Combined use of photocatalyst and adsorbent for the removal of inorganic arsenic(III) and organoarsenic compounds from aqueous media

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Abstract

A novel method for the removal of inorganic arsenic(III) (As(III)), monomethylarsonate (MMA), and dimethylarsinate (DMA) from aqueous media, was proposed and investigated. This method involves the combined use of TiO_2-photocatalyst and an adsorbent, which has a high ability of As(V) adsorption, under photo-irradiation. When an aqueous solution of As(III) was stirred and irradiated by sunlight or xenon lamp in the presence of TiO_2 suspension, the oxidation of As(III) into As(V) was effectively attained. By use of the same photocatalytic reaction, MMA and DMA were also degraded into As(V), while the total organic carbon (TOC) in the aqueous phase was decreased. When an aqueous solution of As(III) was stirred with a mixed suspension of TiO_2 and an adsorbent for As(V) (activated alumina) under sunlight irradiation, the arsenic removal reached 89% after 24 h. By use of the same photocatalyst–adsorbent system, 98% of MMA and 97% of DMA were removed. The mechanism of the removal of arsenic species by the photocatalyst–adsorbent system was discussed.
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1. Introduction

Arsenic is a carcinogen and a toxic element for humans [1] and other living organisms [2]. Arsenic is present in natural waters in both inorganic and organic forms. The most common form of inorganic arsenic in surface water is arsenate (As(V)), while under highly reducing conditions, such as anaerobic ground waters, arsenic may form reduced arsenite (As(III)) forms [3]. The toxicity of As(III) is much higher than that of As(V).

Although the inorganic species are predominant in natural waters, the presence of organoarsenic compounds, such as monomethylarsonate (MMA) and dimethylarsinate (DMA),

has been reported. Considerably high concentrations of DMA were observed in Mexico [4] and Taiwan [5], while 10–24% of arsenic species detected in lake water and groundwater in some places in USA were methylated species [6,7]. Further, various organoarsenic compounds, such as MMA, DMA, and phenylarsonic acid derivatives, are used in agriculture in USA, and these compounds may contaminate agricultural wastewaters [8,9].

It has been thought that organoarsenic compounds are much less toxic than inorganic species. However, recent studies have demonstrated the carcinogenic ability of methylated arsenic compounds, especially DMA [10,11]. Also, the methylated species of trivalent arsenic, which is likely to produce during the metabolism of MMA and DMA, are equally or more toxic than As(III) in terms of cytotoxic effect [12].

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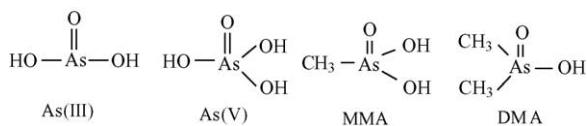 *E-mail address:* ohki@be.kagoshima-u.ac.jp (A. Ohki).

Fig. 1. Arsenic compounds used in this study (acid-forms are shown).

For inorganic arsenic compounds, especially As(V), there have been many studies about the removal from aqueous media; coprecipitation and adsorption are mainly used [13–15]. Compared to As(V), the removal efficiency of As(III) by use of those separation methods is inadequate [16], while those of MMA and DMA are also insufficient [17,18]. Therefore, the oxidation of As(III) into As(V) by use of oxidants, such as MnO_2 [19], H_2O_2 [20], O_3 [21], and Fenton reagent [22], has been attempted for the improvement of removal efficiency. The photocatalytic oxidation of As(III) using TiO_2 was reported [23–25], while we briefly mentioned the application of the photocatalytic reaction to the degradation of DMA into As(V) in our previous paper [26]. Also, the photochemical degradation of organoarsenic compounds has been studied on the purpose of analytical procedure [27,28]. However, to our knowledge, the combined use of photocatalyst and an adsorbent has not yet been attempted for the removal of arsenic species.

