



Capacity and recycling of polyoxometalate applied in As(III) oxidation by Fe(II)-Amended zero-valent aluminum

Liang-Ching Hsu^a, Yen-Lin Cho^b, Yu-Ting Liu^{b,*}, Yu-Min Tzou^{b,**}, Heng Yi Teah^c

^a Scientific Research Division, National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu 300, Taiwan

^b Department of Soil and Environmental Sciences, National Chung-Hsing University, 145 Xingda Rd., Taichung 402, Taiwan

^c Division of Environmental Studies, Graduate School of Frontier Sciences, The University of Tokyo, 332 Building of Environmental Studies, 5-1-5 Kashiwanoha, Kashiwa City, Chiba 277-8563, Japan

HIGHLIGHTS

- Polyoxometalate boosts As(III) oxidation in Fe(II)-amended ZVAL at acidic pH.
- Reduced polyoxometalate reacts with O₂ to generate H₂O₂.
- Polyoxometalate is recycled via the re-polymerization at pH 1.
- Recycled polyoxometalate performs comparable efficiency in As(III) oxidation.

ARTICLE INFO

Article history:

Received 5 November 2017

Received in revised form

24 January 2018

Accepted 10 February 2018

Available online 12 February 2018

Keywords:

Arsenic

Oxidation

Polyoxometalate

Zero-valent aluminum

Recycling

ABSTRACT

Arsenic remediation is often initiated by oxidizing As(III) to As(V) to alleviate its toxicity and mobility. Due to the easy availability, zero-valent Al (ZVAL) like Al can was considered as potential alternatives to facilitate As(III) oxidation. This study determined the capability and recycling of polyoxometalate (POM) to catalyze As(III) oxidation in Fe(II)-amended ZVAL systems. POM acquired electrons from ZVAL more effectively at pH 1 than at pH 2. While 76% of the reduced POM [POM(e⁻)] reacted with O_{2(g)} to generate H₂O₂ at pH 1, only 60% of POM(e⁻) was used to produce H₂O₂ at pH 2. The remaining POM(e⁻) was oxidized by the generated H₂O₂. Such additional consumption of POM(e⁻) and H₂O₂ led to the incomplete As(III) oxidation in the system without residual ZVAL and emphasized the need for a continuous electron supply from ZVAL to compensate the depletion of POM(e⁻). After the hydrolyzation at pH 6.0, the XANES data evidenced that not only As(V) but WO₄ released from the POM retained on surfaces of Al/Fe hydroxides. The competition for sorption sites on Al/Fe hydroxides between As(V) and WO₄ led to the incomplete As removal. Despite the loss of WO₄, the POM re-polymerized at pH 1 still showed the comparable capability to catalyze As(III) oxidation with original POM. This study revealed electron transfer pathways from ZVAL to As(III) as catalyzed by POM and evidenced the effective POM recycling after As removal, which lowers the cost of POM application and turns the ZVAL/Fe(II)/POM/O₂ system into a practical strategy for As remediation.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

The widely distributed As in water, groundwater, sediment, and other areas particularly enriched with pyrite or sulfide has posed the potential threat to the ecosystem and public health (Moore et al., 1994; Schreiber et al., 2000; Minnesota Department of

Health, 2001; Williams, 2001; Appleyard et al., 2004). In most natural waters, both As(III) and As(V) are common As oxyanions (Smedley and Kinniburgh, 2002). Given that As(III) shows a greater toxicity and a lower affinity to natural adsorbents such as ferrihydrite than As(V) does, the oxidation of As(III) to As(V) is considered as a strategy to alleviate the As impact in environments. In addition to the microbial catalysis (Bruneel et al., 2003), As(III) oxidation could be induced through a Fenton or Fenton-like reaction by zero-valent metals (Katsoyiannis et al., 2008). Our previous studies reported that As(III) could be effectively oxidized in the ZVAL/O₂

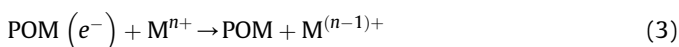
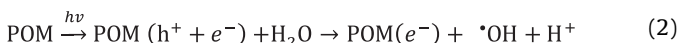
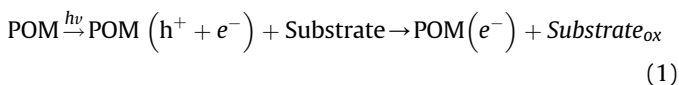
* Corresponding author.

