

Arsenic(III) Remediation from Contaminated Water by Oxidation and Fe/Al Co-Precipitation

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Abstract

Battery grade γ -MnO₂ powder was investigated as an oxidant and an adsorbent in combination with Fe/Al coagulants for removal of arsenic from contaminated water. Simultaneous oxidation of As(III) and removal by coprecipitation/adsorption (one step process) was compared with pre-oxidation and subsequent removal by coprecipitation/adsorption (two step process). The rate of As(III) oxidation with MnO₂ is completed in two stages: rapid initially followed by a first order reaction. As(III) is oxidised to As(V) by the MnO₂ with a release of approximately 1:1 molar Mn(II) into the solution. No significant pH effect on oxidation of As(III) was observed in the pH range 4 - 6. The rate showed a decreasing trend above pH 6. The removal of As(V) by adsorption on the MnO₂ decreased significantly with increasing pH from 4 to 8. The adsorption capacity of the γ -MnO₂ with particle size 90% passing 10 μ m was determined to be 1.5 mg/g at pH 7. MnO₂ was found to be more effective as an oxidant for As(III) in the two step process than in the one step process.

Keywords: Manganese Oxides, Iron Hydroxides, Arsenic Remediation, Fe/Al Coagulants, Contaminated Water

1. Introduction

Arsenic in contaminated groundwater occurs largely as arsenite (As(III)). [1] Effective and complete removal of arsenic by adsorption/coprecipitation methods requires pre-oxidation of As(III) to As(V). Oxygen or air is a cheap but kinetically slow oxidant for As(III). Various other oxidants for As(III) have been reported in the literature, including permanganate (MnO₄⁻), [2-4] ozone (O₃), [5] hydrogen peroxide (H₂O₂), [6] chlorine (Cl₂), [7-10] or hypochlorite (ClO⁻), [11-13] catalyzed sulphite/O₂ (air) mixture, [14,15] and UV catalyzed systems. [16-19] These oxidants are effective but are either costly, or need rigid process controls for efficient oxidation. In recent years, manganese oxides, in both synthetic and natural forms, have been investigated for oxidation of As(III) [20-26].

Oscarson *et al.* [27] found that the oxidation of As(III) by birnessite, cryptomelane, and pyrolusite obeyed the first-order rate law with the rate constants at 298 K being 0.267, 0.189 and $0.44 \times 10^{-3} \text{ h}^{-1}$, respectively. However, Chen and Fang [28] reported that the oxidation rate of As(III) by MnO₂ was rapid initially followed by a first-

order kinetics with respect to As(III) concentration. The activation energies for the oxidation reaction by the MnO₂ were measured to be in the range 26.0 - 32.3 kJ/mol [27]. The oxidation process was reported to be limited by diffusion of the reactant As(III) to or the reaction products away from the surface [27-29].

Scott and Morgan [29] proposed a surface mechanism that As(III) anion forms an inner-sphere complex followed by electron transfer between the surface metal ion and As(III) anion. The adsorption of As(III) on the surface was the slowest step. The surface mechanism was supported by the observation that the rate of As(III) oxidation directly depended on the concentration of surface-bound As(III) [30]. A mechanism of production of an intermediate reaction product, Mn(III) hydroxyl (MnOOH*), was proposed by Nesbitt *et al.* [31].



Various forms of Mn oxides as adsorbent for arsenic removal have also been investigated, including pyrolusite and cryptomelane, [32] combination of pyrolusite with granular ferric hydroxide, [30] natural manganese oxides

in a packed bed or column, [33] ferruginous manganese ore (FMO), [34] Mn dioxide-coated sand (MDCS), [35, 36] and Bi-enhanced Mn oxides [37]. Chiu and Hering [30] compared the adsorption capacities for different types of Mn oxides. They found that the surface saturation for pyrolusite and cryptomelane at pH 6.5 for As(V) species were 0.75 and 1.87 mg/g, respectively. The difference in the adsorption capacity was attributed to their crystallinity and specific surface areas. Poorly crystalline birnessite and cryptomelane possess higher specific surface areas than highly ordered pyrolusite [29].

