Oxidation of As(III) by potassium permanganate

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Abstract

The oxidation of As(III) with potassium permanganate was studied under conditions including pH, initial As(III) concentration and dosage of Mn(VII). The results have shown that potassium permanganate was an effective agent for oxidation of As(III) in a wide pH range. The pH value of tested water was not a significant factor affecting the oxidation of As(III) by Mn(VII). Although theoretical redox analyses suggest that Mn(VII) should have better performance in oxidization of As(III) within lower pH ranges, the experimental results show that the oxidation efficiencies of As(III) under basic and acidic conditions were similar, which may be due to the adsorption of As(III) on the $Mn(OH)_2$ and MnO_2 resulting from the oxidation of As(III).

Key words: arsenite; arsenate; oxidation; potassium permanganate

Introduction

Arsenic (As) is a naturally occurring toxic element which exists in both organic and inorganic forms in nature. Organic arsenic species in water supplies are seldom above 1 μg/L (Anderson and Bruland, 1991) and have no significant effect on drinking water treatment. Inorganic arsenic in water mainly exists in two forms, As(III) and As(V). In the normal pH range of natural water, As(V) exists in the form of anions such as $H_2AsO_4^-$ and $HAsO_4^{2-}$ while As(III) is in the form of neutral molecular, i.e., H_3AsO_3. As(V) and As(III) are present mainly in surface water and anaerobic groundwater.

Arsenic contamination of drinking water has received increasingly intensive attention in recent years because of its carcinogenic properties (Smith *et al.*, 1992). Arsenic poisoning has affected millions of people worldwide, especially in Bangladesh (Smith *et al.*, 2000). Accordingly, the Environmental Protection Agency of the United States recently reduced the maximum contaminant level of arsenic in drinking water from 50 to 10 μg/L. In order to meet the new stringent standard, different As removal methods have been developed.

As(III) is more toxic and mobile than As(V), so its removal efficiency is much lower than that of As(V) when conventional arsenic removal technologies are used. Therefore, oxidation of As(III) to As(V) is necessary to

improve total arsenic removal efficiency.

Chlorine is one of the oxidizers so far explored by many researchers. However, harmful Cl-based byproducts could be generated during this oxidation process. The other oxidants reported for oxidation of As(III) include ozone, pure oxygen (Kim and Nriagu, 2000), hydrogen peroxide (Ryu and Choi, 2004), manganese oxides (Manning *et al.*, 2002; Tournassat *et al.*, 2002), UV/iron (Emett and Khoe, 2001; Hug *et al.*, 2001), TiO$_2$/UV (Kocar and Inskeep, 2003; Lee and Choi, 2002), and ferrate (Lee *et al.*, 2003). Each oxidant as an As(III) oxidizing agent has its advantages and disadvantages.

Potassium permanganate is powerful oxidant. Commercial potassium permanganate is in solid form and it does not generate seriously concerned byproducts. Therefore, it can potentially be used to oxidize As(III) in water treatment. This research aims at investigating the oxidation of As(III) by potassium permanganate and examining the factors affecting the oxidation of As(III).

1 Experiments

1.1 Materials and chemicals

All solutions used in the research were prepared with deionized water, which was further degassed with purging helium for at least 10 min to exclude oxygen from water. All the chemicals were analytic grade and were used as

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received. Sodium arsenite, NaAsO$_2$, used as the source of As(III), was purchased from Aldrich, and KMnO$_4$ was supplied by Fisher Scientific.

1.2 Solution preparation

A stock 100 mg/L As(III) solution was prepared by dissolving 0.1734 g of NaAsO$_2$ in 1000 ml of degassed deionized water. For each test, 1000 ml of 200–600 μg/L As(III) solution was prepared by diluting the stock solution with predetermined volumes of degassed deionized water. A stock 0.01 mol/L KMnO$_4$ solution was prepared by dissolving 1.58 g of KMnO$_4$ in 1000 ml of degassed deionized water. The buffer solutions used in this study are CH$_3$COOH-CH$_3$COONa (0.001 mol/L, respectively) and NaHCO$_3$-Na$_2$CO$_3$ (0.001 mol/L, respectively).