In the present work, we proposed and investigated the photocatalyst–adsorbent system for the removal of As(III), MMA, and DMA from aqueous media. Aqueous solutions of As(III), MMA, and DMA in the presence of TiO_2 and an adsorbent, such as activated alumina, were stirred and irradiated by sunlight. The effectiveness of this removal system was discussed. The structures of As(III), As(V), MMA, and DMA are shown in Fig. 1.

2. Materials and methods

2.1. Chemicals

Sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$), sodium arsenite ($NaAsO_2$), dimethylarsinic acid, titanium dioxide (TiO_2: anatase-type), activated alumina (AA), and activated carbon (AC) were purchased from Wako Pure Chemical Industries (Osaka, Japan). The average diameters of TiO_2, AA, and AC were 1.0 μm, 75 μm, and 3.5 mm, respectively, while the specific surface areas of those materials were 13, 200, and 950 m^2/g, respectively. Methylarsonic acid was obtained from Tri Chemical Laboratories Inc. (Yamanashi, Japan).

2.2. Photocatalytic reaction and adsorption

Aqueous TiO_2 suspension was prepared by adding 0.10 g of TiO_2 powder to a Pyrex round-bottomed flask with 10 mg-As/L of arsenic compound solution (100 mL). The flask was irradiated by sunlight, while the suspension was stirred with a magnetic stirrer. The sunlight irradiation was per-

formed July–October under cloudless sky on the roof of the Department of Bioengineering (Kagoshima University, Japan, 31°N). The intensity of UV-A light in the range of 310–390 nm at the reaction vessel measured by an actinometer (UIT-150, Ushio Inc., Tokyo, Japan) was 17–57 W/m^2. The temperature at the reaction vessel was 27–34 °C. For comparison, the irradiation by a 500 W xenon lamp (USH-500D, Ushio Inc.) without filter was performed; the intensity of UV-A light was ca. 50 W/m^2. At given irradiation time intervals, 3-mL aliquots were collected and centrifuged to remove the suspended particulates, and the supernatant was analyzed.

For the photocatalyst–adsorbent system, a proper amount of an adsorbent (AA or AC) was further added to make a mixed suspension of TiO_2 and the adsorbent, and the irradiation was performed. Analysis of the supernatant separated was similarly done. For all cases of the photocatalyst–adsorbent systems, the final pH values in the reaction mixtures were 6.5–7.5; under the pH conditions the adsorption of As(V) onto AA and AC was reported to effectively proceed [13].

2.3. Fractional determination of arsenic species

The fractional determination of arsenic species in the reaction mixture was carried out by an off-line combination of high-performance liquid chromatography (HPLC) and graphite furnace atomic absorption spectrophotometry (GFAAS) as reported in our previous paper [26]. The HPLC was performed with a Shimadzu LC-6A pump equipped with a Hamilton PRP-X100 anion-exchange column (150 mm × 5.0 mm). For the separation of As(III) and As(V), a buffered aqueous solution containing 30 mM ammonium carbonate (pH 8.0) was used, while 15 mM ammonium carbonate solution (pH 8.5) was used when MMA, DMA, and As(V) were separated. The eluent was collected at a fixed interval by a fraction collector. The arsenic concentration of each fraction was determined by a GFAAS instrument (Nippon Jarrel Ash AA-890 spectrometer with FLA-1000 flameless atomizer unit). The determination of total arsenic concentration was also performed by the GFAAS instrument.

When the photocatalytic degradations of MMA and DMA were performed, total organic carbon (TOC) in the aqueous phase of reaction mixture was measured using an automatic TOC analyzer (Shimadzu TOC-V CSH).

