

## Oxidative adsorption of As(III) with $\gamma$ -Al<sub>2</sub>O<sub>3</sub> adding MnO<sub>2</sub>

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### Abstract

Arsenic contamination in ground water has become a big environmental problem all over the world. Arsenic in the ground water exists as arsenite As(III) and arsenate As(V). The adsorbent,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, was used for As adsorption in order to investigate the competitive adsorption of As(III) and As(V). The oxidation of inorganic arsenite As(III) with MnO<sub>2</sub> was also investigated to improve the removal of As(III) from aqueous solution. Combination of adsorbent,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and the oxidation agent, MnO<sub>2</sub>, was applied to oxidize As(III) to As(V) and to remove arsenic as As(V) in the adsorption step. It is known from the previous research that As(V) is adsorbed and removed more easily than As(III). The effects of pH and the additional amount of MnO<sub>2</sub> on the removal of As(III) were examined.

It was found from the removal experiments in the mixed solution of As(III) and As(V) that As(V) was preferentially adsorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The addition of MnO<sub>2</sub> increased the removal of As(III) from 20% to 90% at pH3. The reaction of MnO<sub>2</sub> and As(III) occurred to oxidize As(III) to As(V) in the aqueous solution. The dissolution of Mn<sup>2+</sup> due to As(III) oxidation decreased with increasing pH. Above pH6 As(III) was oxidized and adsorbed without residual Mn<sup>2+</sup> due to the adsorption of produced Mn<sup>2+</sup> on MnO<sub>2</sub> surface. The oxidation rate was slow compared with the adsorption rate of As(III) and As(V) on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Keywords: Arsenic, Oxidative adsorption,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>

### 1. DISSOLVED STATE OF As AND PROPERTIES OF $\gamma$ -Al<sub>2</sub>O<sub>3</sub> AND MnO<sub>2</sub>

The dissolved states of As(III) and As(V) shown in Figures 1 and 2 are important for adsorption of them with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The dissolved states of them change as a function of pH. The acid dissociation constants of As(III) (H<sub>3</sub>AsO<sub>3</sub>) are 9.1, 12.1 and 13.4 as pKa values (Smedley, 2002). Then, As(III) exists as a neutral species (H<sub>3</sub>AsO<sub>3</sub>) below pH 9, while above pH 9 it exists as a negatively charged species (H<sub>2</sub>AsO<sub>3</sub><sup>-</sup>, HAsO<sub>3</sub><sup>2-</sup>, AsO<sub>3</sub><sup>3-</sup>). On the other hand, since the pKa values of As(V)(H<sub>3</sub>AsO<sub>4</sub>) are 2.1, 6.7 and 11.2 (Smedley, 2002), As(V) is present as a negatively charged species above pH2.

The physical properties of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> are

examined in this study (See Table 1). The isoelectric points of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> are 8.6 and 3.8. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has a positive zeta potential below pH8.6, whereas MnO<sub>2</sub> has a negative zeta potential in the wide pH range above pH3.8. The specific surface areas of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> are 237 and 68 m<sup>2</sup>/g. It is considered from these measurements that MnO<sub>2</sub> affects as an oxidation reactant rather than adsorption reactant.

### 2. ADSORPTION OF As(III) AND As(V) WITH $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

As shown in Figure 3, The adsorption amounts of As(III) and As(V) increase with an increase in initial concentration

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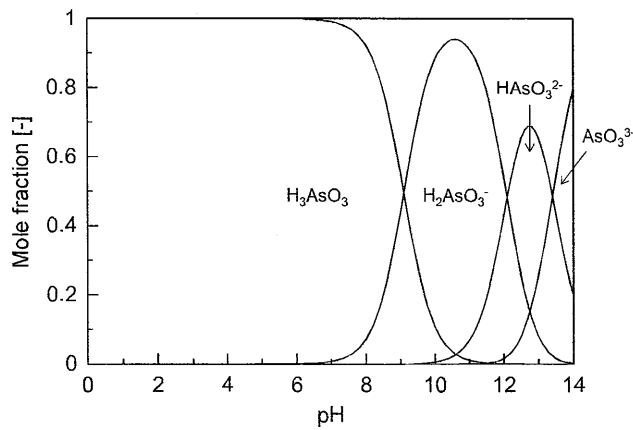


