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Photocatalytical removal of inorganic and organic arsenic species from aqueous solution using zinc oxide semiconductor†

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Abstract

The photocatalytic removal of arsenite [As(III)] and monomethylarsonic acid [MMA(V)] was investigated in the presence of UV light (350 nm) and aqueous suspensions of ZnO synthesized by the sol–gel technique. Photocatalytic removal of these potent arsenic compounds results in the effective and rapid mineralization to less toxic inorganic arsenate [As(V)]. The effect of ZnO loading and solution pH on the treatment efficiency of the UV/ZnO photocatalytic process was evaluated. The optimal conditions for the removal of 5 mg L⁻¹ [As(III)] and [MMA(V)] aqueous solutions were observed at catalyst loadings of 0.25 and 0.50 g L⁻¹ with solution pH values of 7 and 8, respectively. Under these conditions, the activity of photocatalyst sol–gel ZnO was compared with TiO₂ Degussa P25 and commercial ZnO catalyst. The results demonstrate that the high adsorption capacity of ZnO synthesized by sol–gel gives enhanced removal of arsenic species from water samples, indicating that this catalyst is a promising material for treatment of arsenic contaminated groundwater.

1. Introduction

Arsenic is a carcinogenic and highly toxic element for humans. Chronic arsenic exposure *via* drinking water has been reported in several countries around the world.¹ Both inorganic and organic forms of arsenic have been found in natural waters.² Arsenic exists mainly as [As(III)] and [As(V)] oxyanions, arsenite (H₃AsO₃) and arsenate (H₃AsO₄) in the aquatic environment. Under groundwater conditions, [As(III)] is the predominant form of arsenic, which is much more toxic and mobile than [As(V)]. Although the inorganic species are predominant in natural waters, organoarsenic compounds, such as monomethylarsonic acid [MMA(V)] and dimethylarsinic acid [DMA(V)], are problematic pollutants in groundwater at sites with a history of pesticide manufacturing and improper disposal.

A relatively high concentration of arsenic in the aquatic system has many implications for the health of humans, animals and plants. The World Health Organization (WHO) has established a guideline of 0.01 mg L⁻¹ as the maximum allowable level of arsenic in drinking water.³ A simple, low-cost and effective technology for arsenic removal is thus highly desirable to ensure safe drinking water to the people in contaminated areas.

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Commonly used removal technologies include coagulation and precipitation employing iron and aluminum salts, adsorption onto activated alumina and activated carbon, ion exchange and reverse osmosis.^{1,4} These techniques have however been found to be more efficient for [As(V)] as a result of the stronger adsorption affinity of negatively charged [As(V)] oxyanions to solid surfaces compared to the neutral [As(III)] molecule.¹ Current treatments require oxidation of [As(III)] to [As(V)] prior to adsorption of the arsenic species to achieve efficient total arsenic removal. TiO₂ photocatalytic oxidation has been used for the efficient oxidation of [As(III)]/organic arsenic species to [As(V)]^{5–12} followed by adsorption of [As(V)] by TiO₂.^{9,10} The photocatalytic removal of [MMA(V)] and [DMA(V)] using Degussa P25 and nanocrystalline TiO₂ has also been investigated.^{11,12} In this context, TiO₂ materials have been recognized as an excellent material for photocatalysis due to their photoactivity, modest cost, nontoxic nature, and large band gap.¹³ Although TiO₂ is generally considered as the most important photocatalyst, ZnO is also an attractive alternative to TiO₂ due to the similar band gap energy (3.2 eV) and its lower cost for large-scale water treatment.¹⁴ Moreover, larger quantum efficiency and higher photocatalytic activity have been reported for ZnO compared to TiO₂ for the photocatalytic destruction of specific pollutants.^{15–18} However enhancing the photocatalytic activity of ZnO for water treatment is desirable to obtain better removal efficiency. Different synthesis techniques have been adopted to prepare catalysts with suitable characteristics that can reduce the recombination rate of photogenerated electrons and holes.¹⁹ The sol–gel method allows flexibility in parameter control with its relatively slow reaction process. This technique allows tailoring the photocatalysts to obtain desired structural characteristics such as compositional homogeneity, grain size, particle morphology and porosity.²⁰

The primary aim of this work was to accomplish the photocatalytic removal of [As(III)] and [MMA(V)] from aqueous solution using ZnO synthesized by sol–gel as the catalyst under UV radiation at different solution pH and catalyst loading. The activity of sol–gel ZnO on the removal efficiency of arsenic species was compared with TiO₂ Degussa P25 and commercial ZnO. To the best of our knowledge, the removal of [As(III)] and [MMA(V)] from aqueous solution by the UV/ZnO system has not been previously reported.