3. Results and discussion

3.1. Photocatalytic oxidation of As(III) into As(V)

To examine the validity of the TiO_2 photocatalytic oxidation of As(III), a set of experiments were performed. An aqueous solution of 10 mg-As/L As(III) was irradiated by sunlight in the presence of 1.0 g/L TiO_2 suspension. As shown in Fig. 2, the oxidation of As(III) into As(V) was effectively
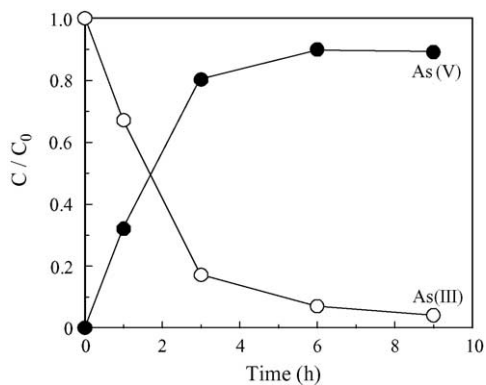
Fig. 2. Photocatalytic oxidation of As(III) under sunlight irradiation (10 mg-As/L As(III), 1.0 g/L TiO$_2$). C and C_0 denote the concentration (mg-As/L) of arsenic species in the aqueous phase at each reaction time and that initially added, respectively.

achieved after 6 h of reaction. Considering the mass balance of arsenic in the reaction, some portion of arsenic initially added was lost, probably due to the adsorption onto TiO$_2$ surface. Bissen et al. [24] reported that the adsorption of arsenic onto TiO$_2$ occurred in a similar photocatalytic reaction. When the photocatalytic reaction was carried out under dark conditions or without TiO$_2$, almost no oxidation of As(III) took place, suggesting that the oxidation of As(III) into As(V) is caused by the photocatalytic reaction for which both the photo-irradiation and the existence of TiO$_2$-photocatalyst are needed.

For comparison, the photo-irradiation was artificially conducted by a xenon lamp. As indicated in Fig. 3, almost similar oxidation profile to that for sunlight irradiation was obtained. Therefore, it is proved that the photocatalytic oxidation of As(III) into As(V) by sunlight irradiation is as effective as that for the artificial irradiation.

3.2. Adsorption of As(V) and As(III) by adsorbents

The adsorption of inorganic arsenic species, As(V) and As(III), were tested by use of two general adsorbents, AA
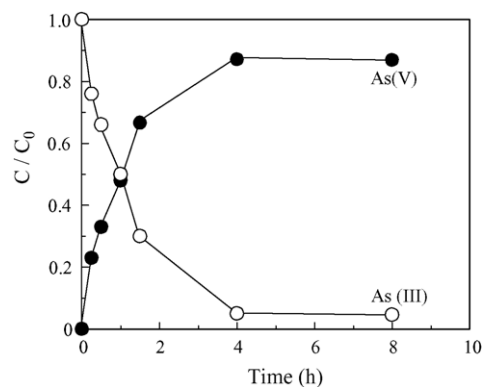

Fig. 3. Photocatalytic oxidation of As(III) under xenon lamp irradiation (10 mg-As/L As(III), 1.0 g/L TiO$_2$). The explanation of C and C_0 is seen in Fig. 2.
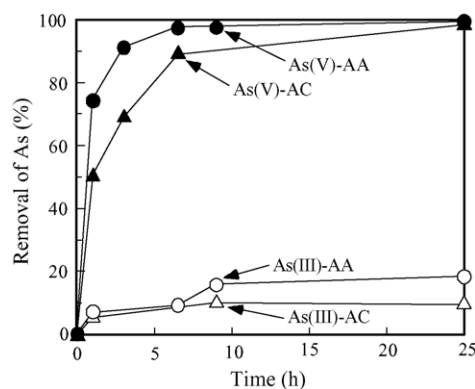

Fig. 4. Adsorption of As(III) and As(V) by two adsorbents (10 mg-As/L As(III) or As(V), 1.0 g/L adsorbent).

and AC. The results are presented in Fig. 4. When an aqueous solution of 10 mg-As/L As(V) was stirred with 1.0 g/L AA, the adsorption of As(V) favorably occurred and reached 97% removal after 7 h of reaction. However, the adsorption of As(III) was not effective and only 18% removal was attained even after 25 h. The use of AC instead of AA resulted in a little decrease in the removal efficiency for both As(V) and As(III). Consequently, the adsorption of As(III) is much inferior to that of As(V) when AA and AC are used as an adsorbent.

