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Promotion effect of $KMnO_4$ on the oxidation of As(III) by air in alkaline solution

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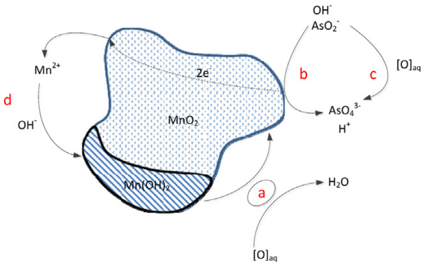
HIGHLIGHTS

- $KMnO_4$ shows superstoichiometric oxidation for arsenic in solution.
- Adding $KMnO_4$ to alkaline solution could improve the kinetics of arsenic oxidation.
- MnO_2 acts as a catalyst to prompt reaction between As(III) and dissolved oxygen.
- The mole ratio of As/Mn and pH has significant effects on As(III) oxidation.
- The adsorption and desorption of MnO_2 with As(III) and oxygen occurs.

GRAPHICAL ABSTRACT

The mechanism of the oxidation of arsenic by air in the presence of $KMnO_4$: (a) Oxidation of Mn^{2+} and formation of MnO_2; (b) Catalytic oxidation of arsenic; (c) Oxidation of arsenic by dissolved oxygen; (d) Dissolution and precipitation of Mn^{2+}.



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ABSTRACT

The mechanism of oxidation of As(III) in alkaline solution by air with promotion effect of $KMnO_4$ was studied. The experimental results indicated that the superstoichiometric oxidation of As(III) by $KMnO_4$ could be attributed to the catalytic effect of reductive product of $KMnO_4$. The XRD and XPS results demonstrated that the catalyst was nascent MnO_2 rich in potassium. The results also showed that the mole ratio of Mn/As and the initial pH had significant effects on the oxidation of As(III). The time for the oxidation by air was less than 2 h with the mole ratio of Mn/As less than 1/10.5 and the initial pH higher than 13. The kinetics of the catalytic oxidation of arsenic was interpreted using the pseudo first order reaction, and the apparent active energy was about 15.01 kJ/mol. The study suggested that the initial oxidation was firstly dominated by the direct oxidation of $KMnO_4$ followed by the catalytic oxidation with the nascent MnO_2.

1. Introduction

Arsenic is a toxic element for human and animals, and the long-term intake of small doses of arsenic has led to the increased occurrence of many cancers particularly those of the skin and bladder [1]. The behavior of arsenic in aqueous solution is strongly affected by the valency of arsenic [2,3]. Since As(III) is much more toxic and more transportable than As(V), it is necessary to oxidize As(III) to As(V) in the treatment of arsenic bearing solution [4,5]. The current methods on oxidation of arsenic include direct chemical oxidation [6–8], which is characterized with high efficiency (>99%) but costly, photocatalytic oxidation [9–12] and biological oxidation [13,14]. For the photocatalytic oxidation using visible radiation, there is still a large gap when compared to the case of using high-energy radiations, such as ultraviolet radiation [9]. The research of biological oxidation has been employed to oxide As(III)

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in drinking water plants, but this method was only suitable for low levels of arsenic due to the lack of bacterial strain of high inhibitory concentration for As(III) [15]. More recently, the advanced oxidation processes, using reactive oxygen species ($O_2^{\bullet-}$, H_2O_2, $^{\bullet}OH$, or other oxidizing intermediates) as the oxidants, have been successfully developed to treat arsenic bearing groundwater or drinking water, but most of them use UV radiation instead of sunlight to promote the oxidation of arsenic, resulting in large cost of treatment [1,16,17]. Therefore, strong oxidants such as H_2O_2 [6], Cl_2 [18], NaClO [19], O_3 [20] and $KMnO_4$ [7] are normally used, especially for the solution containing high concentration of arsenic. Although the efficiency of oxidation by these strong oxidants is satisfactory, for example, it has been reported that a 1.0 mg/L free chlorine dose was able to oxidize 100 μg/L As(III) in less than 5 s [21], the high cost limits their industrial application. It is urgent to explore a method with low cost on the oxidation of arsenic.

Undoubtedly, the oxidation of arsenic by air is a promising method, however, the slow kinetics/oxidation rate limit its application [19,22]. For example, some researchers found that only 57% and 54% As(III) is oxidized at pH of 7.6–8.5 with oxygen and air after 5 days, respectively [20]. Scott and Morgan even concluded that dissolved oxygen had no effect on the oxidation of the As(III) [21,23].

Although it was feasible for the oxidation of As(III) with dissolved O_2 thermodynamically ($\Delta G_{AsO_4^{3-}/AsO_2^{-}} = -457.79$ kJ/mol), the reaction was kinetically controlled by the high activation energy. The key to solve this barrier is to reduce the activation energy to improve reaction kinetics of the oxidation of As(III) by air. The introduction of a catalyst in the reaction system is a way. Actually, some metal ions have been found to exist a certain promotion for the oxidation of As(III), such as Fe(III), Fe(II) and Cu(II) [24–26]. Kim et al. [20] reported that As(III) cannot be oxidized at pH 3.5–7.5 by dissolved O_2 but in the presence of Fe(II). Emett and Khoe [10] confirmed that dissolved Fe(III) would act as a catalyst for the reaction between arsenic and oxygen by emitting near-UV light. In addition, it is reported that the rate of oxidation of As(III) with dissolved oxygen could be improved in the presence of peroxydisulfate by using sonochemical methods [27]. The latest study indicated Fe–Mn binary oxide was positively correlated with As(III) oxidation in the aeration-direct filtration (AF) process [28,29].

