Coagulation of methylated arsenic from drinking water: Influence of methyl substitution

Chengzhi Hu*, Qingxin Chen, Huijuan Liu, Jiuhui Qu

Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

HIGHLIGHTS

- FeCl_3 was more efficient than Al salts in methylated As removal by coagulation.
- As removal was negatively correlated with the degree of methyl substitution.
- Adsorption on Fe/Al hydroxide flocs was major coagulation mechanism of methylated As.
- As–O group of methylated As substituted O–H group of Fe/Al hydroxide to form complex.

GRAPHICAL ABSTRACT

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ABSTRACT

Methylated arsenic can be found in virtually all earth surface environments. So far, however, little information has been collected regarding their removal by coagulation. In this study, the removal of monomethylarsenate (MMA) and dimethylarsenate (DMA) from drinking water by coagulation was investigated from the viewpoint of methyl substitution. Results indicated that FeCl_3 was more efficient than AlCl_3 and polyaluminum chloride (PACl) in methylated As removal. For the initial arsenic concentration of $200 \mu\text{g/L}$, an FeCl_3 dosage of 0.2 mmol Fe/L was sufficient to attain about 95% removal of MMA, while a dosage of 0.6 mmol Fe/L achieved about 57% removal of DMA. Arsenic removal efficiency was negatively correlated with the degree of methyl substitution. With the increase in methyl group number, the quantity of negatively charged arsenic species decreased and molecular size increased, leading to the decrease of methylated As removal by coagulation. Adsorption on preformed hydroxide flocs was the major mechanism during coagulation. Both FTIR and XPS results indicated that the As–O group of As might substitute the O–H group of Fe/Al hydroxide to form a Fe/Al–O–As complex. Furthermore, the use of traditional oxidants and coagulation aids exhibited limited help for improving coagulation removal of DMA.

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1. Introduction

Arsenic (As) is of considerable environmental concern due to its toxicity [1], with drinking water, the main source of As exposure for

* Corresponding author. Tel.: +86 10 6284960; fax: +86 10 62849160.
E-mail address: czhu@rcees.ac.cn (C. Hu).

Fig. 1. Effect of coagulant dose on As(V), MMA, DMA removal and treated water pH (a) FC coagulation (b) AC coagulation (c) PACl coagulation (d) treated water pH. Initial As concentration was 200 $\mu\text{g As/L}$.

humans [2]. Although inorganic As(V) and As(III) are the most common arsenic species in the environment, organic forms of As can also be found in nature, typically occurring as monomethylarsenate (MMA) and dimethylarsenate (DMA) [3]. Previous research reported that 19.4% and 5.0% of total As occurred as DMA and MMA, respectively, in a Californian lake [4], and 24.1% of total As occurred as DMA (3.5 $\mu\text{g As/L}$) in a southwest Spanish river [5], where methylated As may threaten the safety of drinking water. In addition, MMA and DMA concentrations were found to be 35.4–233.9 $\mu\text{g As/L}$ and 3.5–13.1 $\mu\text{g As/L}$ from a source of drinking water in Inner Mongolian, respectively [6]. Some bacteria and fungi can produce MMA and DMA through the methylation of inorganic As [7]. Furthermore, MMA and DMA can be introduced into the environment through agricultural activities [8] with both used as herbicides and pesticides over the past several decades [7,9]. Although inorganic As has long been considered more toxic than organic As [10], some methylated As, such as MMA(III), is reportedly much more toxic than inorganic As [11]. Thus, the reduction of MMA and DMA can produce very toxic MMA(III) and DMA(III), respectively.

As a result of the widespread distribution and toxicity of methylated As in the environment, research on methylated As removal from water has grown in importance. The adsorption of MMA and DMA on several minerals has been studied previously [9,12–16]. Results found that adsorption of DMA on goethite and ferrihydrite was reportedly low compared with As(V) and MMA [13], adsorption of As(V) on aluminum oxide reached 100% within 5 min, while 78% and 15% of MMA and DMA were adsorbed, respectively [15], and adsorption of MMA on nanocrystalline TiO_2 achieved 100% at pH 7.5, with DMA removal reaching 65% at pH 5.5 [17].

