Reduction and removal of mercury from water using arginine-modified TiO$_2$

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Abstract

The photocatalytic removal of mercury(II) ions from water was investigated using titanium dioxide (TiO$_2$) nanoparticles (45 Å in diameter) surface-modified with arginine (ARG). TiO$_2$ sols were prepared by the controlled hydrolysis of titanium tetrachloride. ARG-modified TiO$_2$ was placed in water and purged anoxically with an inert gas. Suspensions were spiked with elevated mercury concentrations (from mercuric chloride) and equilibrated for 10 min in darkness (with continuous stirring). Suspensions were either illuminated with 253.7 nm light or kept in darkness while mixing continuously. Samples were periodically withdrawn from the reactor via syringe and filtered anoxically. Precipitate collected on the filters was tested for elemental mercury; filtrate was analyzed for mercury using cold vapor atomic absorption spectrometry. Results showed that in the absence of light, approximately 60% of initial mercury could be sorbed onto the ARG-modified TiO$_2$ [ARG (1.67×10^{-3} M), TiO$_2$ (5.00×10^{-3} M)]. ARG-modified TiO$_2$ removed greater than 99.9% of the initial mercury (150 ppm) present in solution within 128 min of illumination through sorption and reduction processes. This removal time was reduced to 32 min when methanol was added as a hole scavenger. These sorption and reduction processes were catalytic in nature. The presence of 30 ppm iron(III) greatly inhibits both the sorption and the reduction of mercury on ARG-modified TiO$_2$. © 2002 Elsevier Science B.V. All rights reserved.

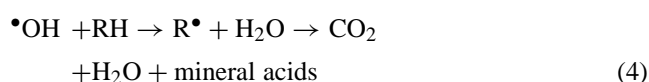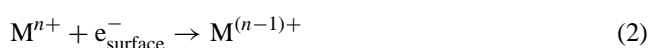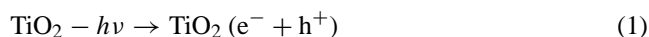*Keywords:* Titanium dioxide; Mercury; Reduction; Photocatalysis

1. Introduction

Both inorganic and organic mercury in waters pose considerable risk to aquatic biota since mercury in both forms is cumulatively toxic. Numerous physical and chemical treatment methods have been used to remove mercury contamination from waters and waste streams. These methods include precipitation, sorption, ion exchange, and reverse osmosis. Although these processes are effective, they generate wastes that must often be disposed as hazardous.

Various studies have explored metal removal by photocatalysis. Zinc oxide powder has been used as a photocatalyst, reducing mercury(II) ions to metallic mercury in the presence of ultraviolet light [1]. TiO$_2$ also has been used as a photocatalyst to eliminate mercury from solutions. Various forms of aqueous mercury including chloride salts, cyano species, and organic species can be removed and reduced by TiO$_2$ in the presence of ultraviolet light [2–9]. Reduction can occur by several mechanisms, including direct reduction, where the electrons are transferred to sorbed mercury,

and indirect reduction, whereby an organomercury complex is oxidized resulting in metallic mercury deposition on TiO$_2$ [3]. Photocatalytic mercury removal by TiO$_2$ often requires that the solution should first be purged with an inert gas since dissolved oxygen, an electron acceptor, inhibits the photoreduction of mercury by TiO$_2$ [2,5,6].

Our study builds on the results from our previous work in metal reduction. This work has included reduction and removal of aqueous cadmium, copper, and lead by surface-modified TiO$_2$ nanoparticles [10–13]. As TiO$_2$ is illuminated, electrons and holes are produced. These charges can either recombine to produce heat, or can be used to reduce or oxidize species in solution at the TiO$_2$ surface as indicated by Eqs. (1)–(5) [2,14].

$$\text{TiO}_2 - h\nu \rightarrow \text{TiO}_2\,(\text{e}^- + \text{h}^+) \tag{1}$$

$$\text{M}^{n+} + \text{e}^-_{\text{surface}} \rightarrow \text{M}^{(n-1)+} \tag{2}$$

$$\text{OH}^- + \text{h}^+_{\text{surface}} \rightarrow \text{OH}^\bullet \tag{3}$$

$$^\bullet\text{OH} + \text{RH} \rightarrow \text{R}^\bullet + \text{H}_2\text{O} \rightarrow \text{CO}_2$$
$$+ \text{H}_2\text{O} + \text{mineral acids} \tag{4}$$

$$2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+ \tag{5}$$

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In Eqs. (1)–(5), M represents the metal ion, R represents an organic species, and n is an integer.