Fig.1 Distribution diagram of As(III) in aqueous solution

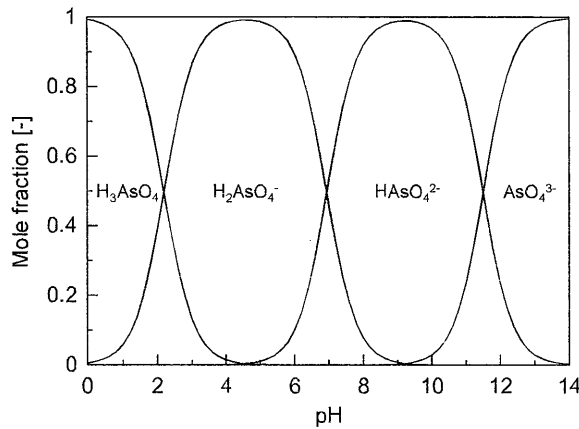


Fig.2 Distribution diagram of As(V) in aqueous solution

Table1 Physical property of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>

Material	Isoelectric point	Specific surface area [m <sup>2</sup> /g]	Pore size [Å]	Median diameter [μm]
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (Adsorbent)	8.6	237	51	55.3
MnO <sub>2</sub> (Oxidant)	3.8	68	25	44.1

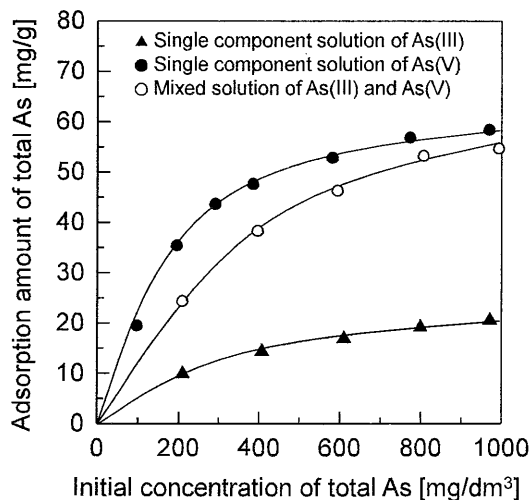


Fig.3 Adsorption amount of total As with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at pH3

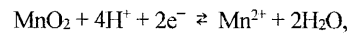
of them and the maximum adsorptions are 20.6mg/g and 58.4mg/g in the equilibrium pH of 3.3-3.6. As the isoelectric point of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is at 8.6,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has a positive zeta

potential in the pH range of 3.3-3.6 and As(V) has a negatively charged species (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>). This is a reason why the adsorption amount of As(V) is larger than that of As(III).

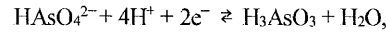
Using the mixed solution of As(III)/As(V) (mixing ratio of 1:1), the adsorption behavior was investigated. The adsorption of As(V) increased with increasing the concentration and the maximum adsorption was 54.7mg/g. The adsorption was almost the same as that of a single component solution. The preferential adsorption of As(V) takes place compared with As(III). Based on the adsorption experiments of As(III) and As(V) from the mixed solution of different concentration ratio As(III)/As(V), it is clear that the adsorption of As(V) is much higher than that of As(III).

### 3. OXIDATION OF As(III) WITH MnO<sub>2</sub>

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> preferably adsorbs As(V) compared with As(III) and then it is not suitable for the adsorption of As(III). We added MnO<sub>2</sub> as an oxidation agent of As(III) (Driehaus *et al.*, 1995 ; Nicy *et al.*, 2013 ; Xiujuan *et al.*, 2010). The reaction of MnO<sub>2</sub> and As(III) and the standard potential of the half reactions as follows (Nihon Kagakukai, 1984 ; Driehaus *et al.*, 1995),



$$V^\circ = +1.23\text{V} \quad (1)$$



$$V^\circ = +0.56\text{V} \quad (2)$$

From the above half reactions, the oxidation reaction of As(III) with MnO<sub>2</sub> is expressed as,