The number of methyl groups of As(V), MMA and DMA is 0, 1 and 2, respectively. Variation in methyl substitution degree can lead to

remarkable differences in the adsorption behavior of As onto Fe/Al oxides. Coagulation by Fe- and Al-based salts have been used as the most practical choice for As removal from drinking water [18,19]. Many studies have investigated the coagulation removal of inorganic As [20–23]. However, only limited information is available on the removal of organic As by coagulation [24], and the removal of methylated As from drinking water by coagulation has not yet been studied. Furthermore, the influence of methyl substitution on As coagulation by Fe/Al-based salts is still unclear.

We investigated the coagulation efficiency and behavior of methylated As in drinking water from the viewpoint of methyl substitution. The removal of As(V), MMA and DMA was examined under various conditions including coagulant type, coagulant dose, and water pH. The mechanisms of methylated As removal by Al/Fe-based coagulants were also studied through particular coagulation/adsorption experiments. The interaction of flocs with As(V), MMA and DMA was characterized using Fourier transform infrared spectrometry (FTIR) and X-ray photoelectron spectrometry (XPS). We also evaluated the addition of common oxidants and coagulant aids to enhance methylated As removal by coagulation.

2. Material and methods

2.1. Materials and analysis methods

All chemical solutions used in this study were prepared using de-ionized water and analytical (or better) grade chemicals. FeCl_3 (FC), AlCl_3 (AC) and polyaluminum chloride (PACl) were used as coagulants. PACl was prepared by an electrochemical process [25]. The predominant Al species of PACl was Al_{13} polymer, which accounted for 86.3% of total Al

Fig. 2. Effect of pH on As(V), MMA and DMA removal (a) FC coagulation (b) AC coagulation (c) PACl coagulation. Initial As concentration was 200 $\mu\text{g As/L}$. Coagulant dosages were 0.1 mmol/L.

concentration as analyzed by the Ferron colorimetric method [26]. $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma, USA), $\text{CH}_3\text{AsNaO}_3 \cdot 1.5\text{H}_2\text{O}$ (Sigma, USA) and $\text{C}_2\text{H}_6\text{AsNaO}_2 \cdot 3\text{H}_2\text{O}$ (J&K, China) were used to prepare 400 mg/L As(V), MMA and DMA stock solutions, respectively. The initial concentration of As in the experiments was approximately 200 $\mu\text{g/L}$.

Arsenic analysis was conducted using inductively coupled plasma mass spectrometry (Thermo Scientific, USA). The collision cell was switched on to eliminate Cl^- interference from $^{40}\text{Ar}^{35}\text{Cl}^+$. Each sample was measured three times and the value of RSD could not exceed 5%.

2.2. Jar tests

Jar tests were performed on a six-paddle stirrer. Sample water (400 mL) was transferred to a 500 mL beaker. The process included 2 min of rapid stirring (200 rpm), 15 min of slow stirring (40 rpm) and 30 min of settling, after which the supernatants were filtered by 0.45 μm pore size membranes and measured by ICP-MS for As. Water pH was accurately adjusted to the expected values by adding HCl or NaOH solution after dosing with coagulants during the rapid stirring period, after which water pH was almost constant in the following processes.

Fig. 3. As(V), MMA and DMA removal by coagulation and adsorption on preformed hydroxide flocs (a) FC coagulation (b) AC coagulation (c) PACl coagulation. Initial As concentration was 200 $\mu\text{g As/L}$. pH value was 5.

Some common oxidants and coagulant aids were used to enhance DMA removal by coagulation. A certain amount of KMnO_4 , NaClO and powdered activated carbon (PAC) were added into the sample water at the beginning of the coagulation process, and FC was then added after 20 min. A certain amount of chitosan (deacetylation degree 80–95%) was added into the sample water after FC addition in the rapid stirring period. The treated water was taken for As measurement.