2. Experimental details

2.1 Materials

Sodium arsenate (Na₂HAsO₄·7H₂O, [As(V)]) and sodium arsenite (NaAsO₂, [As(III)]) were purchased from Sigma-Aldrich. Monosodium methanearsonate (CH₃AsO₃Na·6H₂O, [MMA(V)]) was purchased from Chem Service Inc. (West Chester, PA, USA). Stock solutions of different arsenic species (100 mg L^{−1}) were prepared in volumetric glassware. The required working standards were prepared daily from the stock solutions. All other reagents were reagent grade and used as received. HCl was trace metal grade from Fisher. All solutions were prepared with ultra-pure water (18 MΩ cm^{−1}) from a Millipore Milli-Q system. Titanium dioxide was P25 (80% anatase and 20% rutile, Degussa, Germany) and commercial ZnO (minimum purity 99%) was purchased from Acros Organics.

2.2 Synthesis of ZnO

It was prepared by the sol–gel technique using zinc acetate, Zn-(CH₃COO)₂·2H₂O, as a precursor according to a procedure reported in previous work.²¹ Briefly, 13.5 g of zinc acetate was dissolved in 216 mL of water. An aqueous solution (50% v/v) of NH₄OH was added under continuous stirring to reach a pH of 9.0. The reaction mixture was kept at room temperature until gel was formed. Once the colloidal ZnO was observed, it was aged for 24 h and filtered; then the material was washed with 0.1 M NH₄NO₃ and dried by heating the sample slowly to 90 °C until the solvent was completely evaporated. The dried powder

(fresh sample) was annealed at 350 °C for 5 h in air. BET surface areas were calculated from N₂ adsorption-desorption isotherms obtained in an Autosorb-1 instrument (Quantachrome Co., Boynton Beach, FL, USA). The band gap energy (E_g) values of the studied catalysts were calculated from the UV-Vis diffuse reflectance spectra using a Thermo Scientific Evolution 300 UV-Vis spectrophotometer (Thermo Fisher Scientific, Massachusetts, USA) equipped with an integrating sphere TFS-Praying Mantis. The powder X-ray diffraction patterns of the ZnO catalysts (commercial and prepared by the sol-gel method) were observed in accordance with the zincite phase of ZnO (International Center for Diffraction Data, JCPDS).²²

2.3 Adsorption experiments

FTIR spectra of sol-gel ZnO and arsenic species adsorbed on the catalyst samples were obtained in transmission mode using a Perkin Elmer model Paragon 1000 PC Spectrometer. The spectra were all recorded in the form of KBr pellets.

2.4 Photocatalytic experiments

The catalyst was added to a Pyrex cylindrical reaction vessel (12 × 1 in, 160 mL capacity) containing an aqueous solution of 5mgL⁻¹ [As(III)] or [MMA(V)]. The pH of the solution was adjusted to the desired values (5 to 9) using diluted solutions of HNO₃ (0.1 M) and NaOH (0.1 M). Under stirring, the mixture was kept in the dark for 60 min to ensure equilibrium adsorption prior to illumination. Thereafter, the photocatalytic reaction was carried out in a Rayonet Model RPR-100 reactor equipped with 16 phosphor-coated low-pressure mercury lamps that had a spectral energy distribution with a maximum intensity at $\lambda = 350$ nm, and yielding an incident light intensity of $5.2 \pm 0.1 \times 10^6$ photon s⁻¹ cm⁻³. The temperature was kept close to room temperature by a cooling fan and the reaction rate was followed by taking aliquots at desired time intervals. The catalyst was separated by filtration through a 0.45 μ m syringe filter and subsequently analyzed to determine the individual arsenic species concentrations present in the solution. Arsenic speciation analysis was performed within 6 h of sampling, using a PS Analytical Millenium Excalibur Atomic Fluorescence System (AFS, PSA 10.055) coupled to a high-performance liquid chromatography (HPLC) instrument. An anion exchange column, PRP X-100 (250 mm × 4.6 mm × 10 μ m), was used for the separation of arsenic species. The mobile phase was a 15 mM monosodium phosphate solution (pH 5.7). The flow rate was 1.0 mL min⁻¹, and the injection volume of the sample was 100 μ L. The separated As species were subjected to hydride generation with HCl (12.5% v/v, 2 mL min⁻¹) and NaBH₄ (1.4% w/v in 0.1 M NaOH, 2 mL min⁻¹). This was followed by the introduction of Ar into a gas/liquid separation chamber to efficiently carry the gases to the atomic fluorescence spectrometer.²³ The effect of the pH of the solution (5–9) and the catalyst loading (0.25 and 0.50 g L⁻¹) on the photocatalytic removal of [As(III)] and [MMA(V)] was studied. All the experiments were performed in triplicate.

