

## Modeling arsenic removal by co-precipitation under variable redox conditions

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**ABSTRACT:** Drinking water companies in the Netherlands are actively investigating routes to reduce arsenic (As) to  $<1 \mu\text{g L}^{-1}$  in drinking water. Co-precipitation of As with iron during groundwater treatment is a promising method. When As(III) is present in raw water, permanganate ( $\text{MnO}_4$ ) can be dosed to oxidize As(III) to As(V) in order to improve As removal efficiency. The dosages of  $\text{MnO}_4$  and Fe(III) to achieve  $<1 \mu\text{g L}^{-1}$  As in the treatment effluents depend on the composition of raw water. The coprecipitation of As(III) and As(V) with ferrihydrite under variable raw water composition and redox environments, controlled by oxygen ( $\text{O}_2$ ) or  $\text{MnO}_4$  is modeled in this study by the generalized double layer model, and redox equilibrium reactions. Results show that the pH of the treatment process is critical to determine the As removal efficiency. At pH = 8 the highest As removal is obtained, followed by pH = 6 while pH = 7 gives the least removal.  $\text{HCO}_3^-$ ,  $\text{PO}_4$  and  $\text{H}_4\text{SO}_4$  hamper the adsorption of As(V). In future work, the model outcome will be assessed by experiments. Furthermore, the model will be extended with oxidation kinetics in case oxidation (by e.g. oxygen) occurs at a slower rate than the (mean) residence time of the water in the process.

### 1 INTRODUCTION

Drinking water companies in the Netherlands are actively investigating methods to reduce As to  $<1 \mu\text{g L}^{-1}$  in drinking water (Ahmad *et al.*, 2014). At groundwater treatment plants (WTPs), indigenous Fe(II) in raw water is oxidized to form insoluble ferrihydrite. Also, Fe(II) or Fe(III) may be dosed in the filter influent to introduce or increase As removal. After Fe(II) gets oxidized to Fe(III) by  $\text{O}_2$ , Fe(III) undergoes hydrolysis which results in the formation of ferrihydrite which in turn can adsorb As (coprecipitation). These As-laced ferrihydrite precipitates are then removed in a filter placed downstream. The raw water at most WTPs in the Netherlands contain As(III) in variable proportions. In order to achieve higher As removal efficiency, complete oxidation of As(III) to As(V) is necessary through dosing a strong oxidant, such as permanganate ( $\text{MnO}_4$ ) (Ahmad *et al.*, 2017). The dosages of  $\text{MnO}_4$  and Fe(III) to achieve  $<1 \mu\text{g L}^{-1}$  As in the treatment effluent depend on the composition of raw water. The objective of this study is to model the coprecipitation of As(III) and As(V) with ferrihydrite under variable raw water composition and redox environments, controlled by oxygen ( $\text{O}_2$ ) or  $\text{MnO}_4$ .

### 2 METHODS

#### 2.1 Model description

The treatment process is simplified to batch mode and the raw water composition represents typical groundwater quality in the Netherlands (see Table 1). It is assumed that As only coprecipitates with ferrihydrite. Adsorption of ferrihydrite is modeled with the Generalized Double Layer Model (DLM) based on the work of (Dzombak & Morel, 1990). For this work, a modified PHREEQC database *wateq4f* is used. Arsenic adsorption constants and reactions are modified according to the average values presented in (Gustafsson & Bhattacharya, 2007). The  $\log(k)$  values of (de)protonation of As species is also set equal to what Gustafsson & Bhattacharya, 2007 used to maintain consistency of the database. The adsorption of  $\text{H}_4\text{SiO}_4$  is modeled according to (Stollenwerk *et al.*, 2007), adsorption of carbonate is described by reactions and constants as reported by (Appelo *et al.*, 2002). Furthermore, the system is assumed to be in thermodynamic equilibrium as most kinetics are much faster than the modeled residence time of the water. This means that  $\text{MnO}_4$  is assumed to be fully reduced to Mn(II) (1 mole  $\text{MnO}_4$  is assumed to oxidize 5 moles

Table 1. Overview of the concentrations used in the simulations.