2.3. Adsorption experiments

Adsorption experiments were initiated to evaluate As(V), MMA and DMA removal by adsorption on preformed Al/Fe hydroxide flocs. In the water samples without As, hydroxide flocs formed during the slow stirring period. A certain amount of As was then added into the preformed flocs suspension and another 15 min of slow stirring was performed to allow for As adsorption. The settling step was applied after the adsorption step. The experimental conditions for adsorption were the same for coagulation. The removal performance of As by adsorption was then compared with that by coagulation.

Fig. 4. FTIR spectra for flocs obtained from coagulation by FC/AC. (a) FC coagulation (b) AC coagulation. As/Fe = As/Al = 1.2 (w/w).

2.4. Flocs characterization by FTIR and XPS

When coagulation finished, the flocs were accumulated by settling and centrifuging, and then freeze-dried for FTIR and XPS characterization. FTIR spectra were collected on a Nicolet 5700 spectrometer using absorbance mode. Samples for FTIR were ground with spectral grade KBr in an agate mortar. A fixed sample ratio (2% w:w) was used to prepare the pellet. XPS data were collected on an ESCA-Lab-220i-XL spectrometer with monochromatic Al K α radiation (1486.6 eV). C1s peaks were used as an inner standard calibration peak at 284.7 eV.

3. Results and discussion

3.1. Effect of coagulant dose on arsenic removal

Fig. 1 shows the results of As(V), MMA and DMA removal by FC, AC and PACl. With the increase in coagulant dosage, the concentration of As gradually decreased, except at high dosages of AC. Results showed that FC was more effective than Al-based coagulants for methylated As removal. The removal efficiency of MMA by FC reached above 95% at dosages of more than 0.2 mmol Fe/L, while the maximum removal efficiency by Al-based coagulants was about 84.1% at the AC dosage of 0.4 mmol Al/L. The removal of DMA by FC was also notably higher than that by the two Al

salts at the same dosage. Fig. 1 shows the removal efficiency of As as As(V) > MMA > DMA. The removal efficiency of methylated As decreased with the increase in the degree of methyl substitution. After the addition of 0.2 mmol/L FC, the removal efficiencies of As(V), MMA and DMA were 98.3%, 94.7% and 22.1%, respectively. MMA removal exhibited a similar trend as As(V) during the FC coagulation process. MMA concentrations in the treated water met the required maximum contaminant level (10 μ g As/L) when adding more than 0.2 mmol/L FC. Fig. 1 also indicates that AC exhibited better coagulation performance than that of PACl. DMA removal by PACl coagulation was almost negligible. Accordingly, with respect to DMA, coagulation by Fe and Al-based coagulants was not an effective removal method.

The pH of treated water was depressed by coagulant addition (Fig. 1(d)). The most significant decline in water pH was observed by FC coagulation. For Al-based coagulants, the extent of pH decrease was inverse to coagulant basicity ($[\text{OH}^-]/[\text{Al}_\text{T}]$). With the addition of 1.0 mmol/L Al salts, the pH with AC addition decreased from 7.6 to 4.8, which was larger than the pH range observed with PACl. With the addition of more than 0.6 mmol/L AC, water pH was less than 6, under which most hydrous Al oxides are soluble and less solid Al hydroxides are formed [27]. Accordingly, As removal decreased at dosages of more than 0.6 mmol Al/L. The effect of pH on methylated As removal by coagulation was further investigated, as discussed below.