TiO$_2$ nanoparticles, synthesized from the controlled hydrolysis of titanium tetrachloride, are 40–60 Å in diameter, allowing for 40% of the titanium to be located on the surface of the particle [15]. Nanosized surface-modified TiO$_2$ offers several advantages over the commercially available (e.g. Degussa) TiO$_2$: (1) a high surface area for reactions to occur; (2) selective sorption of metal ions to the TiO$_2$ surface through chelation; and (3) introduction of deeper trapping sites outside the TiO$_2$ particle resulting in greater separation of photogenerated charges and "enhanced" reduction properties of photogenerated electrons [16–20].

In unmodified nanosized TiO$_2$, a large percentage of Ti(IV) atoms lie on the particle surface and act as electron trapping sites [16]. These charges, along with holes trapped directly on oxygen atoms bound to surface Ti(IV) atoms, are injected into particles localized at surface defect sites [17,18]. Surface modification of TiO$_2$ with carboxylic acids results in the replacement of surface OH groups and coordination of surface titanium atoms with a carboxyl group [19]. New trapping sites (outside the semiconductor) are formed that localize photogenerated holes and electrons [20,21]. The modifier increases the distance between trapped electrons and holes, preventing recombination from occurring. Modification also leads to the accumulation of trapped electrons, permitting multi-electron injection into a sorbed species. This is advantageous since multi-electron transfers usually require lower reduction potentials than one electron transfer [21]. This modification allows reactions to occur on the TiO$_2$ surface that were not previously possible [19].

2. Experimental details

Anatase TiO$_2$ was prepared by the controlled hydrolysis of titanium tetrachloride (TiCl$_4$, Aldrich). This procedure is described elsewhere and produces TiO$_2$ colloids that are 40–60 Å in diameter with an average particle diameter of 45 Å [20,22]. For this particle size, approximately 40% of the titanium atoms are located on the particle surface [15]. After synthesis, the colloid concentration was determined by dissolving the TiO$_2$ in concentrated sulfuric acid (Aldrich) and forming peroxotitanium(IV) [23]. The peroxo complex was analyzed using a Beckman DU 640 Spectrophotometer to determine its concentration. Prepared colloid was stable for several months and maintained the initial particle size. The colloid either remained unmodified or its surface was modified with L-arginine (ARG, C$_6$H$_{14}$N$_4$O$_2$, Aldrich). Arginine was used as a modifier because it effectively binds both to the TiO$_2$ surface through the carboxyl functional group and to mercury ions in solution through the amino functional groups [20]. The concentration of arginine needed to coat the colloid was chosen based upon previous sorption studies of various modifiers to the TiO$_2$ colloids [21].

Solutions of TiO$_2$ (5.0×10^{-3} M) or arginine-modified TiO$_2$ [ARG (1.67×10^{-3} M), TiO$_2$ (5.00×10^{-3} M)] were prepared and allowed to equilibrate for 1 day under an anoxic atmosphere (argon-purged, AGA 99.995%). Mercuric chloride (Aldrich) from a prepared stock solution was injected anoxically into the modified or unmodified TiO$_2$ solution, diluted to 500 ml in a quartz flask, and allowed to equilibrate 10 min in darkness with continuous mixing. After the equilibration period, the sample either remained in darkness, or, was illuminated by an eight-light Rayonet Photochemical Chamber Reactor (RMR Model 600) producing 253.7 nm light. Four milliliters of samples were periodically withdrawn from the reactor via syringe and filtered anoxically using Amicon Diaflo pressure filters with Amicon YM100 membranes. Precipitate on the filter was tested for the presence of elemental mercury using a saturated solution of potassium iodide (oxides of mercury are soluble in this solution, elemental mercury is not) [5]. Filtrate was analyzed using cold vapor atomic absorption spectroscopy (Buck Scientific 200 A). The pH's of the solutions were at natural pH.

3. Results and discussion

Sorption and reduction of mercury on unmodified and arginine-modified TiO$_2$ were investigated. Fig. 1 shows the results of anoxic experiments with unmodified TiO$_2$; Fig. 2 shows the results of experiments with arginine-modified TiO$_2$.