These results triggered researchers that it is feasible to employ some catalysts to promote the oxidation of As(III) by air. Most of the studies involving the interactions of arsenic and Mn oxides only focused on the removal of arsenic in groundwater, while little attention was given to the mechanism, especially for the treatment of high concentrations of arsenic. In our tentative experiments, it is found that the addition of $KMnO_4$ greatly improved the oxidation efficiency of As(III) with air, but the mechanism was unknown. In this paper, a new process for catalytic oxidation of As(III) in which air is used as an oxidant with the addition of $KMnO_4$ is further investigated at laboratory scale. The study is expected to motivate the researchers' interest on the catalytic oxidation of arsenic and to develop a new method for the oxidation of arsenic with low cost and high efficiency.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and used without further purification. All solutions were prepared using deionized water (resistivity 18.2 MΩ cm; TOC < 10 μg/L). A stock of 0.334 mol/L As(III) solution was made by dissolving 43.35 g of $NaAsO_2$ (>99%, Sinopharm) in 1000 mL of deionized water. 2 M stock solutions of NaOH (>96%, Xilong) and HNO_3 (>65%, Xilong) were used as pH adjuster. The reagents used for spectroscopic determination, including $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (>99%, Sinopharm), $K(SbO)C_4H_4O_6\cdot 0.5H_2O$ (>99%, Sinopharm) and ascorbic acid (>99%, Sinopharm), were those quoted by the ISO norm [30].

2.2. Methods

For each test, 500 mL of 0.0667–0.334 mol/L As(III) solution was made by diluting the stock solution with predetermined volumes of deionized water, and the initial pH measured with a combined glass electrode was adjusted using NaOH or HNO_3 solution for the experiments at pH 12–14. The resultant solution was stirred at 300 rpm and heated by a thermostat circulating water bath. A designated quantity of $KMnO_4$ (0.13, 0.25, 0.50, 0.75, 1.05 g) was then added into the solution after it reached the setting temperature (15, 40, 60, 80, 90 °C) while the air was conducted into the flask at a certain flow rate (0, 0.1, 0.2, 0.3, 0.4, 0.5 m^3/h). Each of 10 mL slurry was sampled and filtered immediately through a cellulose acetate membrane of 0.45 μm pore size every 30 min, and the liquor filtered from the sample was acidified with 20% HCl for the determination of As(III) and the total As. The precipitates were collected, washed with deionized water and dried at 50 °C for 48 h in a vacuum drying oven before sampled for X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis.

2.3. Characterization

As(V) was determined by molybdate-bule method [31], which was an optimization of the colorimetric method of Johnson and Pilson [32] to accurately measure arsenic concentrations in the 2–400 μg/L range in water. Total As was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). All samples and standards were treated according the standard methods [33]. The concentration of As(III) was obtained from the difference between total As and As(V). The residue was identified by X-ray diffraction (Siemens D5000, Cu Kα, $\lambda = 1.541874$ Å), and scans from 10° to 70° 2θ were made at rates of 5° 2θ/min. The valence state of Mn element in the solid was performed by X-ray photoelectron spectroscopy (PHI5300, PERKIN-ELMER) using a monochromated Al Kα X-ray source ($h\nu = 1486.6$ eV) at a spot size of 500 μm in diameter.

3. Results and discussion

3.1. Factors affecting the oxidation of As(III)

The performance of $KMnO_4$ in catalytic oxidizing As(III) with air under different conditions, including the mole ratio of Mn/As, pH, temperature, and air flow rate, was investigated.

3.1.1. Effect of the mole ratio of Mn/As

The results shown in Fig. 1 revealed that the oxidation of arsenic increased with the increase of the molar ratio of Mn/As. More than 5 h were needed to completely oxidize As(III) with the molar ratio of Mn/As of 1/21 in comparison to that of 2 h with the molar ratio of Mn/As of 1/10.5. According to Eqs. (1) and (2), the theoretical mole ratio of Mn/As for complete oxidation of As(III) with $KMnO_4$ was about 1/2.5. Lee et al. also confirmed that the stoichiometry ratio of Mn(VII)/As(III) was 1/(2.49 ± 0.09), when As(III) was in excess of permanganate [34]. However, the experimental results indicates that the amount of $KMnO_4$ for complete oxidation of As(III) was much less than the theoretical value under the condition of aeration. Given that only air could be involved in the oxidation reaction except for $KMnO_4$, it can be inferred that oxygen was involved in the reaction as an oxidant. However, the previous study demonstrated that oxygen was not an effective oxidant for As(III) oxidation in