3. Results

3.1 Effect of the pH on the adsorption of arsenic species

The solution pH can have a pronounced effect on the speciation of arsenic species and the surface charge of sol-gel ZnO, and therefore plays a key role in the ZnO adsorption and removal of arsenic species. In order to better understand the process, the adsorption of [As(III)] and [MMA(V)] was studied as a function of the solution pH (structures shown in Table 1).

In the initial adsorption experiment an aqueous solution of 5 mg L⁻¹ arsenic at a ZnO loading of 0.25 g L⁻¹ was placed in the dark to equilibrate for 60 min followed by the filtration and analysis. The results are summarized in Table 2.

The adsorption process is favored for both species in the range of pH from 7 to 9. At pH 7 the adsorption of [As(III)] was 53 ± 4%, while the adsorption of [MMA(V)] was 33 ± 3%. The pK_a values of H₃AsO₃ [As(III)] are 9.2, 12.1, and 12.7 and those of [MMA(V)] (CH₅AsO₃) are 4.1 and 8.7¹, respectively. At the pH range of 7–9, [As(III)] exists predominantly in the neutral H₃AsO₃ form while [MMA(V)] exists predominantly as a monoanion. Under the neutral or slightly basic conditions (pH between 7 and 9) of the experiments, the catalyst surface charge is mainly positive since the reported zero point charge (zpc) of ZnO is 9.0 ± 0.3.²⁴ While electrostatic interactions are important in the adsorption process especially for the anion [MMA(V)] species, the [As(III)] is neutral at pH zpc and thus the adsorption is related to surface complexation rather than to electrostatic interactions.²⁵ The surface hydroxyl groups of ZnO can act as chelating groups for [As(III)] species.¹¹

On the other hand, the adsorption of [MMA(V)] is mainly the result of the electrostatic attraction between the positively charged catalyst surface and the negatively charged [MMA(V)] species. The presence of the methyl groups in [MMA(V)] reduces capacity and efficiency of the adsorption and thus overall removal compared to [As(III)] adsorption onto ZnO. The adsorption behavior of [As(V)] at pH 7 was also evaluated since this is the final product from the photocatalytic oxidation of [As(III)] and [MMA(V)] using the TiO₂ catalyst.^{1,4} The adsorption percentage of [As(V)] was 95 ± 3% using 0.25 g L⁻¹ of ZnO after 60 min in the dark. The pK_a values of H₃AsO₄ [As(V)] are 2.3, 6.9, and 11.5,¹ thus, at pH 7, [As(V)] predominantly exists in a di-anion H₂AsO₄²⁻ form while the surface of the catalyst at the same pH has an overall positive charge. Thus strong electrostatic attraction and surface complexation lead to strong adsorption of [As(V)] onto the catalyst. The presence of four oxygen atoms on [As(V)] available for complexation to the catalyst surface increases the potential adsorption capacity onto ZnO compared to [As(III)] with three oxygen atoms. The adsorption capacity onto sol–gel ZnO followed the order [As(V)] > [As(III)] > [MMA(V)]. We proposed that the adsorption processes of arsenic species onto sol–gel ZnO are mediated by operative mechanisms similar to those reported for TiO₂.²⁶ The adsorption mechanisms for TiO₂ surfaces involve the formation of bidentate inner sphere complexes for [As(V)], [As(III)], and [MMA(V)].^{27–29}