3.2. Effect of pH on arsenic removal

Fig. 2 shows the effect of pH on As(V), MMA and DMA removal when 0.1 mmol/L of coagulants were used. Dosages of 0.6 mmol/L were also used and exhibited more pronounced removal performance than that of 0.1 mmol/L dose, although the trend was similar as that observed for As removal (Fig. S1). In the range of pH 4–9, methylated As removal efficiencies with FC were clearly higher than those using the two Al-based coagulants. The optimal pH levels for MMA and DMA removal by FC, AC and PACl were 4–6, 5–7 and 5–8, respectively. Generally, in weakly acidic pH conditions, Fe and Al hydroxide flocs readily and largely form due to the minimum solubility of Fe and Al in water in this pH region [27]. Hydroxide flocs may favor methylated As removal through coprecipitation into growing hydroxides and adsorption on preformed hydroxide flocs. The solubility product constant of aluminum hydroxide and that of ferric hydroxide was reported to be about 10^{-33} and 10^{-38} , respectively [27]. Accordingly, hydrous Fe oxide was found to be more insoluble than hydrous Al oxide [18], which produced more flocs during coagulation and which could be helpful for methylated As removal. In addition, the structure of Fe hydroxide appears to be more open and loose than that of Al hydroxide [28], thereby supplying a large available surface area for complexing or adsorbing MMA and DMA. Such factors might contribute to the better performance of FC in As removal. Fig. 2(b) and (c) show that MMA removal by AC was higher than those by PACl in the pH range 5–8. Previous research indicated that, in this pH region, Al_{13} species was largely in situ formed during AC coagulation process, which supported the higher removal of As [29]. Fig. 2 also shows DMA removal by AC and PACl coagulation was almost negligible. PACl performance in regards to As removal was less dependent on pH than was AC. This might be the result of the stable characteristics of preformed Al hydroxide polymers during the PACl coagulation process.

3.3. Mechanism of methylated As removal by coagulation

MMA and DMA are anionic species in water, as shown in Fig. S2. The possible coagulation mechanism, by which anionic contaminants are converted into insoluble products, includes precipitation, coprecipitation, and adsorption [28,30]. Precipitation refers to the

Fig. 5. XPS for flocs obtained from coagulation by FC/AC (a) FC coagulation (b) AC coagulation. As/Fe = As/Al = 1.2 (w/w).

insolubilization of contaminants by exceeding a solubility product. Coprecipitation is defined as the incorporation of contaminants into a growing hydroxide phase via inclusion or occlusion. Adsorption refers to the formation of a surface complex between anionic contaminants and a solid hydroxide surface [30]. To explore which mechanism was predominant for methylated As removal in coagulation, the degree of As removal via coagulation was compared with the adsorption removal on preformed hydrous Fe/Al oxide under identical conditions [31,32].

As shown in Fig. 3, the coagulation removal efficiencies of MMA and DMA were much higher than that of adsorption. Adsorption of As occurred as well as precipitation and co-precipitation during coagulation. However, the gap in As removal efficiency between adsorption and coagulation was small. The difference was much more pronounced at low dosages than at high dosages of coagulants for As(V) and MMA, but the trend for DMA was obscured due to ineffective removal by coagulation. Consequently, results indicated that adsorption on Fe/Al hydroxide was the most important mechanism for As removal and precipitation or co-precipitation might also play certain roles, especially at low coagulant dosage. Incorporation of As into the growing hydroxide phase via inclusion or occlusion was difficult due to the fewer hydroxide flocs formed at low coagulant dosage. As removal by both coagulation and adsorption increased with the increase in coagulant dose. Fig. 3 shows that FC exhibited better As removal performance than that of AC or PACI, which may be attributed to the lower solubility of hydrous Fe oxide and open structure of Fe hydroxide flocs, ensuring a large available surface area for adsorption [28]. The flocs generated from AC coagulation were larger and looser than those generated from

PACI coagulation [29]. Consequently, AC exhibited much better performance than PACI for MMA and DMA removal.

3.4. Characterization of coagulation flocs by FTIR and XPS

Fig. 4(a) shows the FTIR spectra for FC flocs generated from coagulation. The two peaks at 1121 and 1048 cm^{-1} were assigned to the symmetrical and asymmetrical stretching vibration of the O–H group of ferric hydroxide, respectively [33]. After coagulation with As, the two peaks at 1121 and 1048 cm^{-1} disappeared obviously for As(V) and MMA, while the intensities of the two peaks became weaker for DMA. These results implied that the O–H group of Fe hydroxide might play an important role in As removal. It could be deduced that the As–O group of As might substitute the O–H group of Fe hydroxide, i.e., the interaction between As and surface hydroxyl of Fe hydroxide was responsible for the attachment of As onto Fe hydroxide. This might be the mechanism for methylated As removal by coagulation and has also been proposed by other researchers when using Fe oxide adsorbents to adsorb As(V) and As(III) [34–36]. The obscure change in the O–H group of Fe hydroxide for DMA might be ascribed to lower consumption of the O–H group during the coagulation process.