Compound	$\mu\text{mol/L}$	$\text{mg L}^{-1}$
Fe(II)	0–70	0–3.9
Mn(II)	3.6	0.2
As(III)	0.3	0.02
Ca	1497	60
Mg	329.1	8
Cl	3840.9	136.2
Na	3229.1	74.2
HCO <sub>3</sub>	2458.2	150
Si	356	10
PO <sub>4</sub>	5.3	0.5

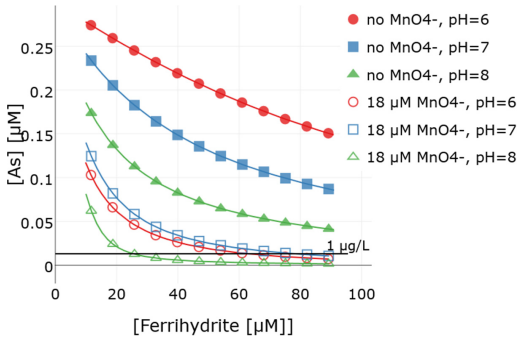


Figure 1. Removal of As(V) as function of ferrihydrite formed at different pH and MnO<sub>4</sub> dosages. The horizontal line indicates the target As in drinking water in the Netherlands.

of Fe(II) to produce ferrihydrite). The only exception to this thermodynamic equilibrium is the slow oxidation of As(III) and Mn(II) by oxygen.

### 3 RESULTS AND DISCUSSION

Figure 1 presents residual As(V) as a function of the precipitated ferrihydrite at different pH and MnO<sub>4</sub> dosages. The simulation shows that the amount of ferrihydrite is limited by the amount of available Fe(II) in raw water and MnO<sub>4</sub> dose. Interestingly, As(V) removal is higher for pH = 6 compared to pH = 7, while pH = 8 yields the highest As(V) removal. This observed trend may be due to the presence of H<sub>4</sub>SiO<sub>4</sub>, PO<sub>4</sub> and HCO<sub>3</sub> in water. Figure 2 shows the removal of As(III) as function of the amount of formed ferrihydrite at different pH and MnO<sub>4</sub> dosages. It confirms that the oxidation of As(III) by MnO<sub>4</sub> significantly improves As(III) removal. Figure 3 and 4 show the effect of HCO<sub>3</sub>, PO<sub>4</sub> and H<sub>4</sub>SiO<sub>4</sub> on the removal of As(V) and As(III) respectively. Both figures simulate the same system but the difference is the dosage of MnO<sub>4</sub>. In Figure 3 MnO<sub>4</sub> is dosed and thus As(III) is oxidized to As(V) while in Figure 4 MnO<sub>4</sub> is not dosed. Moreover, in Figure 3 Fe(II) is oxidized by MnO<sub>4</sub> while

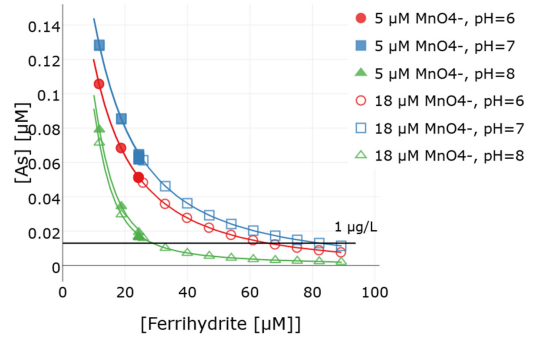


Figure 2. Removal of As(III) for different pH and MnO<sub>4</sub> dosages. The horizontal line indicates the target As in drinking water in the Netherlands.

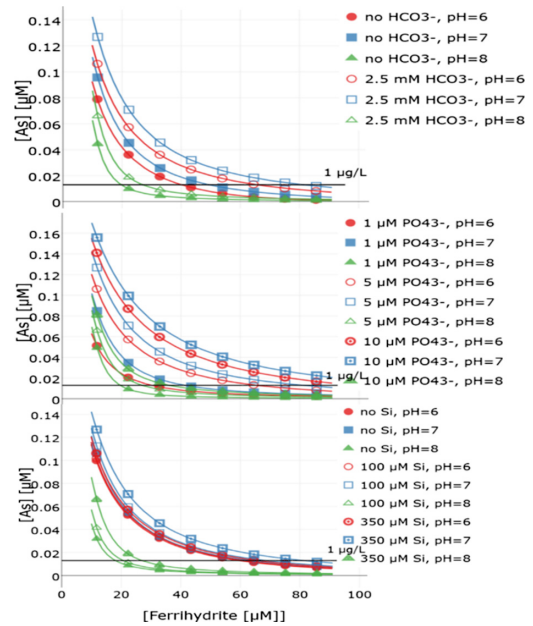


Figure 3. Removal of As(III) with MnO<sub>4</sub> dosing for different pH as function of the amount of ferrihydrite formed.

