

Supplementary Information

Experimental Section

1. Ferrihydrite

Based on Schwertmann and Cornell [1], 40 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9(\text{H}_2\text{O})$ were dissolved in distilled water under constant stirring for 30 min. The pH was adjusted by adding KOH in order to keep in control the acidity of the system. Afterwards, the residue was washed using deionized water and then filtered using a 0.45 μm cellulose membrane filter. Finally it was dried at 35 °C.

1.1. Arsenic Co-Precipitated with Ferrihydrite

Using the same technique described before, 0.07 g of AsO_3 was added during the initial stage but with an extended stirring time of 40 min.

1.2. Arsenic Adsorption on Ferrihydrite

Twenty milliliters of deionized water with 0.1 g of AsO_3 were mixed with 1.7 g of ferrihydrite under constant stirring for 24 h and at constant pH 5. Afterwards, the residue was washed using deionized water and then dried at 35 °C.

2. Schwertmannite

Following the method described by Regenspurg *et al.* [2], 10 g of iron sulphate (II) were dissolved in distilled water under continuous stirring for 1 h. Hydrogen peroxide was incorporated until the color of the solution changed to dark ochre (5 min) in order to accelerate the oxidation from ferrous to ferric and then a new 1 h stirring process was applied. The sample was kept for 1 day at a constant pH 2.4. Afterwards, the residue was washed using deionized water and then filtered using a 0.45 μm cellulose membrane. Finally it was dried at 35 °C.

2.1. Arsenic Co-Precipitated with Schwertmannite

Natural sample (SCH-1) containing arsenic 0.57 wt % from Monte Romero mine located in the Iberian Pyrite Belt, Spain [3], was selected to conduct this experiment. Diffraction pattern in this sample showed a highlighted peak around 4.2 Å, which displays a mixture between goethite and schwertmannite.

2.2. Arsenic Adsorption on Schwertmannite

Given a solution containing 15 mL of H_2AsO_4 (1000 mg/L), 5 ml of deionized water, and 450 μL of NH_4OH , 1.7 g of schwertmannite was added and the whole system stirred for 24 h. Finally the sample was cleaned and dried at a temperature of 35 °C.

3. Jarosite

Jarosite synthesis was based on several works [4–6]. It was started by heating 100 mL of deionized water to a temperature between 70 and 90 °C under constant stirring. Afterwards, 15 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

were added under constant stirring for 5 min, then, 5 g of KSO_4 were added to the solution. When pH reached 1.3, 5 mL of KOH were added under constant stirring for 1 h. Subsequently, 25 mL of KOH were added until pH 1.6 was reached and the color of the solution changed from yellow to ochre-brown. Stirring continued for another 5 h and then allowed to stand. The precipitate was washed with deionized water, filtered with a 0.45 μm membrane, and submitted to a one-day drying process at 110 °C.

3.1. Arsenic Co-Precipitated with Jarosite

Using the same described technique, 15 mL of H_2AsO_4 (1000 mg/L) were added before the 5 mL KOH addition. One hour stirring process was applied. During this period, pH was adjusted to 1.6 by adding an extra 2 mL KOH solution.

3.2. Arsenic Adsorption on Jarosite

Given a solution containing 15 mL of H_2AsO_4 (1000 mg/L), 5 mL of deionized water, and 450 μL of NH_4OH , 1.7 g of jarosite was added and the whole system stirred for 24 h. Finally, the sample was cleaned and dried at a temperature of 35 °C.

4. Goethite

For this synthesis, 13.9 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in 1 L of deionized water with a constant N_2 bubbling for 30 min [7]. Afterwards, 110 mL of NaHCO_3 were added and the N_2 was changed by an air flux of 30–40 mL/min. A 48 h stirring process at neutral pH was also applied. Finally, the sample was washed with deionized water and filtered with a 0.45 μm membrane, the drying was carried out at 35 °C.

4.1. Arsenic Co-Precipitated with Goethite

Using the same procedure but before adding the air flux, 0.04 g of As(III) were added, which result in a faster oxidation rate with a constant pH 8 during co-precipitation.

4.2. Arsenic Adsorption on Goethite

Twenty milliliters of deionized water with 0.1 g of AsO_3 were mixed with 1.7 g of goethite under constant stirring for 24 h and at constant pH 5. Afterwards, the residue was washed using deionized water and then dried at 35 °C.

Table S1. Point of zero charge (PZC) for Fe(III) hydroxides.

Mineral	PZC	Electrolyte	Reference
Ferrihydrite	7.8–8.7	0.01–0.5 KNO_3	[8]
Schwetmannite	6.6–7.2	-	[9]
Goethite	7.5–9.4	0.001–0.1 M NaCl	[8]
Jarosite	3.9	-	[10]

Table S2. Specific reaction surfaces for Fe(III) hydroxides.

Mineral	Area (m ² /g)	Reference
Ferrihydrite	>200	[11]
	347	[12]
	200–600	[1]
Goethite	19	[12]
	34	[13]
	98	[14,15]
	100–300	[1]
Jarosite	2.6	[16]
	5–20	[15]
Schwertmannite	117.5	[17]
	5.3–210	[18]
	250	[1]

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