** Corresponding author.

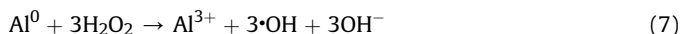
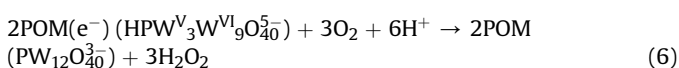
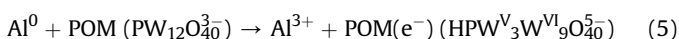
E-mail address: yliu@nchu.edu.tw (Y.-T. Liu).

system with amendments of Fe(II) or POM (Wu et al., 2013; Hsu et al., 2016), however, related mechanisms are still unclear.

Polyoxometalate (POM) consists of cations and polyanion clusters (Pope, 1983), which generally contains early transition metals such as W and Mo and main-group elements like P and S. While the nature of cations in POM controls the crystallographic property and solubility (Pradeep et al., 2010; Yan et al., 2010), polyanions in POM show the redox nature to bear and release electrons due to their ability to play as the Lewis acid and Lewis base under different conditions (Wang and Yang, 2015). The combination of notable redox properties with remarkable hydrolytic and oxidative stabilities makes POM a preponderant catalyst, although subunits of polyanions might release from the skeletons in the aqueous solution at a certain pH range (Wang and Yang, 2015). In POM, the charge could transfer from an oxygen atom to the d orbital of trace element in the presence of UV or near visible light. For example, the photocatalysis of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ induces the charge transfer from O^{2-} to W^{6+} , resulting in a pair of a hole center (O^-) with a trapped electron center (W^{5+}) (Guo and Hu, 2007). Upon the excitation, POM serves as a strong oxidant to decompose organic substances directly [equation (1), Hiskia et al. (2006)] or indirectly via the OH radicals ($\cdot\text{OH}$) produced from the reaction of excited POM with water molecules [equation (2), Mylonas and Papaconstantinou (1996)]. In both scenarios, the reduced POM [$\text{POM}(\text{e}^-)$] could further transfer electrons to metal ions [equation (3), Gkika et al. (2005)]. Such concomitant process was recognized as a prominent strategy for Cr(VI) remediation (Gkika et al., 2006).



Besides the photocatalysis, POM could also receive electrons from the reductant to form the $\text{POM}(\text{e}^-)$. Lee et al. (2007) reported that POM reacted as an electron shuttle to gain electrons from zero-valent iron (ZVI). The $\text{POM}(\text{e}^-)$ subsequently transferred electrons to oxygen atoms and boosted H_2O_2 production, which initiated the $\cdot\text{OH}$ -mediated oxidation through a Fenton-like reaction. Compared with the ZVI, zero-valent aluminum (ZVAL) has a higher oxidation potential [$E^\circ(\text{Al}^0/\text{Al}^{3+}) = 1.66 \text{ V}$ versus $E^\circ(\text{Fe}^0/\text{Fe}^{3+}) = 0.04 \text{ V}$] (Lin et al., 2009; Wu et al., 2013) and an easier access. For example, beverage cans that contain >95% of Al (AlSaffar and Bdeir, 2008) could be considered as the alternative material of ZVAL (Hsu et al., 2016). These preponderances make ZVAL a promising substitute for ZVI to serve as a reductant for POM. In an aerated condition, both O_2 and POM could gain electron from the oxidation of ZVAL to generate H_2O_2 [equation (4), Bokare and Choi (2009)] and $\text{POM}(\text{e}^-)$ [equation (5), Wu et al. (2013)], respectively. The $\text{POM}(\text{e}^-)$ could further react with O_2 to produce additional H_2O_2 . While H_2O_2 reacted with residual ZVAL, a strong oxidant of $\cdot\text{OH}$ was formed [equations (6) and (7), Wu et al. (2013)]. Therefore, the ZVAL/POM/ O_2 system has been tentatively applied for As(III) oxidation to As(V) (Katsoyiannis et al., 2008; Wu et al., 2013; Hsu et al., 2016).