As Fig. 1 reveals, the unmodified TiO$_2$ in the dark reaction sorbed very little mercury. No significant increase in mercury sorption was noticed in the light reaction. Mercury reduction did not occur in either the light or dark reaction with unmodified TiO$_2$.

Fig. 2 shows that arginine greatly enhances the amount of mercury sorbed to the colloid. After the 10-minute equilibration period, approximately 50% of the mercury in solution is sorbed to arginine-modified TiO$_2$ compared to only 5%
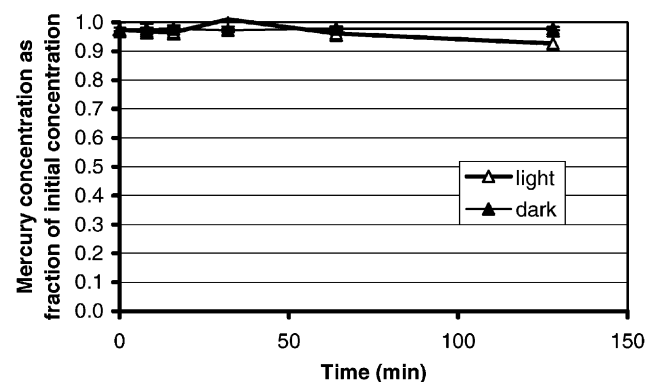

Fig. 1. Removal of mercury by TiO$_2$. [TiO$_2$] $= 5.0 \times 10^{-3}$ M, [Hg] $= 7.5 \times 10^{-4}$ M (150 ppm). Error bars are derived from the standard deviation of light and dark duplicate reactions.
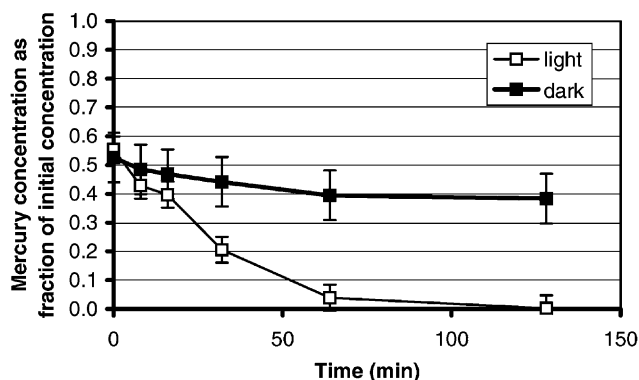
Fig. 2. Removal of mercury by arginine-modified TiO$_2$. [TiO$_2$] = 5.0×10^{-3} M, [ARG] = 1.67×10^{-3} M, [Hg] = 7.5×10^{-4} M (150 ppm). Error bars are derived from the standard deviation of light and dark duplicate reactions.

Fig. 3. Removal of mercury by TiO$_2$ in the presence of methanol. [TiO$_2$] = 5.0×10^{-3} M, [ARG] = 1.67×10^{-3} M, [Hg] = 150 ppm, [methanol] = 9.9×10^{-3} M. Error bars are derived from the standard deviation of light and dark duplicate reactions.

that was sorbed to unmodified TiO$_2$ (Fig. 1). The dark reaction of Fig. 2 continues to sorb mercury for approximately 60 min until the system reaches equilibrium. At this equilibrium point, 60% of the mercury initially present is sorbed to the arginine-modified TiO$_2$. In the corresponding light reaction, both sorption and reduction processes occur until all of the mercury (99.98%) is removed from solution (to less than detection limits, 30 ppb). Removal occurs within 1 h of illumination.

A distinct visual change (a color change due to mercury reduction) occurs on the arginine-modified colloid during the illumination period. As time progressed during the illuminated reaction, the solution (colloid) darkened, indicating the reduction of mercury. The dark precipitate was confirmed chemically to be elemental mercury by a procedure described earlier (using potassium iodide). No color change was observed in the dark reaction, indicating that mercury was only sorbed but not reduced.

To improve photogenerated charge transfer from TiO$_2$ to mercury, methanol was added as a hole scavenger. We expect that without methanol, arginine is oxidized as mercury is reduced (previous work shows that TiO$_2$ photocatalytically degrades amino acids [24]). Methanol, a hole scavenger, inhibits arginine oxidation and electron–hole recombination, thereby increasing the rate of mercury reduction. In addition, methanol has been shown to have a current doubling effect on the TiO$_2$ surface [20]. With methanol present, absorption of one photon leads to the injection of two electrons into the TiO$_2$ conduction band, thus doubling the current [20]. This phenomenon is manifested by the much faster removal of mercury, as shown in Fig. 3.