3.3. Removal of As(III) by photocatalyst–adsorbent system

The removal of As(III) was attempted by the combined use of TiO$_2$-photocatalyst and an adsorbent. As shown in Fig. 5, when an aqueous solution of 10 mg-As/L As(III) was stirred in the presence of both 1.0 g/L TiO$_2$ and 1.0 g/L AA under sunlight irradiation, the arsenic removal increased with time and reached 89% after 24 h. When the same photocatalyst–adsorbent system was carried out without the irradiation, the arsenic removal was greatly retarded, which was comparable to that in the case of As(III)–AA in Fig. 4. These results suggest that the photocatalytic oxidation of
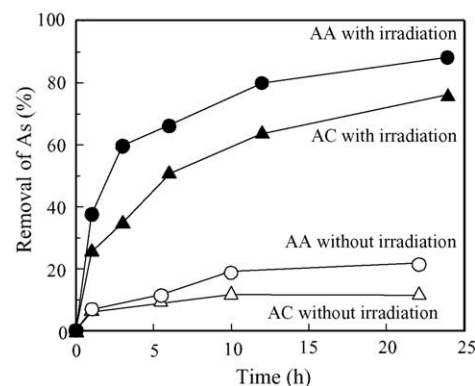

Fig. 5. Removal of As(III) by the combined use of TiO$_2$ and adsorbent under sunlight irradiation (10 mg-As/L As(III), 1.0 g/L TiO$_2$, 1.0 g/L adsorbent).
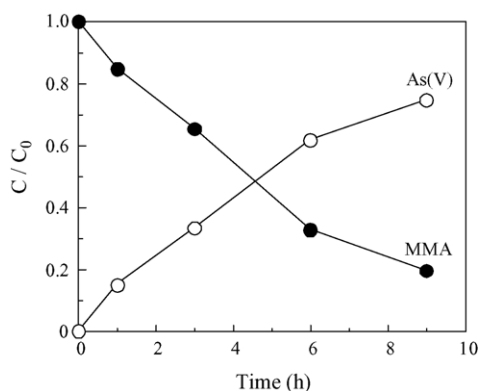
Fig. 6. Photocatalytic degradation of MMA under sunlight irradiation (10 mg-As/L MMA, 1.0 g/L TiO$_2$). The explanation of C and C_0 is seen in Fig. 2.

As(III) occurs and the resulting As(V) produced is adsorbed by AA. Compared with the simple adsorption of As(V) by AA, the photocatalyst–AA system provided a low removal rate. This result indicates that the oxidation of As(III) is the rate-determining step in the photocatalyst–AA system. The use of AC instead of AA leads to a little decrease in the arsenic removal, which may be ascribed to the relatively low As(V) adsorption ability of AC.

3.4. Photocatalytic degradation of MMA and DMA into As(V)

The photocatalytic degradation of MMA and DMA was examined, and the results for MMA and DMA are seen in Figs. 6 and 7, respectively. When an aqueous solution of 10 mg-As/L MMA was stirred with 1.0 g/L TiO$_2$ under sunlight irradiation, the concentration of MMA was decreased with irradiation time and reached 20% of the initial concentration after 9 h, while the almost comparable concentration of As(V) was increased, considering the adsorption of As(V) onto TiO$_2$.

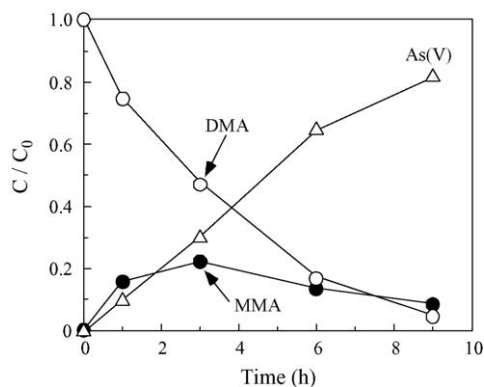When the same photocatalytic reaction was performed for DMA, the concentration of DMA was decreased and reached

Fig. 7. Photocatalytic degradation of DMA under sunlight irradiation (10 mg-As/L DMA, 1.0 g/L TiO$_2$). The explanation of C and C_0 is seen in Fig. 2.

