Influence of Fe(II), Fe(III) and Al on arsenic speciation in treatment of contaminated water by Fe and Al (hydr)oxides co-precipitation

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ABSTRACT: Arsenic is considered a highly toxic metalloid, but the toxicity depends on its speciation. Inorganic species are considered more toxic than organic ones and the As(III) more toxic than As(V). This study evaluated the speciation of soluble arsenic after treatment of contaminated water by co-precipitation of Fe and Al (hydr)oxides. The results showed that the valence of Fe and presence of Al play an important role on As speciation in soluble phases resulting from water treatment.

1 INTRODUCTION

Arsenic is considered a very toxic metalloid that is usually found associated to gold deposits. Acid mine drainage (AMD) is among the major environmental problems in base metal exploitations. Therefore, contamination of water, soil and sediments with As associated to AMD is a major concern in mining industry. This study aimed to evaluate arsenite and arsenate removal from highly contaminated water and redox changes due to co-precipitation of Fe(II), Fe(III) and Al (hydr)oxides.

2 EXPERIMENTAL

2.1 Fe and Al (hydr)oxides synthesis

Synthesis of Fe and Al (hydr)oxides were performed following Schwertmann and Cornell (2000) guidelines with some adaptations in order to approach AMD. Iron and Al (hydr)oxides were precipitated from sulfates salts of Fe(II), Fe(III) and Al in a solution containing high concentrations of As (500 mg L⁻¹). Three Fe:Al molar ratios were considered (100:0, 80:20 and 60:40), in order to obtain pure Fe (hydr)oxides, Al substituted Fe (hydr)oxides and Al (hydr)oxides. The pH was buffered to 8 with KOH in the beginning of the experiments and whenever necessary.

2.2 Arsenic speciation

Arsenic concentrations in supernatants were monitored by hydride generation atomic fluorescence spectrometry (AFS-HG) during the experimental period (84 days). At the end of the experimental period, speciation of soluble arsenic in supernatants was performed by HPLC-AFS-HG.

3 RESULTS AND DISCUSSION

3.1 Removal efficiency

Efficiencies of As removal from water reached high percentages just after precipitation (>93%), for both As species, with a slightly lower efficiency for arsenite (As(III)) treated with Fe(II) in the presence of Al (Table 1).

3.2 Arsenic speciation

Goethite, lepidocrocite and gibbsite were identified by XRD in precipitates from Fe(II). No significant differences were identified in Fe and Al (hydr)oxides after synthesis with arsenite or arsenate (Fig. 1).

In these treatments, soluble As(III) was oxidized to As(V), mainly in the presence of Al, suggesting that Al favors As oxidation (Table 2).

Table 1. Efficiencies for As (III and V) removal from water by co-precipitation of Fe and Al (hydr)oxides at different Fe:Al molar ratios 2 h after precipitation.

Treatments	Fe:Al	Efficiency mean after 2 h
Fe(II): Al: As(V)	100:0	99.98 a
Fe(III): Al: As(V)	100:0	99.98 a
Fe(III): Al: As(III)	100:0	99.98 a
Fe(III): Al: As(V)	80:20	99.98 a
Fe(III): Al: As(V)	60:40	99.98 a
Fe(III): Al: As(III)	80:20	99.96 a
Fe(II): Al: As(III)	100:0	99.93 a
Fe(III): Al: As(III)	60:40	99.90 a
Fe(II): Al: As(V)	80:20	99.89 a
Fe(II): Al: As(V)	60:40	99.89 a
Fe(II): Al: As(III)	80:20	99.33 a
Fe(II): Al: As(III)	60:40	93.49 b

Figure 1. Diffractograms of precipitates from Fe(II) treatments (a) and Fe(III) treatments (b), with the three Fe:Al molar ratios 100:0, 80:20 and 60:40. (Fy: ferrihydrite, Gb: gibbsite, Gt: goethite, Lp: lepidocrocite).

Table 2. Soluble arsenite and arsenate concentrations in supernatants at the end of incubation period for treatments with 500 mg L⁻¹ of As(III) or As(V).

Arsenic valence	Fe(II):Al ratio	Total [As] (μg L ⁻¹)	[As (III)] (μg L ⁻¹)	[As (V)] (μg L ⁻¹)
As(III)	100:00	1352	818	534
	80:20	232	25	207
	60:40	441	20	421
As(V)	100:00	198	43	155
	80:20	83	22	61
	60:40	140	0	140

	Fe(III):Al ratio	Total [As] (μg L ⁻¹)	[As (III)] (μg L ⁻¹)	[As (V)] (μg L ⁻¹)
As(III)	100:00	161	137	25
	80:20	330	330	0
	60:40	663	660	3
As(V)	100:00	77	70	7
	80:20	135	106	30
	60:40	112	110	2

This behavior is similar to oxidation of Fe(II) in the presence of Al, as it favors precipitation of goethite in detriment to magnetite (Mello *et al.*, 2018). On the other hand, ferrihydrite and gibbsite were identified in precipitates from Fe(III) treatments (Fig. 1), but As(III) was not oxidized to As(V). Differently from Fe(II), Al did not favor As oxidation in Fe(III) system. This difference can be related to Fenton Reactions that take place in Fe(II) systems, leading to Fe oxidation, but not in Fe(III) systems (Ona-Nguema *et al.*, 2010). On the other hand, As(V) was reduced to As(III) in a higher extent in Fe(III) treatments, but apparently, there are not reported reasons for that.

4 CONCLUSIONS

Considering the higher toxicity of arsenite compared to arsenate, the main contribution of this study was to demonstrate the As(III) oxidation in treatments with Fe(II), in the presence of Al. On the contrary, As(V) was reduced to As(III) in Fe(III) treatments.

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