1.3 Analyses of As(III)

The concentrations of As(III) were measured using silver-diethyldithiocarbamate-based method as outlined in Standard Methods for the Examination of Water and Wastewater (Eathon *et al.*, 1995). This method is based on the fact that As(III) and As(V) can be selectively reduced by sodium brohydride (NaBH$_4$) to arsine (AsH$_3$) under different pH conditions. Under an acetate buffer condition of pH approximately 5.5, only As(III) can be reduced to AsH$_3$, but when the pH value of the solution is lower than 1, both As(III) and As(V) can be reduced. The generated AsH$_3$ will be carried by N$_2$ gas and absorbed with silver diethyldithiocarbamate. The concentration of As in AsH$_3$ was measured using a Varian DMS-100 UV/VIS with a detection limit of 3 μg/L at a wavelength of 520 nm.

1.4 Measurement of redox potentials

The redox potentials of solutions after oxidation of As(III) were measured by EW-59521-80 LABCOR Consort R305 Proportional pH/mV/Ion Controller with Dual Electrode Inputs.

1.5 Procedures

The performance of KMnO$_4$ in oxidizing As(III) under different oxidation conditions, including different initial concentrations of Mn(VII) and As(III), and pH, was investigated. The first step of the oxidation tests was to add the diluted As(III) solution as prepared to a 1000-ml of deionized water in a volumetric flask, which was followed by adjusting the pH of the As(III) solution with an appropriate amount of the prepared buffer solutions. The second step was to add a designated quantity of potassium permanganate solution to the As(III) solution and shake the solution for about 10 min. The solution was left to oxidize without being disturbed for either 24 or 48 h. Then, 10–100 ml of treated water sample was taken for As(III) analysis. The volumes of samples taken for As(III) measurements depended on the residual concentrations of As(III). Each As(III) oxidation test was conducted at room temperature (22–23°C).

2 Results and discussion

The residual concentrations of As(III) in water samples collected after one and two days of oxidation are shown in Fig.1. It shows that the average variations (ε), defined as the difference of the residual As(III) concentration achieved in the first and second days of tests was 0.9 μg/L, and the corresponding standard deviation of variances for the system was 17 μg/L. As the standard deviation was larger than the average variations, the differences of As(III) residual concentrations obtained in two days are statistically negligible. In other words, 24 h was sufficient to take representative samples for studying the performance of Mn(VII) in the oxidation of As(III).

The results of the oxidation of As(III) by Mn(VII) under different pH and oxidizer dosages are shown in Fig.2. Fig.2 indicates that residual As(III) concentrations of solutions were not affected substantially by the pH value of As(III) solution. For example, when pH values were increased from 4.5 to 9.8 at the dosage of 1.78×10^{-6} mol/L Mn(VII), residual As(III) concentrations decreased only from 50 to 30 μg/L. Fig.2 shows that the As(III) oxidation efficiencies were affected by the dosages of oxidizers added to As(III) solutions. For example, when the Mn(VII) dosage increased from 1.78×10^{-6} to 7.11×10^{-6} mol/L, the residual As(III) concentration decreased from 50 to 0 μg/L.
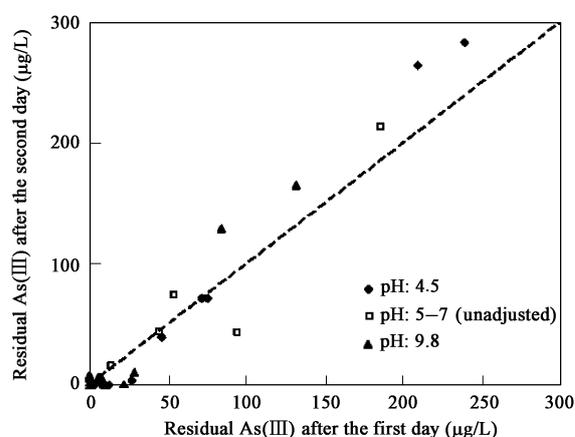

Fig. 1 Changes of residual As(III) concentrations after one day and two days of oxidation.
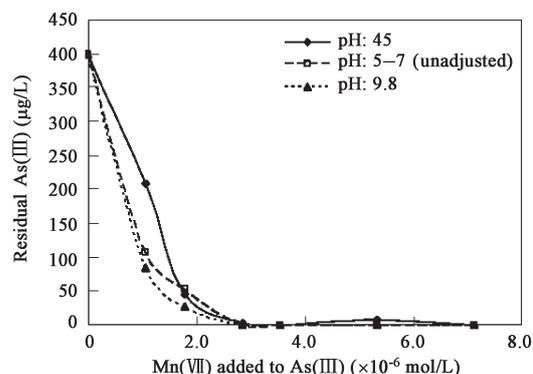