3.2 FTIR study of adsorbed As species

FTIR spectra of sol–gel ZnO before and after adsorption with 5 mg L⁻¹ arsenic species for 6 h were studied in order to determine the behavior of arsenic species on the catalyst. The solution pH was 7 for [As(III)] and [As(V)] species, and 8 [MMA(V)], respectively. The FTIR spectrum of sol–gel zinc oxide is shown in Fig. 1a. The adsorption peaks of low intensity at 720–600 cm⁻¹ and the broad absorption band centered at 450 cm⁻¹ had been attributed to the ZnO stretching frequency of the Zn–O bond.³⁰ A new band at 830 cm⁻¹ in the FTIR spectrum of sol–gel ZnO was found after adsorption and reaction, which matched well with the stretching frequencies of the As–O band in the arsenite group (see Fig. 1d). The spectrum of ZnO–As(III) displayed a peak that weakly adsorbed at 780 cm⁻¹ due to the symmetry stretching vibration of As–OH. The results agree well with previous FTIR studies of As(III) adsorption on iron oxides published by Goldberg and Johnston.³¹

The spectrum after sorption of [MMA(V)] (Fig. 1b) showed a broad peak at around 839 cm⁻¹ (stretching frequency of the As–O band), and the peak at 730 cm⁻¹ due to the symmetric stretching vibration of As–OH disappeared. This could be due to an apparent increase in molecular symmetry upon the sorption or to the peak shifting to a lower wave

number. Peaks from a methyl group were not observed in the ZnO–MMA(V) spectrum. This is likely due to the weak peak signal from a single methyl group being overshadowed by the intense As–O peak.^{31,32} During the adsorption process of [MMA(V)], the As–O(H) group from [MMA(V)] may go through ligand exchange reactions with OH groups from the ZnO surface, forming inner-sphere complexes. Similar results were observed for [As(V)] (Fig. 1c). During As(V) sorption on sol–gel ZnO, the As–O peak (945 cm^{-1}) downshifts to 862 cm^{-1} as a result of inner-sphere complex formation at the catalyst surface.³¹ Previous results indicated that arsenic species are adsorbed onto the TiO_2 surface by an inner-sphere mechanism.^{27–29} From the FTIR spectrum analysis results, it was concluded that specific adsorption mechanism should occur at the aqueous solution of arsenic species and the solid sol–gel ZnO interface.

3.3 Effect of the pH on the photocatalytic removal of arsenic species

Since maximum adsorption of [As(III)] and [MMA(V)] species was achieved between pH 6 and 8, this pH range was selected for further studies. According to a previous study, the stability of ZnO can be maintained at this pH range.²⁴ Fig. 2 shows the effect of pH on the removal of [As(III)] and [MMA(V)].

The ZnO mediated photocatalytic treatment of [MMA(V)] was lower compared to As(III) oxidation. In the presence of UV light, the complete ZnO photocatalytic oxidation of As(III) was achieved within 180 min and it was not significantly influenced for the pH. Hence, further experiments for As(III) were performed at pH 7, near the pH of natural waters. At pH 8 the ZnO photocatalysis of [MMA(V)] resulted in 94% removal after 360 min, and thus pH 8 was selected for further experiments with [MMA(V)].