This paper reports the investigation of MnO₂ as an oxidant for As(III) and as adsorbent in combination with Fe/Al coagulants for As(V) removal. The adsorption capacity of MnO₂ for As(V) was compared with commonly used iron and aluminium hydroxide adsorbents under similar experimental conditions. Simultaneous oxidation and coprecipitation/adsorption (one step process), and pre-oxidation followed by coprecipitation/adsorption (two step processes) were investigated for various combinations of MnO₂ with in-situ formed Fe/Al hydroxides. The objectives of this work were to determine the suitability of MnO₂ as an oxidant and adsorbent in combination with Fe/Al hydroxide for arsenic removal.

2. Materials and Methods

First, Battery grade γ -MnO₂ powder with particle size 90% passing 10 μ m, supplied by Aldrich Australia, was used for all the experiments. All the other chemicals used were of AR grade without further treatment. As(III) stock solution was prepared from As₂O₃ in accordance with the procedure provided by Vogel [38]. As(V) stock solution was prepared by dissolving Na₂HAsO₄ in deionized water. Fe(III) and Al(III) stock solutions were prepared from their chloride salts. Solution pH was adjusted with dilute HCl and NaOH solutions.

All the experiments were conducted at 25°C in 250 ml conical flasks equipped with magnetic stirring units for liquid-solid mixing. In the one step process, a dose of MnO₂ and a desired volume of equal molar Fe(III)/Al(III) solution were simultaneously added to water containing known amount of As(III) or As(V). Solution pH was adjusted and maintained at the desired value throughout the experiment. Samples were taken and filtered through a 0.2 μ m membrane filter. The filtrate was analysed for As(III) and As(V) by hydride generation followed by inductively coupled plasma and atomic emission spectroscopy (ICP-AES), and for total soluble Mn by ICP-AES at the Marine and Freshwater Research Institute, Environmental Science, Murdoch University, Western Australia. For the two step process, the arsenic bearing

solution was first treated with MnO₂ followed by adsorption/precipitation with Fe(III)/Al(III) coagulants at pH 7. All the other procedures were the same as the one step process.

3. Results and Discussion

3.1. Oxidation of Arsenic(III) by MnO₂

3.1.1. Stoichiometry of Oxidation of As(III)

The stoichiometry of oxidation of As(III) by MnO₂ was determined by measuring residual reactants and reaction products after 2 hours contact of one gram of the MnO₂ powder with initial 1 ppm As(III) solution at pH 7 in the absence of oxygen maintained by bubbling nitrogen gas through the solution. The analysis results for residual concentrations of As(III), As(V) and Mn(II) in the final solution are given in **Table 1**. The important observations are:

No As(III) remained in the solution, indicating that all the As(III) was oxidized to As(V).

The residual arsenic in the solution accounted for only 80% of the amount initially present in the reaction mixture.

The solid phase contained the remaining 20% of the arsenic which could be assumed to be As(V).

The solution contained Mn(II) as much as would be expected if all the reacted MnO₂ were converted to Mn(II) during its reaction with As(III). Thus, the oxidation of As(III) was accompanied by a reduction of MnO₂ yielding Mn(II) into solution at an approximately equal molar stoichiometry with respect to the total oxidized As(III):



3.1.2. Rate of Oxidation of As(III)

The rate of As(III) oxidation are plotted in **Figure 1** and analyzed with respect to the first order rate law:

$$\ln[\text{As(III)}]_t / [\text{As(III)}]_0 = -kt \quad (4)$$

where [As(III)]₀ is the initial As(III) concentration (mg/L), [As(III)]_t the concentration at time t (min), k the rate constant (min⁻¹) which is a function of MnO₂ dose and tem-

Table 1. Concentrations of reaction products in the final solutions after 2 hour contact time at pH 7 and 25°C. Initial 1 ppm As(III), 1 g/L MnO₂.