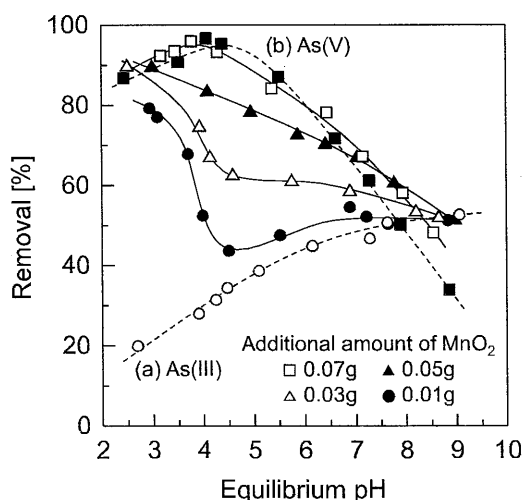
$$E^\circ = +0.67\text{V} \quad (3)$$

By the oxidation of As(III) with MnO<sub>2</sub>, As(V) is produced and the dissolution of Mn<sup>2+</sup> takes place. The free energy of the oxidation reaction  $\Delta G^\circ$  is calculated as bellow,

$$\Delta G^\circ = -nFE^\circ = -129\text{kJ} \quad (4)$$

### 4. OXIDATION ADSORPTION OF As(III) WITH $\gamma$ -Al<sub>2</sub>O<sub>3</sub> AND MnO<sub>2</sub>

We investigated the oxidative adsorption of As(III) with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> using the mixed solution of As(III) and As(V) (See Figure 4). By the oxidation reaction with MnO<sub>2</sub>, the adsorption of As(III) remarkably increased and the adsorption behavior of As(III) is close to that of As(V). As the oxidation of As(III) with MnO<sub>2</sub> easily happens at the lower pH such as 3-5, the higher adsorption of As(III) appeared in these pH values. On the other hand, oxidation with MnO<sub>2</sub> decreases with an increase in pH and then oxidation of As(III) to As(V) goes down over the pH of 5. The additional amount of MnO<sub>2</sub> brings the increase in



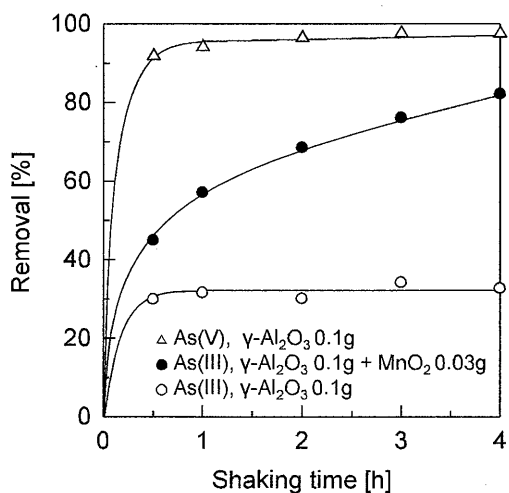
**Fig.4** Removal of As(III) with mixture of  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{MnO}_2$

oxidation adsorption of As(III). The adsorption of As(III) as As(V) becomes predominant at all pH with the enough additional amount of  $\text{MnO}_2$ .

$\text{MnO}_2$  dissolution due to oxidation reaction of As(III) is very low. At pH 3 the dissolution of  $\text{MnO}_2$  is highest, while it decreases with increasing pH. The  $\text{Mn}^{2+}$  concentration in aqueous solution disappears in the pH region more than 6. The isoelectric point of  $\text{MnO}_2$  is at pH 3.8. Therefore, it is considered that  $\text{Mn}^{2+}$  is adsorbed on the  $\text{MnO}_2$  surface.

## 5. ADSORPTION RATE

The adsorption rates of As(III) and As(V) with  $\gamma\text{-Al}_2\text{O}_3$  were studied and also the oxidation adsorption rate of As(III) with  $\gamma\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$  was investigated. The adsorption of As(III) and As(V) with  $\gamma\text{-Al}_2\text{O}_3$  shown in Figure 5 is fast and the adsorption equilibrium is attained within 60min. When  $\text{MnO}_2$  is used as an oxidation agent, the adsorption of As(III) with  $\gamma\text{-Al}_2\text{O}_3$  is increased quantitatively and



**Fig.5** Effect of As(III) removal on shaking time with mixture of  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{MnO}_2$  at pH4

kinetically. Oxidation reaction is kinetically slow compared with adsorption reaction.

The addition of 0.01g of  $\text{MnO}_2$  to the solution containing As(III) at  $200\text{mg}/\text{dm}^3$  is 2.1 times larger than stoichiometric amount. Though there is the excess amount of  $\text{MnO}_2$ , the adsorption of As(III) with  $\gamma\text{-Al}_2\text{O}_3$  is lower than that of As(V). This comes from the lateness of oxidation reaction. The oxidation reaction is a rate determining step on the oxidation-adsorption of As(III).

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