3.4 Effect of the ZnO loading

Experiments were conducted to assess the effect of catalyst loading on the overall [As(III)] and [MMA(V)] removal rate. The evaluated catalyst loadings were selected on the basis of preliminary experiments using a catalyst mass ranging from 0.10 to 1.00 g L^{-1} . The lowest amount of catalyst was found to be ineffective for arsenic species removal. On the other hand, the removal of arsenic species was completed at the highest loading level (1 g L^{-1}); however, the process was controlled by the adsorption. Thus, the catalyst dosages of 0.25 and 0.50 g L^{-1} were studied for a 5 mg L^{-1} arsenic species concentration in aqueous solutions. The removal efficiencies of As(III) and [MMA(V)] are depicted in Fig. 3. The removal of As species increased with increasing catalyst loading. The increase in the catalyst loading dose provides more active sites on the photocatalyst surface, which in turn increases the number of hydroxyl radicals.⁸ On a reported study using isopropanol and acetonitrile as radical scavengers and iodine anions as hole scavengers was demonstrated that the reaction mechanism for the photocatalytic oxidation on the ZnO surface mainly proceeded by $\text{HO}^\cdot$ radicals and to a lesser extent by the contribution of holes.³³ This result was in agreement with the mechanism proposed by Daneshvar *et al.* for the photocatalytic degradation of a reactive dye using ZnO.¹⁶ For [As(III)], 120 min of treatment results in complete removal employing 0.25 and 0.50 g L^{-1} sol–gel ZnO loading. While the oxidation of [As(III)] is significantly enhanced in the presence of 0.50 g L^{-1} catalyst, a lower loading of sol–gel ZnO was selected for the removal of [As(III)] in order to reduce the amount of used catalyst. The photocatalytic removal of [MMA(V)] was 92% in 120 min when the loading of sol–gel ZnO was 0.50 g L^{-1} , illustrated in Fig. 3. However, when the amount of catalyst was lowered to 0.25 g L^{-1} , the efficiency of photocatalytic oxidation of [MMA(V)] declined to 70% removal. The lower removal observed in [MMA(V)] compared with [As(III)] is a consequence of the lower adsorption capacity of the [MMA(V)] species on the sol–gel ZnO surface. The trend suggests that the optimal catalyst loading for removal of As

species in a sol–gel ZnO suspension under our experimental conditions was 0.25 g L⁻¹ for [As(III)] and 0.50 g L⁻¹ for [MMA(V)].

3.5 Control experiments

The UV photolysis on the removal of arsenic species was evaluated for an initial concentration of arsenic species of 5 mg L⁻¹. The oxidation of [As(III)] and [MMA(V)] to [As(V)] occurred by UV irradiation in the absence of sol–gel ZnO, but to a much less extent with only 17–18% of [As(III)] and [MMA(V)] oxidized in 6 h. Otherwise, the adsorption capacity of [As(III)] and [MMA(V)] without irradiation under the same reaction conditions was 53 and 33%, respectively. The adsorption of arsenic species occurred within the first hour and remained almost unchanged for up to 6 h. In contrast, the photocatalytic oxidation of [As(III)] and [MMA(V)] was highly efficient in the suspensions as illustrated in Fig. 2 for optimum catalyst loading. These control experiments clearly illustrated that the removal of [As(III)] and [MMA(V)] predominantly involves ZnO surface mediated photocatalysis.

The photocatalysis of arsenic species using TiO₂ has been adequately modeled by the first-order reaction rate expression.^{7,12,34,35} Then the kinetic parameters for removal of [As(III)] and [MMA(V)] can be calculated according to eqn (1):

$$\ln(C_0/C) = kt \quad (1)$$

where C_0 is the equilibrium concentration after adsorption; C the concentration at time t , and k the observed first-order rate constant.

The plots of $\ln(C_0/C)$ as a function of time gave linear relationships, with regression coefficients, R^2 , >0.9725 (see Table 3). The rate constants k were obtained as 1.66×10^{-2} and $3.84 \times 10^{-2} \text{ h}^{-1}$ for [MMA(V)] and [As(III)], respectively. The results were consistent with the observation that the initial photocatalytic oxidation of [As(III)] was faster than the [MMA(V)] removal process.

3.6 Comparison of the photocatalytic activity of sol–gel ZnO, commercial ZnO and TiO₂ Degussa P25

For the evaluation of the photocatalytic activity of sol–gel ZnO on the removal of [As(III)] and [MMA(V)], Degussa P25 and commercial ZnO were used as the reference under identical experimental conditions. The photocatalytic removal of [As(III)] is shown in Fig. 4a.