Elements	In solution (μ M)	In solid (μ M)	Total (μ M)
As(III)	<0.05 (DL)	-	-
As(V)	10.7	2.7	13.4
Mn(II)	14.0	-	14.0
Reaction product ratio As:Mn \cong 1			

perature. As can be seen in **Figure 1**, the oxidation of As(III) by MnO_2 could be characterized by very fast kinetics within the first 30 minutes, followed by a first order rate which is indicated by the fact that $\ln[\text{As(III)}]/[\text{As(III)}]$ vs reaction time t is graphically linear. The rate increases with MnO_2 dose, suggesting that the reaction depends on surface area or available reaction sites on the surface of MnO_2 . This two stage kinetic feature was also observed by Chen and Fang [28]. The slow-down in the rate at later stage of the reaction is indicative of competition for active adsorption sites between As(III) and As(V).

3.1.3. Effect of pH on Oxidation of As(III)

The pH effect was investigated by varying solution pH in the range 4 - 8 and measuring the residual As(III) in solution after 2 hour contact time for each fixed pH. The initial As(III) concentration was 6 mg/L. It was observed that about 80% of the As(III) ions was oxidized for each pH in two hours in the pH range 4 - 6. Above pH 6, a decreased trend occurred up to pH 8. This is likely to be caused by formation of manganese hydroxide on the surface which blocks some sites for reaction with As(III) on the surface.

3.2. MnO_2 as Adsorbent

3.2.1. Effect of pH on As(V) adsorption on MnO_2

Figure 2 shows that the %As(V) adsorption decreases linearly when solution pH increases from pH 4 to pH 8. This effect can be explained by the surface charge characteristics of the MnO_2 phase. The point of zero charge (PZC) of chemically or electrochemically prepared MnO_2 materials such as $\alpha\text{-MnO}_2$, $\gamma\text{-MnO}_2$ and $\delta\text{-MnO}_2$ lies in the pH range 1.5 - 4.15 [39,40]. Therefore, it is not surprising to observe the decreasing effect because the adsorption of As(V) species must overcome the increased

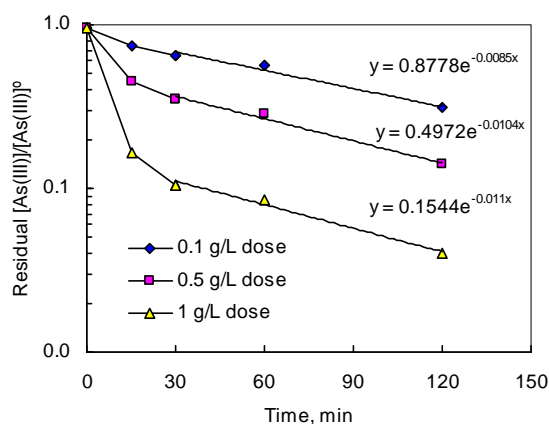


Figure 1. $\ln [\text{As(III)}]/[\text{As(III)}]^0$ vs time. Initial 5 mg/L As(III), pH 7, 25°C.

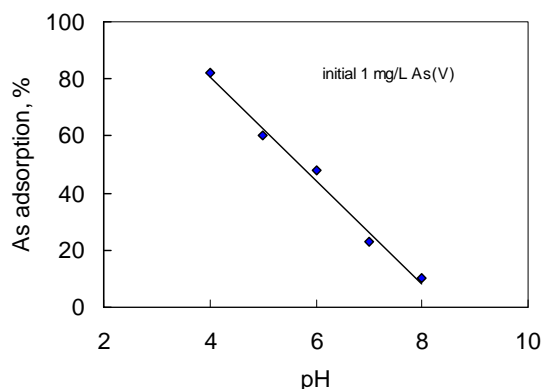


Figure 2. Effect of solution pH on adsorption of As(V) on the MnO_2 .

repulsion force as pH rose above the PZC. Additionally, the proportion of the more negatively charged As(V) species increases as the solution pH increases, e.g. H_2AsO_4^- ions dominate in pH range 2 - 6.5. The $\text{H}_2\text{AsO}_4^{2-}$ ions on the other hand dominate in pH range 6.5 - 11.8. This should also contribute to the observed pH effect.