Simultaneously, the new peaks that appeared at 831 , 811 and 821 cm^{-1} were assigned to As–O stretching vibration of As(V), MMA and DMA, respectively [33]. The differences in the As–O vibration position might be attributed to the structural variations of As(V), MMA and DMA. Methyl groups, attached with As, could donate electrons, which would influence the chemical environment around the As–O group. In addition, the peak intensity at 821 cm^{-1} for DMA was much weaker than the peak intensities of 831 cm^{-1} for As(V) and 811 cm^{-1} for MMA. This might also be attributed to the lower removal of DMA by FC coagulation and less DMA attached to Fe hydroxide. The peak at 1270 cm^{-1} was assigned to the As–CH₃ group [37], which only exist in the spectrums of MMA and DMA. This phenomenon was consistent with the molecular structure of methylated As.

Fig. 4(b) shows the FTIR spectra for the flocs of AC coagulation. The weak band at 1293 cm^{-1} was assigned to the As–CH₃ group [37]. The band at 1123 cm^{-1} was assigned to the stretching vibration of the O–H group of Al hydroxide [38,39]. After coagulation with As(V), MMA and DMA, the peak at 1123 cm^{-1} obviously disappeared for As(V) and weakened for MMA, while little change was observed for DMA. The lower removal of MMA and DMA compared with that of As(V) by AC coagulation might explain the obscure changes at 1123 cm^{-1} . The three peaks that appeared at 871 , 861 and 850 cm^{-1} were assigned to As–O stretching vibration for As(V), MMA and DMA, respectively [33]. The peak at 606 cm^{-1} was assigned to the stretching vibration of the Al–O group of Al hydroxide [39,40]. After coagulation with As(V), MMA and DMA, the position of the Al–O group shifted to 559 , 591 and 599 cm^{-1} , respectively. It was concluded that the As–O group of As might substitute the O–H group of Al hydroxide and a surface complex in the form Al–O–As could be constructed during coagulation. With the increase in methyl group number in methylated As, the electron atmosphere above the Al–O bond in the surface complex would move towards the center of Al and O. This could lead to an increase in the force constant of the Al–O bond. As a result, the vibration frequency of Al–O would increase, resulting in an increase in Al–O wavenumber.

The XPS of Fe 2p and Al 2p of the flocs obtained from FC and AC coagulation are illustrated in Fig. 5. The Fe 2p binding energy of pure Fe hydroxide flocs was 710.8 eV . After coagulation with As(V), MMA and DMA, the Fe 2p binding energies shifted to 711.9 , 710.9 and 710.4 eV , respectively, which were negatively correlated with the degree of methyl substitution. The binding energy change of Fe 2p might be attributed to surface complexation between As and

Fig. 6. Interaction mechanism between methylated As and Fe/Al (Me) hydroxide during coagulation.

Fe hydroxide. With the increase in methyl substitution degree, the electron density around the Fe atom increased. This change might have caused the binding energy of Fe 2p to decrease gradually. The Al 2p binding energy of pure Al hydroxide flocs was 74.5 eV. After coagulation with As(V), MMA and DMA, the Al 2p binding energies shifted to 74.8, 74.3 and 74.0 eV, respectively, showing similar trends to FC coagulation.

During the coagulation process, the As–O group of As(V), MMA and DMA substituted the O–H group of Fe/Al hydroxide to form a M–O–As complex. Methyl substitution significantly influenced

the interaction between As and Fe/Al hydroxide, leading to the remarkable differences in As removal by coagulation. The influence of methyl substitution on coagulation could be explained by the following points. Firstly, as shown in Fig. S2, the number of de-protonation sites for As(V), MMA and DMA were 3, 2 and 1, respectively. As a result, As(V) had the largest quantity of negatively charged species, while DMA had the smallest quantity at any pH environment. Consequently, electrostatic attraction with positively charged metal hydroxide was highest for As(V) and lowest for DMA. This would influence the coagulation removal efficiency of As(V),

Fig. 7. Performance of some methods to enhance DMA removal (FC dosage was 0.2 mmol/L. Initial pH was 7.80. Initial DMA concentration was 200 $\mu\text{g As/L}$).