The results clearly indicated that Degussa P25 was found to be the most active in the oxidation of [As(III)]. By using sol–gel ZnO, the complete removal of [As(III)] was achieved in 150 min. The order of photocatalytic activity was Degussa P25 > sol–gel ZnO > commercial ZnO. While these results clearly demonstrated that [As(III)] was readily removed by these catalysts, it was important to identify the reaction by-products of the treated solutions. The results are shown in Fig. 4b. During the oxidation of [As(III)], [As(V)] species was formed in the solution. This behavior was in agreement with previous reports on a TiO₂ surface where the photocatalytic oxidation of [As(III)] was extremely fast, involving oxidation of the arsenic atom to the pentavalent oxidation state.^{10,36–40} By using TiO₂, the As(V) concentration that was formed as a by-product increased up to 4.9 mg As L⁻¹ in the first 2 h and remained constant thereafter. The observed difference between TiO₂ and sol–gel ZnO semiconductors was due to the excellent adsorption capability of sol–gel ZnO semiconductor shown for [As(V)], thus the [As(V)] concentration in the treated solution was largely decreased in spite of the continuous generation of [As(V)] by the oxidation of [As(III)]. Overall, the results demonstrated complete removal of [As(V)] even below the WHO drinking water limit of 10 µg L⁻¹ using the sol–gel ZnO catalyst.

Similar behavior was observed during the removal of [MMA(V)] (see Fig. 5a).

The results clearly demonstrated that photocatalytic oxidation of [MMA(V)] was faster in TiO₂ than in sol-gel ZnO. By using commercial ZnO, the removal efficiency of [MMA(V)] was approximately 55% after 300 min. Although TiO₂ exhibited better photocatalytic performance on the removal of [MMA(V)] than sol-gel ZnO, the [As(V)] generated during the photocatalytic removal process remained in solution since it was not adsorbed on the TiO₂ surface (Fig. 5b). By using commercial ZnO, 0.7 mg L⁻¹ [As(V)] remained in solution, conversely, complete adsorption of [As(V)] on the catalyst surface was observed with sol-gel ZnO.

The BET surface area and band gap energy (E_g) of the studied catalyst are shown in Table 4. With respect to Degussa P25, the ZnO catalysts showed lower BET surface area values. As can be observed in Fig. 4 and 5, the sol-gel ZnO showed better performance than commercial ZnO and TiO₂ on the removal of these two arsenic species. This fact can be a consequence of the structural defects formed on the semiconductor during the sol-gel preparation method, which in turn produced a shift on the E_g values. As can be seen in Table 4, the E_g value of sol-gel ZnO slightly decreased compared to the band gap value of commercial ZnO due to the elimination of the OH groups that are bound to the synthesized material. The sol-gel method using inorganic salts as precursors causes formation of M-OH₂ bonds which produces through the condensation several types of bridges and an infinite network.^{20,21} Additionally, the hydroxyl groups that are lost during the thermal treatment cause a certain degree of defects and yield oxygen vacancies that act as active sites improving the catalytic activity of sol-gel ZnO with respect to TiO₂ Degussa P25.²¹ According to Zheng *et al.*,⁴¹ defects in an oxide semiconductor have an important role in photocatalysis since the oxygen defects could benefit the efficient separation of electron-hole pairs in the photocatalytic process.

Thus, the high adsorption capacity observed in the ZnO synthesized by the sol-gel method provided the advantage that this material could be used as a combined catalyst and adsorbent to remove toxic arsenic species from groundwater samples.

4. Conclusions

The heterogeneous photocatalysis using ZnO prepared by sol-gel is effective for the oxidation of inorganic and organic arsenic species leading to the complete removal of [As(III)] and [MMA(V)] from aqueous solutions under UV irradiation. The [As(V)] generated as a by-product during the removal of these arsenic species was completely and strongly adsorbed onto the ZnO surface under a variety of conditions. This material has promising potential to consistently produce arsenic free water (<10 µg L⁻¹) from highly arsenic contaminated water. The photocatalytic method using ZnO prepared by the sol-gel technique may be applied as a relatively inexpensive method to treat arsenic contaminated groundwater of emerging regions of the world.