Fig. 2 Effects of Mn(VII) dosage on residual As(III) concentration. Initial As(III) concentration: 400 μg/L.
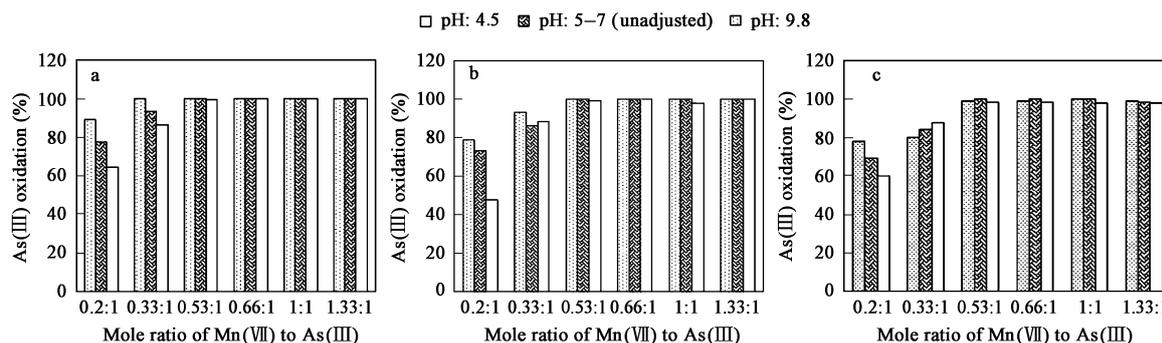
Fig. 3 Effects of Mn(VII):As(III) ratios and pHs on the oxidation of As(III). Initial As(III) concentration was (a) 200 μg/L; (b) 400 μg/L; (c) 600 μg/L.

When the dosage of Mn(VII) added was 2.0×10^{-6} mol/L the residual concentrations of As(III) under three different pH conditions were less than 40 μg/L.

The effects of the mole ratios of Mn(VII):As(III) on As(III) oxidation under different initial As(III) concentrations and pH conditions are presented in Fig.3. Fig.3 shows that about 100% As(III) oxidation efficiency can be achieved when the mole ratio of Mn(VII):As(III) is greater than 0.53:1. Furthermore, the As(III) oxidation efficiencies obtained under basic conditions for Mn(VII)-As(III) system are higher than those under acidic conditions.

The relationships between the dosages of oxidizers added and the quantity of the oxidized As(III) are shown in Fig.4 to further study the mechanism of oxidation of As(III) by Mn(VII) under different conditions. Fig.4 indicates that the dosages of Mn(VII) added are linearly related to the amount of As(III) oxidized under the given oxidation conditions. The slopes in Fig.4, represents the moles of As(III) oxidized by each mole of Mn(VII). Fig.4 indicates
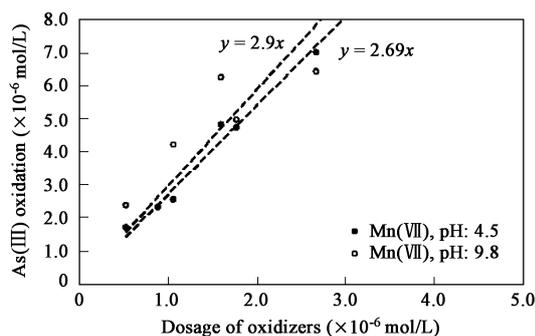

Fig. 4 Relationships used for indicating mechanism of As(III) oxidation by Mn(VII).

that 2.69 and 2.9 moles of As(III) disappeared from water due to the addition of one mole of Mn(VII) under acidic (pH approximately 4.5) and basic (pH approximately 9.8) conditions, respectively. The proposed mechanisms for the oxidation of As(III) with Mn(VII) under acidic and basic environment are shown in Reactions (1) and (2), respectively:

$$5As^{3+} + 2MnO_4^- + 16H^+ \longrightarrow 5As^{5+} + 2Mn^{2+} + 8H_2O \quad (1)$$

$$5As^{3+} + 2MnO_4^- + 8H_2O \longrightarrow 5As^{5+} + 2Mn(OH)_2 + 12OH^- \quad (2)$$
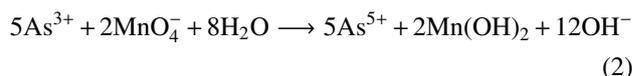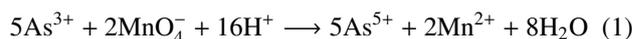
Reactions (1) and (2) indicate that 2.5 moles of As(III) could be theoretically oxidized with one mole of Mn(VII) under both acidic and basic conditions. Under acidic conditions, As(III) oxidation efficiencies obtained from experiments for the Mn(VII)-As(III) oxidation systems were slightly higher than those calculated from Reaction (1). Under basic conditions, As(III) oxidation efficiencies obtained from experiments for the Mn(VII)-As(III) oxidation systems were obviously greater than those calculated from Reaction (2).