In this study, we aimed to determine how the simultaneous addition of Fe(II) and POM affected the As(III) oxidation in relation to the capability of POM catalysis with the reductant of ZVAL via the stoichiometric calculation for the generation and consumption of $\text{POM}(\text{e}^-)$ and H_2O_2 . Furthermore, we also determined the efficiency of POM recycling after the As(III) oxidation and the subsequent As removal to lower the cost for the POM application in As remediation.

2. Materials and methods

2.1. Materials

All chemicals and reagents used in this study are analytical grade, and all solutions were prepared using the 18 M Ω Millipore water. The ZVAL purchased from Merck was cut into pieces with the dimension of 5 mm \times 5 mm \times 0.3 mm, whose specific surface area is $3.4 \times 10^{-3} \text{ m}^2 \text{ g}^{-1}$ (Lin et al., 2009). The pre-treatment for ZVAL was applied for specific experiments, which was conducted by setting 1 g of ZVAL in 100 mL of 6 M HCl under an anoxic environment for 1 h. This process was repeated twice to remove the oxide layer on ZVAL surfaces. The ZVAL with HCl pretreatment was denoted as HCl-treated ZVAL hereafter.

2.2. Methods

2.2.1. POM reduction by ZVAL with and without HCl pre-treatment and the production of H_2O_2

One mL of POM stock solution (25 mM, $\text{HNa}_2\text{PW}_{12}\text{O}_{40}$, Sigma-Aldrich) was adjusted to pH 1 or pH 2 using 0.1 M HCl and then diluted to 250 mL to achieve the final concentration of 100 μM . The diluted POM solution was purged with a $\text{N}_{2(\text{g})}$ flow at 50 mL min^{-1} for 30 min prior to the addition of ZVAL. The ZVAL or HCl-treated ZVAL was then added into the POM solution with a solid concentration of 4 g L^{-1} . Changes in the absorbance at 650 nm, indicating the production of $\text{POM}(\text{e}^-)$ (Hiskia et al., 2001), were monitored over time using the UV-VIS Spectrophotometer (Varian Cary 50).

For the system with HCl-treated ZVAL, the residual ZVAL was removed from the solution immediately after POM reduction reached the equilibration, i.e. the $\text{POM}(\text{e}^-)$ concentration hit a plateau. The solution containing $\text{POM}(\text{e}^-)$ was purged instantly with a $\text{O}_{2(\text{g})}$ flow at 50 mL min^{-1} . For the other batch of experiment, H_2O_2 (Sigma-Aldrich) was added into the solution containing $\text{POM}(\text{e}^-)$ to achieve a final concentration of 150 μM , and the system was still purged with $\text{N}_{2(\text{g})}$ instead of $\text{O}_{2(\text{g})}$ at a flow rate of 50 mL min^{-1} . The H_2O_2 production from both batches of experiments was determined over time using the colorimetric method (Bader et al., 1988). See Fig. S1 in the Supplementary Data (SD) for the experimental flow chart.

2.2.2. As(III) oxidation by $\text{POM}(\text{e}^-)$

The 100 μM POM solution with pre-adjusted pH of 1 or pH 2 was mixed with HCl-treated ZVAL at solid concentration of 4 g L^{-1} under a $\text{N}_{2(\text{g})}$ flow (50 mL min^{-1}). When the concentration of $\text{POM}(\text{e}^-)$ achieved a plateau, the residual ZVAL was removed from the solution. As(III) (NaAsO_2 , Sigma-Aldrich) and Fe(II) ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Sigma-Aldrich) were then added into the solution to achieve a final concentration of 85 μM and 250 μM , respectively, and the system was purged with $\text{O}_{2(\text{g})}$ at a flow rate of 50 mL min^{-1} . Concentrations of As(III) were determined using the hydride generation-atomic absorption spectrometry (HG-AAS, Hitachi Z-2000) overtime (Wu et al., 2013). The experimental flow chart was summarized in Fig. S1 in SD.

Download English Version:

<https://daneshyari.com/en/article/8851815>

Download Persian Version:

<https://daneshyari.com/article/8851815>

[Daneshyari.com](https://daneshyari.com)