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References

1. Sharma VK, Sohn M. Environ. Int. 2009; 35:743–759. [PubMed: 19232730]
2. Mass MJ, Tennant A, Roop BC, Cullen WR, Styblo M, Thomas DJ, Kligerman AD. Chem. Res. Toxicol. 2001; 14:355–361. [PubMed: 11304123]

3. World Health Organization. Arsenic in drinking water. Oct 26.2008 May 2001.
4. Litter MI, Morgada ME, Bundschuh J. Environ. Pollut. 2010; 158:1105–1118. [PubMed: 20189697]
5. Zheng S, Cai Y, O'Shea KE. J. Photochem. Photobiol., A. 2010; 210:61–68.
6. Yang H, Lin WY, Rajeshwar K. J. Photochem. Photobiol., A. 1999; 123:137–143.
7. Bissen M, Vieillard-Baron MM, Schindelin AJ, Frimmel FH. Chemosphere. 2001; 44:751–757. [PubMed: 11482665]
8. Xu TL, Kamat PV, O'Shea KE. J. Phys. Chem. A. 2005; 109:9070–9075. [PubMed: 16332013]
9. Dutta PK, Ray AK, Sharma VK, Millero FJ. J. Colloid Interface Sci. 2004; 278:270–275. [PubMed: 15450443]
10. Dutta PK, Pehkonen SO, Sharma VK, Ray AK. Environ. Sci. Technol. 2005; 39:1827–1834. [PubMed: 15819243]
11. Xu TL, Cai Y, O'Shea KE. Environ. Sci. Technol. 2007; 41:5471–5477. [PubMed: 17822119]
12. Xu T, Jing C, Li F, Meng X. Environ. Sci. Technol. 2008; 42:2349–2354. [PubMed: 18504964]
13. Fujishima A, Zhang X, Tryk DA. Surf. Sci. Rep. 2008; 63:515–582.
14. Tian C, Zhang Q, Wu A, Jiang M, Liang Z, Jiang B, Fu H. Chem. Commun. 2012; 48:2858–2860.
15. Lizama C, Freer J, Baeza J. Catal. Today. 2002; 76:235–246.
16. Daneshvar N, Salari D, Khataee AR. J. Photochem. Photobiol., A. 2004; 162:317–322.
17. Sakthivel S, Neppolian B, Shankar MV, Arabindoo B, Palanichamy M, Murugesan V. Sol. Energy Mater. Sol. Cells. 2003; 77:65–82.
18. Khodja AA, Sehili T, Pilichowski JF, Boule P. J. Photochem. Photobiol., A. 2001; 141:231–239.
19. Zhou J, Zhang Y, Zhao XS, Ray AK. Ind. Eng. Chem. Res. 2006; 45:3503–3511.
20. Luo H, Wang C, Yan Y. Chem. Mater. 2003; 15:3841–3846.
21. Salinas-Guzmán R, Guzmán-Mar JL, Hinojosa-Reyes L, Peralta-Hernández JM, Hernández-Ramírez A. J. Sol-Gel Sci. Technol. 2010; 54:1–7.
22. Hernández A, Maya L, Sánchez-Mora E, Sánchez EM. J. Sol-Gel Sci. Technol. 2007; 42:71–78.
23. Feng M, Schrlau JE, Snyder R, Snyder GH, Chen M, Cisar JL, Cai Y. J. Agric. Food Chem. 2005; 53:3556–3562. [PubMed: 15853401]
24. Delgado-Balderas R, Hinojosa-Reyes L, Guzmán-Mar JL, Garza-González MT, López-Chuken UJ, Hernández-Ramírez A. Environ. Technol. 2012 DOI: 10.1080/09593330.2012.676070.
25. Bang S, Patel M, Lippincott L, Meng X. Chemosphere. 2005; 60:389–397. [PubMed: 15924958]
26. Jing C, Meng X, Calvache E, Jiang G. Environ. Pollut. 2009; 157:2514–2519. [PubMed: 19339086]
27. Jing C, Liu S, Patel M, Meng X. Environ. Sci. Technol. 2005; 39:5481–5487. [PubMed: 16082984]
28. Jing C, Meng X, Liu S, Baidas S, Patraju R, Christodoulatos C, Korfiatis GP. J. Colloid Interface Sci. 2005; 290:14–21. [PubMed: 16122542]
29. Pena M, Meng X, Korfiatis GP, Jing C. Environ. Sci. Technol. 2006; 40:1257–1262. [PubMed: 16572784]
30. Wang YD, Sun XD, Li HD. Mater. Sci. Eng., B. 2010; 167:177–181.
31. Goldberg S, Johnston CT. J. Colloid Interface Sci. 2001; 234:204–216. [PubMed: 11161507]
32. Catalano JG, Park C, Fenter P, Zhang Z. Geochim. Cosmochim. Acta. 2008; 72:1986–2004.
33. Palominos RA, Mondaca MA, Giraldo A, Peñuela G, Pérez-Moya M, Mansilla HD. Catal. Today. 2009; 144:100–105.
34. Gupta K, Ghosh UC. J. Hazard. Mater. 2009; 161:884–892. [PubMed: 18502578]
35. Yao S, Jia Y, Shi Z, Zhao S. Photochem. Photobiol. 2010; 86:1215–1221. [PubMed: 21039575]
36. Ferguson MA, Hering JG. Environ. Sci. Technol. 2006; 40:4261–4267. [PubMed: 16856744]
37. Yoon S, Lee JH. Environ. Sci. Technol. 2005; 39:9695–9701. [PubMed: 16475354]
38. Xu T, Kamat PV, O'Shea EK. J. Phys. Chem. A. 2005; 109:9070–9075. [PubMed: 16332013]
39. Lee H, Choi W. Environ. Sci. Technol. 2002; 36:3872–3878. [PubMed: 12322763]
40. Ferguson AM, Hoffmann MR, Hering JG. Environ. Sci. Technol. 2005; 39:1880–1886. [PubMed: 15819251]