3.2.2. Effect of As(V) Concentration

The effect of As(V) concentration on As(V) adsorption was investigated by varying initial As(V) concentration at a fixed dose of 1 g/L MnO_2 at pH 7. As shown in **Figure 3**, the results reasonably fit the Langmuir isotherm model:

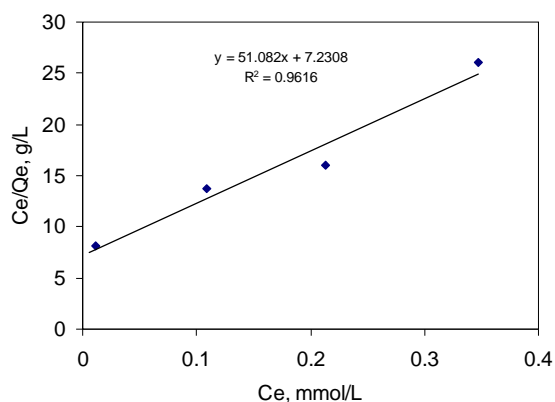
$$C_e/Q_e = 1/bQ^\circ + C_e/Q \quad (5)$$

where, C_e (mmol/L) is the equilibrium concentration in the solution, Q_e (mmol/g) is the amount adsorbed on the adsorbent at equilibrium, Q° and b are the Langmuir constants related to adsorption capacity and binding energy of adsorption respectively. From the slope of best fit, the adsorption capacity of the $\gamma\text{-MnO}_2$ is determined to be 1.5 mg/g.

For comparison, the adsorption capacities of commonly used iron and aluminum hydroxide adsorbents were also similarly studied and the reagents summarized in **Table 2**. The published data from the literature are also included in the table. As seen, the adsorption capacity of MnO_2 increased in the order $\beta\text{-MnO}_2 < \gamma\text{-MnO}_2 < \alpha\text{-MnO}_2 \ll \delta\text{-MnO}_2$. Clearly, the capacity depended on the form of MnO_2 and its preparation method which determine the crystalline properties and surface area. For example, the amorphous $\delta\text{-MnO}_2$ possesses highest surface area and thus highest adsorption capacity compared with other well crystalline forms of MnO_2 . However, the capacity of the amorphous $\delta\text{-MnO}_2$ is found to be significantly lower than the amorphous iron hydroxide (ferrihydrite). The capacity of As(V) removal also depends on the method used. The removal of As(V) by adsorp-

Table 2. Comparison of adsorption capacity of Mn oxides with iron oxides.

	Hydroxides/oxides	Capacity (mg/g)	pH	Ref
Mn Hydroxides/oxides	Cryptomelane (α -MnO ₂)	1.87	6.5	[41]
	Pyrolusite (β -MnO ₂)	0.75	6.5	[41]
	γ -MnO ₂	1.5	7	This work
	Hydrous Mn(IV) oxide (HMO) or δ -MnO ₂	5.5	6.5	[41]
Fe Hydroxides/oxides	Preformed Ferrihydrite	8.2	7	This work
	Fe(III) coagulant in-situ	20 (on dry basis)	7	This work
	Fe(III)/Al(III) coagulant in-situ	30 (on dry basis)	7	This work

**Figure 3. Langmuir plot for adsorption of As(V) on the MnO₂ at pH 7.**

tion/precipitation *in-situ* with Fe(III) or Fe(III)/Al(III) coagulants is much more effective and efficient than the preformed ferrihydrite (Table 2).

3.3. Removal of As(III) by MnO₂ and Fe(III)/Al(III) Coagulants

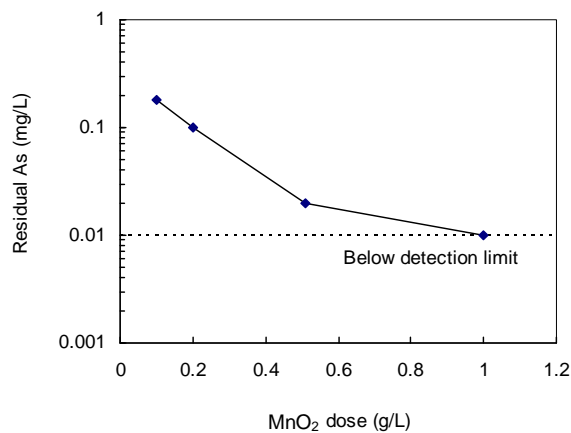
The efficiency of As(III) removal by adsorption on Fe/Al hydroxides was investigated in two ways:

One step process: this involved simultaneous addition of MnO₂ oxidant and the Fe or Fe/Al coagulant followed by pH adjustment.