Fig. 3 shows the methanol enhanced mercury removal from both dark and light systems. In the dark reaction, approximately 70% of the mercury was sorbed to arginine-modified TiO$_2$ in the presence of methanol, whereas in the absence of methanol (Fig. 2), approximately 60% of the mercury had been sorbed in the dark reaction. In the light reaction with methanol present, mercury was
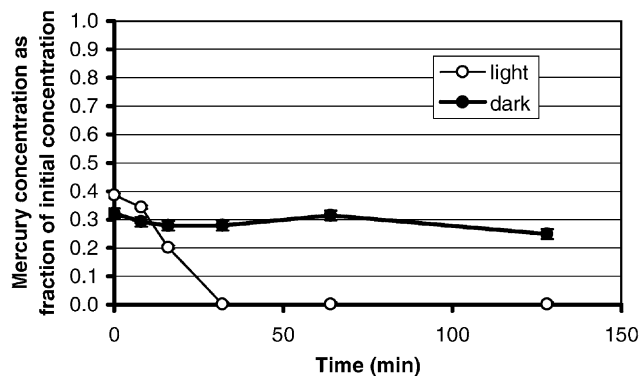
removed and reduced within 32 min. The time required to reduce mercury in the presence of methanol was one-half of what was required in the absence of methanol (Fig. 3).

Previous researchers had noted that the presence of iron(III) significantly inhibited the reduction of mercury on Degussa P25 TiO$_2$ [2]. Our research investigated the effect Fe(III) had on the reduction of mercury using arginine-modified nanosized TiO$_2$. The residual concentrations of total mercury and iron are shown in Fig. 4.

As shown in Fig. 4, during the 10-minute equilibration period, 60% of the total iron introduced to the system was sorbed onto the modified TiO$_2$ compared to only 5% of mercury. In the dark reaction, the amount of mercury sorbed to the TiO$_2$ stayed relatively constant over time, whereas the amount of iron sorbed to arginine-modified TiO$_2$ increased slightly. In the light reaction, mercury slowly but steadily sorbs to the TiO$_2$ over time, whereas 60% of the iron initially sorbed to the colloid desorbs over the illumination period. Visually, no reduction occurred in either the mercury or the iron during the illumination reaction. The lack of mercury reduction was confirmed chemically.
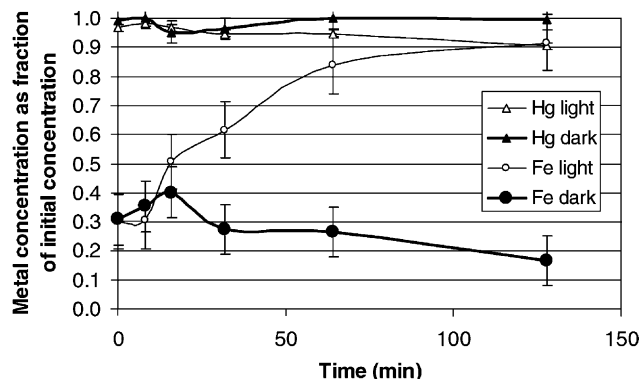

Fig. 4. Removal of mercury by arginine-modified TiO$_2$ in the presence of Fe(III). [TiO$_2$] = 5.0×10^{-3} M, [ARG] = 1.67×10^{-3} M, initial [Hg] = 150 ppm, initial [Fe] = 30 ppm. Error bars are derived from standard deviation of light and dark duplicate reactions.

4. Conclusions

TiO$_2$ surface-modified with arginine is able to effectively remove and reduce mercury to an elemental state, a feat which unmodified TiO$_2$ is unable to do. The modifier: (1) enhances sorption of the mercury to the TiO$_2$ surface; (2) facilitates charge transfer from the TiO$_2$ to the sorbed mercury; and (3) prevents charge recombination from occurring. The addition of methanol increases the rate of mercury removal by a factor of 2. The presence of 30 ppm of iron(III) greatly inhibits both the sorption and the reduction of mercury on arginine-modified TiO$_2$.

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