4% of the initial amount after 9 h (Fig. 7). On the other hand, the concentration of MMA somewhat increased, then decreased, while that of As(V) greatly increased. For all of the sampling time points in Fig. 7, the mass balance of arsenic was almost satisfied considering the adsorption, suggesting that the degradation of DMA produces As(V) through the intermediate of MMA, and there are no notable side reactions.

When the photocatalytic degradation of MMA was performed, the TOC in the aqueous phase was measured. The initial TOC value was 1.5 mg/L, which is comparable to that calculated from the concentration of MMA initially added. The TOC in the aqueous phase after 9 h reaction was 0.3 mg/L, which is also comparable to that calculated from the concentration of MMA unreacted. This result suggests that the organic portion of MMA is probably decomposed into CO$_2$ by the TiO$_2$ photocatalytic reaction, resulting in the production of As(V).
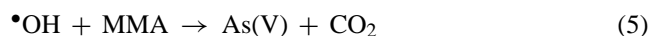
In the photocatalytic reaction, conduction band electrons (e$^-$) and valence band holes (h$^+$) will be generated on the surface of TiO$_2$ by the photo-irradiation:

$$TiO_2 + h\nu \rightarrow h^+ + e^- \tag{1}$$

The holes (h$^+$) may react with MMA to produce As(V) and CO$_2$, and/or react with OH$^-$ or H$_2$O to give hydroxyl radicals ($^\bullet$OH):

$$h^+ + MMA \rightarrow As(V) + CO_2 \tag{2}$$

$$h^+ + OH^- \rightarrow {}^\bullet OH + H^+ \tag{3}$$

$$h^+ + H_2O \rightarrow {}^\bullet OH + H^+ \tag{4}$$

The hydroxyl radical also reacts with MMA:

$${}^\bullet OH + MMA \rightarrow As(V) + CO_2 \tag{5}$$

The electrons (e$^-$) generated may react with oxidants, such as dissolved oxygen, in the aqueous phase:

$$e^- + O_2 \rightarrow {}^\bullet O_2{}^- \tag{6}$$

The measurement of TOC for the photocatalytic degradation of DMA was also carried out, and a similar result
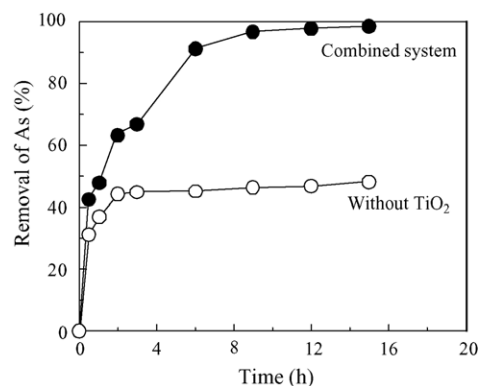

Fig. 8. Removal of MMA by the combined use of TiO$_2$ and AA under sunlight irradiation (10 mg-As/L MMA, 1.0 g/L AA, 1.0 or 0 g/L TiO$_2$).
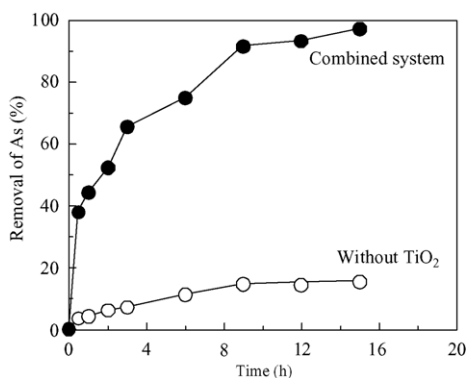
Fig. 9. Removal of DMA by the combined use of TiO_2 and AA under sunlight irradiation (10 mg-As/L DMA, 1.0 g/L AA, 1.0 or 0 g/L TiO_2).

was obtained; the decrease of TOC was comparable to the concentration of DMA degraded. This result suggests that the degradation mechanism of DMA is similar to that of MMA.