Two step process: this involved pre-oxidation of As(III) by MnO₂ and subsequent removal of As(V) by coprecipitation/adsorption on in-situ formed Fe or Fe/Al hydroxides.

- One step process

As shown in Figure 4, the residual arsenic in solution decreased exponentially from 0.2 mg/L to 0.02 mg/L as the MnO₂ dose increased from 0.1 g/L to 0.5 g/L. A dose of 1 g/L of MnO₂ was needed to lower the residual arsenic to 0.01 mg/L (standard drinking water limit by US Environmental Protection Agency). This reflects the relative inefficiency of the one step process for removal

**Figure 4. Effect of MnO₂ dose on removal of arsenic by coprecipitation with Fe/Al coagulant. Initial 1 mg/L As(III), pH 7, molar ratio (Fe:Al = 1:1):As = 50:1.**

of very low level of arsenic.

- Two step processes

The results can be summarized as follows:

Fe/Al alone is an effective adsorbent for As(V) (<0.01 mg/L, Expt. Code 5) but poor for As(III) (0.24 mg/L, Expt. Code 4).

MnO₂ alone is effective for As(III) oxidation (Expt. Code 6) but relatively poor adsorbent for As(V) (Expt. Code 7) compared with Fe/Al adsorbent.

Combination of MnO₂ with Fe/Al in the one step process with initial As(III) effectively lowered the residual As to 0.01 - 0.02 mg/L (Expt. Code 2).

The two step process is more effective for arsenic removal (<0.01 mg/L residual As, Expt. Code 1) than the one step process (0.01 - 0.02 mg/L residual As, Expt. Code 2), but requires additional 2 hours for pre-oxidation.

Soluble Mn(II) was effectively removed from the system in both one-step and two-step processes.

The arsenic removal is not affected when MnO₂, Fe/Al, and As(V) are co-present in the one step process (Expt. Code 3).

The As(III) removal by the one step process is relatively poor compared with the two step process. Two factors are likely to affect the removal process. First, the in-situ formed amorphous Fe/Al 'hydroxide' may partially cover the surface of MnO₂, which slows down the diffusion process of As(III) to its surface. Second, the As(III) initially adsorbed on the surface of Fe/Al "hydroxide" is desorbed by As(V) ions, establishing a new equilibrium. As(III), which is known to occur as unionised H₃AsO₃ in the pH range 2 - 9 is weakly bonded on the surface of ferrihydrite compared with As(V) which occur as H₂AsO₄⁻, H₂AsO₄²⁻. The As(V) species is strongly bonded on the surface via specific inner sphere adsorption mechanism. Furthermore, the As(III) adsorbed on the surface of ferrihydrite may need further treatment to oxidize the As(III) to As(V) for safe disposal. The cost for this treatment may not justify using the one step process in real applications where safe disposal is the prime objective.

4. Conclusions

As(III) is oxidized to As(V) by the γ -MnO₂ with almost equal molar stoichiometric release of Mn(II) into solution. The rate of the oxidation is characterised by an initial fast kinetics followed by a first order rate reaction. No significant variation in the oxidation rate occurs in the pH range 4 - 8, except for a decreased trend at pH above 6, is observed. The adsorption of As(V) with the γ -MnO₂ is favored in low pH 4 and decreases rapidly where the pH rises to 8. The adsorption capacity of MnO₂ (90% passing 10 μ m) is 1.5 mg (As(V))/g at pH 7. The MnO₂ is more efficient when used as an oxidant in the two step process than in the one step process. All the soluble Mn(II) ions are removed in the solution in both the processes.

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