ$  ( $\text{pK}_a = 9.2$ ) is the dominant As(III) species in solution. Therefore, the adsorption of As(III) would be less strongly influenced by the anion repulsion forces that would likely play an important role in the adsorption as As(V) species at high pH. Also, adsorption of  $\text{H}_3\text{AsO}_3^\circ$  would have less influence than the adsorption of negatively charged As(V) species on the total negative charge character at the  $\text{TiO}_2$ -water surface. The adsorption envelopes exhibited broad adsorption maxima extending from approximately pH 6.8 to 9.4 for As(III) and from pH 3 to 6 for As(V). In the case of As(V), there was a significant reduction in adsorption at pH 7 and above, which approximately coincided with the second  $\text{pK}_a$  (6.9) of  $\text{H}_3\text{AsO}_4$ . Bissen et al. reported that the  $\text{TiO}_2$ -catalyst reaction does not significantly depend on the pH value of the samples [8]. Inflections or maxima in the adsorption envelopes of anions at pH values close to their  $\text{pK}_a$ 's are a well-documented phenomenon. As(III) adsorption did increase significantly until pH values were 11. The lower adsorption of As(V) at high pH values (7 and above) is attributable to an increased repulsion between the negatively charged As(V) species and negatively charged surface sites. Since As(III) species have less negative charge character compared to As(V) species at the same pH value, they do not exhibit as much repulsion, and as a result, the adsorption decreases less with increasing pH. Adsorption isotherms at constant pH show that the amount of As(V) adsorbed increases until a condition of surface saturation was reached at some concentration. It has been reported that the adsorption isotherms of orthophosphates on rutile type  $\text{TiO}_2$  surfaces vary with pH [9].

The oxidation of As(III) by  $\text{TiO}_2$  is a slower process at neutral or higher pH values. At low pH, acid catalysis can accelerate the As(III) oxidation; however, the reaction rate is still not sufficient to effectively oxidize As(III). This slower reaction rate can be overcome by increasing light intensity. Experimental results indicated that light could provide energy to enhance As(III) oxidation by  $\text{TiO}_2$ . Low light intensity, e.g., laboratory light, or a stronger light intensity like growth chamber light enhanced As(III) oxidation by  $\text{TiO}_2$ , because the  $\text{TiO}_2$  surface accelerates proton transfer between the reactants. Experimental results indicated that phosphate inhibited or delayed As(III) oxidation by  $\text{TiO}_2$ . Phosphate competes with As(V) for adsorption at the  $\text{TiO}_2$ -water interface and adsorbed phosphate might have blocked  $\text{TiO}_2$  surface sites., thus a slower As(III) oxidation rate was observed. It is likely that  $\text{Ca}^{+2}$  and  $\text{Na}^+$  could exchange proton below the pzc of surface sites and decrease proton transfer tendency, resulting in a decrease in acid catalysis. Thus a slower As(III) oxidation rate was observed.

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