41. Zheng Y, Chen C, Zhan Y, Lin X, Zheng Q, Wei K, Zhu J, Zhu Y. Inorg. Chem. 2007; 46:6675–6682. [PubMed: 17622132]

Fig. 1.

The FTIR spectra of sol-gel ZnO before and after reaction with arsenic species for 6 h. (a) Sol-gel ZnO, (b) ZnO-MMA(V), (c) ZnO-As(V) and (d) ZnO-As(III).

Fig. 2. Effect of pH on the photocatalytic removal of (a) [As(III)] and (b) [MMA(V)].

Fig. 3. Effect of catalyst loading on the photocatalytic removal of [As(III)] and [MMA(V)], using sol-gel ZnO. The initial As species concentration: 5 mg L⁻¹; solution pH: 7 for [As(III)] and 8 for [MMA(V)].

Fig. 4. Concentration of (a) [As(III)] and (b) [As(V)] during the photocatalytic oxidation of As(III) using (■) commercial ZnO, (●) Degussa P25 and (▲) sol-gel ZnO. Solution pH, 7; [As(III)] concentration, 5 mg L⁻¹; catalyst loading, 0.25 g L⁻¹.

Fig. 5.

Concentration of (a) [MMA(V)] and (b) [As(V)] during the photocatalytic oxidation of [MMA(V)] using (■) commercial ZnO, (●) Degussa P25 and (▲) sol-gel ZnO. Solution pH, 8; [As(III)] concentration, 5 mg L⁻¹; catalyst loading, 0.50 g L⁻¹.

Table 1Structure and pK_a values of studied arsenic species

Compound	Structure	Formula	pK_a
[As(III)]		AsO_3^{3-}	9.2, 12.1, 12.7
[As(V)]		AsO_4^{3-}	2.2, 7.0, 11.5
[MMA(V)]		$CH_3AsO(OH)_2$	4.1, 8.7

Table 2

Adsorption of [As(III)] and [MMA(V)] onto the surface of sol-gel ZnO as a function of pH in the dark

pH	<u>Adsorption of As species (%)</u>	
	[As(III)]	[MMA(V)]
5	44 ± 2	31 ± 2
6	42 ± 4	29 ± 3
7	53 ± 4	33 ± 3
8	56 ± 3	36 ± 3
9	52 ± 3	36 ± 3

Table 3

First-order kinetic constants of [As(III)] and [MMA(V)]

Arsenic species	k (h ⁻¹)	R^2	$t_{1/2}$ (h)
[As(III)]	3.84×10^{-2}	0.9725	1.8
[MMA(V)]	1.66×10^{-2}	0.9846	4.3

Table 4

BET surface area and band gap energy (E_g) values of the photocatalysts evaluated for arsenic species removal

Catalyst	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Band gap energy (eV)
Sol-gel ZnO	5.3	3.07
Commercial ZnO	3.2	3.17
Degussa P25	50.5	3.10