As(III) removal in natural groundwaters: influence of HPO_4^{2-} , H_4SiO_4 , Ca^{2+} , Mg^{2+} and humic acid in complex, realistic water matrices

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ABSTRACT: The influence of phosphate, silicate, calcium, magnesium and humic acid on iron flocculation and arsenic removal has been shown in synthetic waters, but these findings may not necessarily be representative for actual groundwaters. In our study, three different groundwaters were selected which varied in composition, and with jar test, the removal of As and changes in iron floc size were monitored. The groundwaters were used as is, or after modification. The main findings are that the iron floc size can be related to the molar (Ca+Mg)/P ratio, and that As removal is closely related to Fe removal, which would indicate that adsorption competition is of lesser importance than hindered flocculation

1 INTRODUCTION

Arsenic removal is well known to be negatively affected by the presence of phosphate, silicate, and humic acid either (directly) due to competition for adsorption sites on iron oxides, or (indirectly) due to hindering the formation of iron oxides themselves (Guan *et al.*, 2009). Ca^{2+} has been shown to (partly) neutralize the latter (Kaegi *et al.*, 2010), and Mg^{2+} is expected to be similarly effective. Natural groundwaters are a mixture of all these ions, and as such, may not be represented well when laboratory experiments are carried out with synthetic water that only includes a selection.

Our aim was to systematically investigate the influence of phosphate, humic acid, calcium and magnesium on As(III) adsorption and Fe(II) flocculation in natural groundwaters. For this purpose, groundwaters were selected with different initial composition, and were used in their original state, and after manipulation of phosphate, calcium, magnesium and humic acid concentrations by either addition or removal by anion/cation exchange. Calcium and magnesium were dosed in equimolar concentrations, in an attempt to separate the effect of potential precipitation (Ca^{2+}) from sole charge neutralization (Mg^{2+}).

2 METHODS/EXPERIMENTAL

Three natural groundwaters with different water composition were selected. The initial concentrations of As and Fe were equalized to $20 \mu\text{g L}^{-1}$ and 5 mg L^{-1} . These waters were used as is, or modified by dosing Ca^{2+} , Mg^{2+} , HPO_4^{2-} , humic acid, or precontacted (anaerobically) with anion exchange resin (Amberlite IRA400) or cation exchange resin (Amberlite IR120). After anion exchange, $150 \text{ mg L}^{-1} \text{HCO}_3^-$ was dosed

back to compensate for its removal, and the pH was corrected to pH 7. Jar tests were carried out with 1 L solution in baffled jars at a mixing rate of 80 rpm and at $15\text{--}16^\circ\text{C}$. In the first 30 s of the jar test, the samples were aerated intensively and an O_2 concentration of 9.7 mg L^{-1} was reached. Water samples were collected before aeration, and after 1, 5, 15, 30 and 60 min, filtered over $0.45 \mu\text{m}$, and analyzed for As, Fe, Ca, Mg, Si, P, S by ICP/MS. Before aeration, HCO_3^- was determined by titration with 0.01 M HCl to an endpoint of pH 4.3, and DOC was measured before aeration and after 60 min. The pH was measured continuously. After 60 min, the particle size and quantity distribution were measured with a particle counter (HIAC Royco model 9703, Pacific Scientific). All experiments were carried out in duplicate.

3 RESULTS AND DISCUSSION

3.1 Baseline

The composition of the three groundwaters after As and Fe equalization is shown in Table 1.

Iron removal was most rapid in KG water, followed by AMD water, followed by AP water. This is in accordance with Morgan and Lahav (2007), who found that iron oxidation rates increase at higher pH values. The total iron floc volume after 60 min was similar for KG and AMD water, but much less for AP water. Nevertheless, adsorption of As was hindered for AMD water, as compared to KG water. Most likely, this can be attributed to adsorption competition with Si.

3.2 Modified groundwaters

The presence of Ca^{2+} and Mg^{2+} was instrumental for iron flocculation. Their removal reduced iron flocculation in all groundwaters, and this effect was

Table 1. Groundwater composition, baseline.

	Fe (mg/l)	As (ug L ⁻¹)	Ca (mg L ⁻¹)	Mg (mg L ⁻¹)	Si (mg L ⁻¹)	P (mg L ⁻¹)	HCO ₃ ⁻ (mg L ⁻¹)	pH
AMD	6.9	23.0	43.5	4.1	11.9	0.18	146	7.01
AP	4.9	21.8	20.9	2.5	7.5	0.34	103	6.83
KG	4.8	25.8	28.4	11.5	5.9	0.26	196	7.31

Figure 1. Floc volume VS (Ca+Mg)/P ratio.

more severe for groundwaters with higher P/Fe ratios. Equimolar addition of Ca²⁺ and Mg²⁺ increased the total floc volume to a similar quantity in KG and AP waters, but Ca²⁺ created significantly larger floc volumes in AMD water. Precipitation of hydroxyapatite could (partially) account for this, but is not strongly supported in literature. Possibly, more voluminous (and less dense) iron flocs are formed at high Si and Ca²⁺ concentrations.

Dosing phosphate slightly reduced iron flocculation in KG and AP water, and actually enhanced it in (Ca²⁺-rich) AMD water. Dosing humic acid either did not influence iron flocculation (KG, AP water), or enhanced it (AMD water). Iron removal was enhanced for all groundwaters after anion exchange.

3.3 (Ca+Mg)/P molar ratio

Since Si is uncharged in our experiments, and humic acid carries a low molar charge density, we used the molar (Ca+Mg)/P ratio to represent the charge balance for iron flocs, and compared this to the total floc volume (Fig. 1). For KG and AP waters, a relatively linear relationship is found, which levels off at ratios higher than 500 where either all Fe has been flocculated, or where complete charge neutralization has occurred. In AMD water, larger iron flocs are created than expected based on this ratio.

3.4 Arsenic removal

Arsenic removal was largely depending on iron removal (Fig. 2). Dosing phosphate did show a reduction in As adsorption at an unrealistically high dose of 10 mg L⁻¹. Adsorption competition with Si was more evident.

Figure 2. Relationship between iron and arsenic removal for AP groundwater.

4 CONCLUSIONS

Removal of As was closely related to removal of Fe, indicating that optimized Fe removal could optimize As removal simultaneously. The (Ca+Mg)/P ratio seems capable to predict iron floc growth and could be used as a tool to optimize iron removal in rapid sand filters. Our results seem to indicate that under environmental conditions, Si can hinder As due to adsorption competition to a larger extent than HPO₄²⁻.

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