The possible intermediate processes involved and their redox potentials, obtained either from reference materials or calculated by the authors, are listed in Table 1. For the Mn(VII)-As(III) system, MnO_4^- can be possibly reduced to either Mn^{2+} or MnO_2 under acidic conditions, and either $Mn(OH)_2$ or MnO_2 under basic conditions. The MnO_2 or $Mn(OH)_2$ formed can adsorb As(III) and co-precipitate, which explains why the As(III) oxidation efficiencies achieved were always higher than those calculated with Reactions (1) and (2).

Table 1 Possible oxidation mechanisms involved and their redox potentials

Reduction half-reaction	Redox potential (V)	Reference
Acidic solution		
$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_{2(s)} + 2H_2O$	1.70	Hill and Petrucci, 2002
$MnO_{2(s)} + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	1.51	Hill and Petrucci, 2002
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	1.224	Calculated
Basic solution		
$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_{2(s)} + 4OH^-$	0.60	Hill and Petrucci, 2002
$MnO_{2(s)} + 2H_2O + 2e^- \longrightarrow Mn(OH)_{2(s)} + 2OH^-$	−0.05	Hill and Petrucci, 2002
$MnO_4^- + 4H_2O + 5e^- \longrightarrow Mn(OH)_{2(s)} + 6OH^-$	0.34	Calculated

3 Conclusions

It has been found that Mn(VII) is efficient for the oxidation of As(III). The performance of Mn(VII) in the oxidation of As(III) is not greatly affected by the pH of the solution. Approximately, two moles of Mn(VII) are needed to oxidize five moles of As(III), and the ending reduction products of Mn(VII) are mainly Mn(II) and Mn(OH)$_2$ under acidic and basic conditions, respectively.

References

Anderson L C D, Bruland K W, 1991. Biogeochemistry of arsenic in natural waters: the importance of methylated species[J]. Environ Sci Technol, 25(3): 420–427.

Eathon A D, Clesceri L S, Greenberg A E, 1995. Standard methods for the examination of water and wastewater[M]. 19th ed. Washington: American Public Health Association.

Emett M T, Khoe G H, 2001. Photochemical oxidation of arsenic by oxygen and iron in acidic solutions[J]. Water Research, 35(3): 649–656.

Hill J W, Petrucci R H, 2002. General chemistry, an integrated approach[M]. Upper Saddle River, New Jersey: Prentice Hall.

Hug S J, Canonica L, Wegelin M *et al.*, 2001. Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters[J]. Environ Sci Technol, 35(10): 2114–2121.

Kim M J, Nriagu J, 2000. Oxidation of arsenite in groundwater using ozone and oxygen[J]. Science of the Total Environment, 247(1): 71–79.

Kocar B D, Inskeep W P, 2003. Photochemical oxidation of As(III) in ferrioxalate solutions[J]. Environ Sci Technol, 37(8): 1581–1588.

Lee H, Choi W, 2002. Photocatalytic oxidation of arsenite in TiO$_2$ suspension: kinetics and mechanisms[J]. Environ Sci Technol, 36(17): 3872–3878.

Lee Y, Um I H, Yoon J, 2003. Arsenic(III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic(V) by iron(III) coagulation[J]. Environ Sci Technol, 37(24): 5750–5756.

Manning B A, Fendorf S E, Bostick B *et al.*, 2002. Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite[J]. Environ Sci Technol, 36(5): 976–981.

Ryu J, Choi W, 2004. Effects of TiO$_2$ surface modifications on photocatalytic oxidation of arsenite: The role of superoxides[J]. Environ Sci Technol, 38(10): 2928–2933.

Smith A H, Hopenhayn-Rich C, Bates M N *et al.*, 1992. Cancer risks from arsenic in drinking water[J]. Environmental Health Perspectives, 97: 259–267.

Smith A H, Lingas E O, Rahman M, 2000. Contamination of drinking water by arsenic in Bangladesh: A public health emergency[J]. Bulletin of the World Health Organization, 78(9): 1093–1103.

Tournassat C, Charlet L, Bosbach D *et al.*, 2002. Arsenic(III) oxidation by birnessite and precipitation of manganese(II) arsenate[J]. Environ Sci Technol, 36(3): 493–500.