in Figure 4 Fe(II) is oxidized by O<sub>2</sub>. For all the cases in Figure 3, the highest removal is achieved at pH = 8, the lowest at pH = 7. The presence of both HCO<sub>3</sub>, PO<sub>4</sub> and H<sub>4</sub>SiO<sub>4</sub> decreases coprecipitation of As. This is in agreement with literature (Antelo *et al.*, 2010; Appelo *et al.*, 2002; Stollenwerk *et al.*, 2007). Indeed, to such an extent that dosage of iron and MnO<sub>4</sub><sup>-</sup> needs to be increased to meet the goal of 1  $\mu\text{g L}^{-1}$ . E.g. due to 2.5 mM HCO<sub>3</sub> at a pH of 8.0, 27  $\mu\text{M}$  instead 20  $\mu\text{M}$  of ferrihydrite is required. For lower pH this difference is larger. It also holds for PO<sub>4</sub> that the influence of PO<sub>4</sub> is larger at lower pH and to an even stronger extent this holds for H<sub>4</sub>SiO<sub>4</sub> as well.

This simulation shows that in order to achieve high process efficiency (i.e. low doses and higher removal of As) operating the treatment process at pH 8.0 is desirable. At pH = 8 the sensitivity of the required

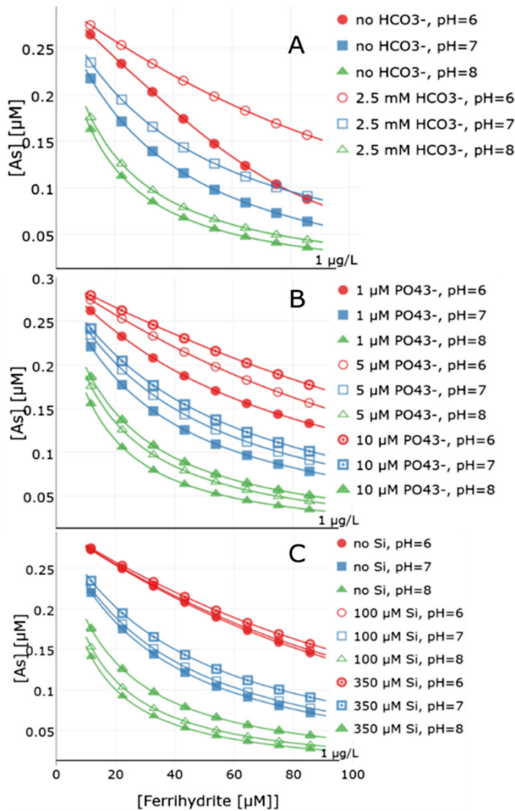


Figure 4. Removal of As(III) with  $O_2$  dosing for different pH as function of the amount of ferrihydrite formed. Figure A, B and C illustrate the competition between the adsorption of As(V) and  $HCO_3^-$ ,  $H_4SiO_4$  and  $PO_4$  respectively.

dosages to  $HCO_3^-$ ,  $PO_4$  and  $H_4SiO_4$  concentrations is relatively low. The results, however, also show that the removal efficiency rapidly decreases when pH decreases to 7.0. This makes pH a critical parameter in designing and operating the As removal at groundwater treatment plants by Fe based coprecipitation under variable redox conditions.

#### 4 CONCLUSIONS AND OUTLOOK

The coprecipitation of As(III) and As(V) with ferrihydrite under variable raw water composition and redox environments, controlled by oxygen ( $O_2$ ) or  $MnO_4$  is modeled by the generalized double layer model, and redox equilibrium reactions. Results show that As(III) and As(V) can be removed by Fe based coprecipitation. The coprecipitation efficiency is much

higher for As(V) than As(III) and this supports that As(III) should be oxidized to improve removal rates. The pH of the treatment process is critical to determine the As removal efficiency. At pH = 8 the highest As removal is obtained, followed by pH = 6 while pH = 7 gives the least removal.  $HCO_3^-$ ,  $PO_4$  and  $H_4SiO_4$  hamper the adsorption of As(V). This is true for all tested pH conditions, but predominantly for pH = 6 and 7. In future work, the model outcome will be assessed by experiments. Furthermore, the model will be extended with oxidation kinetics in case oxidation (by e.g. oxygen) occurs at a slower rate than the (mean) residence time of the water in the process.

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