MMA and DMA. Secondly, the variation in molecular structure also influenced the removal efficiency of methylated As by coagulation. Average As–O distance was found to be about 1.7 Å, and average As–C distance was about 1.9 Å [41,42]. Consequently, the substitution of the –CH₃ group for the –OH group would make the molecular sizes of MMA and DMA larger than As(V), which might hinder surface complexation between As and Fe/Al hydroxide. As a result, the removal efficiency of As was negatively correlated with methyl substitution degree. As(V) can form three different surface complexes on Fe/Al oxide, including monodentate complex, bidentate binuclear complex and bidentate mononuclear complex [41,43], while both MMA and DMA can form bidentate binuclear complexes on Fe/Al oxide [15,42]. As(V) has more possible edge sites than MMA and DMA when forming complexes with Fe/Al oxide due to more hydroxyl groups when compared with methylated As [15]. Fewer reactive sites might result in lower adsorption affinity on Fe/Al hydroxide, leading to the decrease in coagulation removal efficiency of As with the increase in methyl substitution degree. In addition, the formation of a bidentate binuclear complex between DMA and Fe/Al oxide requires that both As=O and the As–OH group are involved in the complexation, while the formation of the complex between MMA or As(V) and Fe/Al oxide only requires the involvement of two As–OH groups [15,42]. Thus, the complex structure between DMA and Fe/Al oxide can be less stable than the complex structure for MMA or As(V) [15]. This can also contribute to the lower adsorption affinity on Fe/Al hydroxide and lower removal by Fe/Al salt coagulation for DMA than that for MMA or As(V). The possible interaction mechanism between methylated As and Fe/Al hydroxide during the coagulation process is illustrated in Fig. 6.

3.5. Evaluation of common methods to enhance DMA removal

As a result of the limited removal of DMA by coagulation, supplementary methods such as pre-oxidation and coagulant aids were used to enhance DMA removal. NaClO and KMnO₄, which are common pre-oxidants in drinking water treatment, were used to pre-oxidize DMA to As(V) or MMA and were subsequently removed by coagulation. As shown in Fig. 7(a) and (b), the removal efficiency of As remained almost unchanged after adding various doses of NaClO or KMnO₄. The results indicated that the –CH₃ group of DMA was difficult to destroy by the oxidants. The use of ozone also exhibits limited destruction of DMA [44].

Previous research demonstrated that PAC was effective at enhancing As(V) removal [45], and high content of basic groups of PAC might favor adsorption of As [46]. In the present study, commercial PAC was used to adsorb DMA, followed by coagulation. Fig. 7 shows that the removal of DMA increased by about 14% after the addition of 5 mg/L PAC, but remained relatively unchanged with the further increase in PAC dosage. Results showed that PAC adsorption was not an efficient option for enhancing DMA removal. Chitosan or modified chitosan derivatives were also used as coagulant aids to remove As, since the amine groups of chitosan can interact with anions [47]. Results showed that chitosan hardly improved the removal of DMA.

4. Conclusions

We showed that FC was much more efficient than AC and PACI in relation to methylated As removal by coagulation. Compared with DMA, As(V) and MMA were more easily removed. The coagulation removal efficiency of methylated As was negatively correlated with the degree of methyl substitution. Adsorption onto Fe/Al hydroxide flocs was the predominant mechanism for MMA and DMA removal, and precipitation or co-precipitation might also play a specific role

at low coagulant doses. Adsorption affinity decreased with the increase in the degree of methyl substitution.

The smallest quantity of negatively charged species of DMA in water and its larger molecular size were mainly responsible for the lower removal efficiency of DMA by coagulation. The As–O group of As substituted the O–H group of Fe/Al hydroxide to form a complex, which might be the interaction mechanism between methylated As and Fe/Al flocs. The unstable structure of the complex formation between DMA and Fe/Al hydroxide might also lead to the poor removal of DMA by coagulation. The DMA methyl group was difficult to destroy by conventional oxidants. PAC and chitosan were also not effective coagulant aids to improve the removal of DMA.

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Appendix A. Supplementary data

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