3.5. Removal of MMA and DMA by photocatalyst–adsorbent system

As shown in Fig. 8, when an aqueous solution of 10 mg-As/L MMA was stirred in the presence of both 1.0 g/L TiO_2 and 1.0 g/L AA under sunlight irradiation, the arsenic removal increased with time and reached 98% of the initial amount after 15 h of reaction. When the same system was carried out in the absence of TiO_2, the arsenic removal was considerably decreased; however, still notable removal of MMA occurred. It appears that MMA itself is adsorbed by AA, although the adsorption of MMA is much inferior to that of As(V).

Also, the removal of DMA was conducted by use of the photocatalyst–adsorbent system, and the results are shown in Fig. 9. In the combined system, in which TiO_2 and AA were present, almost all of arsenic was removed, whereas the absence of TiO_2 led to a great reduction in the arsenic removal. It is anticipated that DMA itself is hard to adsorb
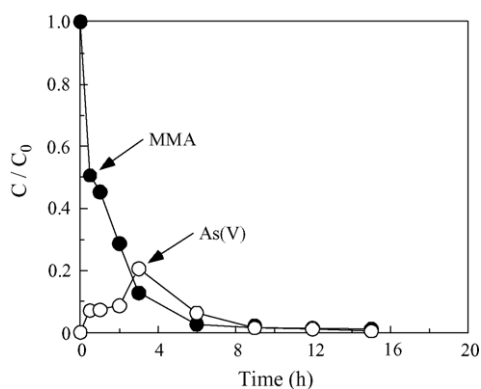

Fig. 10. Concentration of arsenic species in the combined system for the removal of MMA under sunlight irradiation (10 mg-As/L MMA, 1.0 g/L TiO_2, 1.0 g/L AA). The explanation of C and C_0 is seen in Fig. 2.
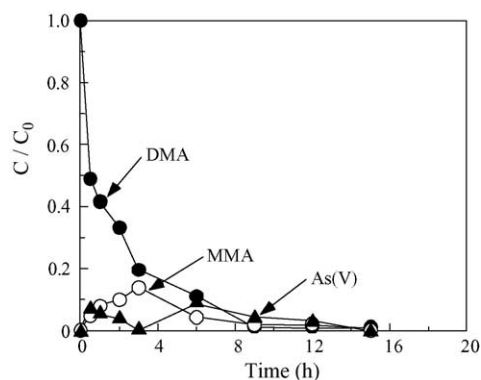

Fig. 11. Concentration of arsenic species in the combined system for the removal of DMA under sunlight irradiation (10 mg-As/L DMA, 1.0 g/L TiO_2, 1.0 g/L AA). The explanation of C and C_0 is seen in Fig. 2.

by AA, so that the arsenic removal is much smaller than that for MMA, when TiO_2 is absent.

Figs. 10 and 11 show the concentration of arsenic species in the combined system for the removal of MMA and DMA, respectively. The degradation products (As(V) for the MMA degradation, and MMA and As(V) for the DMA degradation) were detected during the arsenic removal by the combined system. Therefore, it is concluded that the removal of MMA and DMA from aqueous media can be effectively attained by the combined use of TiO_2–photocatalyst and an adsorbent under sunlight irradiation, and the removal proceeds through the degradation of MMA and DMA, and the resulting products are adsorbed by the adsorbent.

4. Conclusions

The removal of As(III), MMA, and DMA from aqueous media was attempted by the combined use of TiO_2-photocatalyst and an adsorbent under photo-irradiation. It was proved that the arsenic species, which are hard to remove by use of ordinary adsorbents, could be effectively removed by the present photocatalyst–adsorbent system. The recycle use of adsorbent, such as AA, for the As(V) removal has been well-studied [14], and therefore it is hopefully possible to attain the recycle use of adsorbent also in the present system, which will lead to practical use of the present system. The aim of this study is to prove the effectiveness of the combined use of a photocatalyst and an adsorbent in the removal of hazardous materials, and it has been successfully attained. Obviously, the novel concept will offer a new possibility in the application of photocatalytic reaction to the area of environmental clean-up, which certainly deserves further exploration.

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