Comparison between Different Technologies (Zerovalent Iron, Coagulation-Flocculation, Adsorption) for Arsenic Treatment at High Concentrations

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S1. Mechanism for As removal by Fe(0)

The general well-accepted (simplified) mechanism involved in systems using Fe(0) in water for removal of pollutants is indicated in Eqs. (S1)-(S10) (e.g., [1–4]):

$$Fe(0) + 2\ H_2O \rightarrow Fe(II) + H_2 + 2\ HO^- \quad (S1)$$

$$2\ Fe(0) + 2\ H_2O + O_2 \rightarrow 2\ Fe(II) + 4\ HO^- \quad (S2)$$

$$Fe(0) + 2\ H^+ + O_2 \rightarrow Fe(II) + H_2O_2 \quad (S3)$$

$$Fe(0) + 2\ Fe(III) \rightarrow 3\ Fe(II) \quad (S4)$$

$$4\ Fe(II) + 2\ H_2O + O_2 \rightarrow 4\ Fe(III) + 4\ HO^- \quad (S5)$$

$$6\ Fe(II) + 6\ H_2O + O_2 \rightarrow 2\ Fe_3O_4\ (\downarrow) + 12\ H^+ \quad (S6)$$

$$Fe(II) + CO_3^{2-}/HO^- \rightarrow Fe(II)\ (\downarrow) \quad (S7)$$

$$4\ Fe_3O_4\ (\downarrow) + O_2 + 18\ H_2O \rightarrow 12\ Fe(OH)_3(\downarrow) \quad (S8)$$

$$Fe(II) + 2\ Fe(III) + 4\ H_2O \rightarrow Fe_3O_4\ (\downarrow) + 8\ H^+ \quad (S9)$$

$$Fe(III) + 3\ H_2O \rightarrow Fe(OH)_3\ (\downarrow) + 3\ H^+ \quad (S10)$$

Removal of As(V) then occurs by the following reactions:

$$Fe(III) + H_2AsO_4^-/HAsO_4^{2-} \rightarrow FeAsO_4\ (\downarrow) + 2\ H^+/H^+ \quad (S11)$$

$$\equiv Fe(II/III)OH + H_2AsO_4^-/HAsO_4^{2-} \rightarrow \equiv Fe(II/III)AsO_4 \quad (S12)$$

S2. Characterization of the natural clay

The characterization of the natural clay of the Misiones province has been published in a previous work [5]. Briefly, the composition of the clay was determined by elemental analysis by ICP-OES (Perkin Elmer model Optima 2000 DV), after dissolution using a microwave digester oven according to the procedure described in US-EPA 3051 and 3052 standards [6]. Table S1 indicates the chemical composition of the clay with respect to Al, Fe and Mn.

Table S1. Chemical composition of the natural clay.

Element	Al	Fe	Mn
Percentage (g/100 g)	9.26	3.98	0.064

Volatile compounds, determined by weighing the sample before and after calcination at 700 °C for 5 h under air atmosphere, accounted 7% of the clay [**Error! Bookmark not defined.**]. A differential scanning calorimetry analysis under N_2 atmosphere, run from 28 to 550 °C, showed two peaks, one at 74.3 °C, typical of moisture evaporation, and another one at 506.62 °C, corresponding to the loss of hydroxide groups from Al components [**Error! Bookmark not defined.**].

S3. Comparison of kinetic parameters extracted from Figure 4 from the main text

Table S2. Comparison of the kinetic parameters k, r_i, and t_R for As(III) removal with Fe(0) under oxic conditions at circumneutral pH extracted from Figure 4 with Eq. (3) of the main text and data from other authors.

Fe(0) size (mm)	$[As(III)]_0$ (mg L^{-1})	MR As:Fe	pH	EC (mS cm^{-1})[a]	Stirring	$k \times 10^3$ (h^{-1})	r_i (mg L^{-1} h^{-1})	t_R (h)	Ref.
0.074-0.84	5	1:268	7	0.03	No	30	0.15	> 648	This work
0.149	2	1:16109	6.7	≈ 0.9[a]	Orbital, 50 rpm	149	0.298	≈ 48	[7]
NR[1]	2	1:16109	6.7	≈ 0.9[a]	Orbital, 50 rpm	36.2	0.0724	< 96	[**Error! Bookmark not defined.**]
NR[2]	2	1:16109	6.7	≈ 0.9[a]	Orbital, 50 rpm	36.1	0.0722	< 96	[**Error! Bookmar**

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0.045	2	1:16109	6.7	≈ 0.9[a]	Orbital, 50 rpm	7.23	0.0106	NR	[**Error! Bookmark not defined.**]
< 0.149	100	1:13.4	6	0.05-0.8	Magnetic	175	17.5	NR	[8]
< 0.074	0.5	1:6708	8.28	≈ 3[a]	NR	223	0.112	NR	[**Error! Bookmark not defined.**]
1-2	16.9	1:3572	7.5	1.596	Orbital	246	4.16	24	[9]
< 0.005	1	1:1342-1:13416	7	≈ 0.9[a]	Orbital, 185 rpm	80-520	0.08-0.52	≥ 12	[10]
0.297-2.38[1]	3.9	1:38221	7.25	≈ 3.1[a]	Orbital, 50 rpm	8.8	0.034	NR	[11]

[a] When not provided, EC was calculated from the total dissolved solids (TDS) content using the following Eq.: TDS (mg L^{-1}) = 0.65 × EC (µS cm^{-1}) [12]. NR: not reported. [1] Powdered Fe(0), BET: 2.53 m^2 g^{-1}. [2] Powdered Fe(0), BET: 2.33 m^2 g^{-1} .

S4. Kinetics of adsorption of As(III) and formation of As(V) by treatment with the clay

Figure S1 shows the evolution of the As(III) decay and the formation and decay of As(V) by treatment with the clay in the conditions of Figure 6 of the main text.

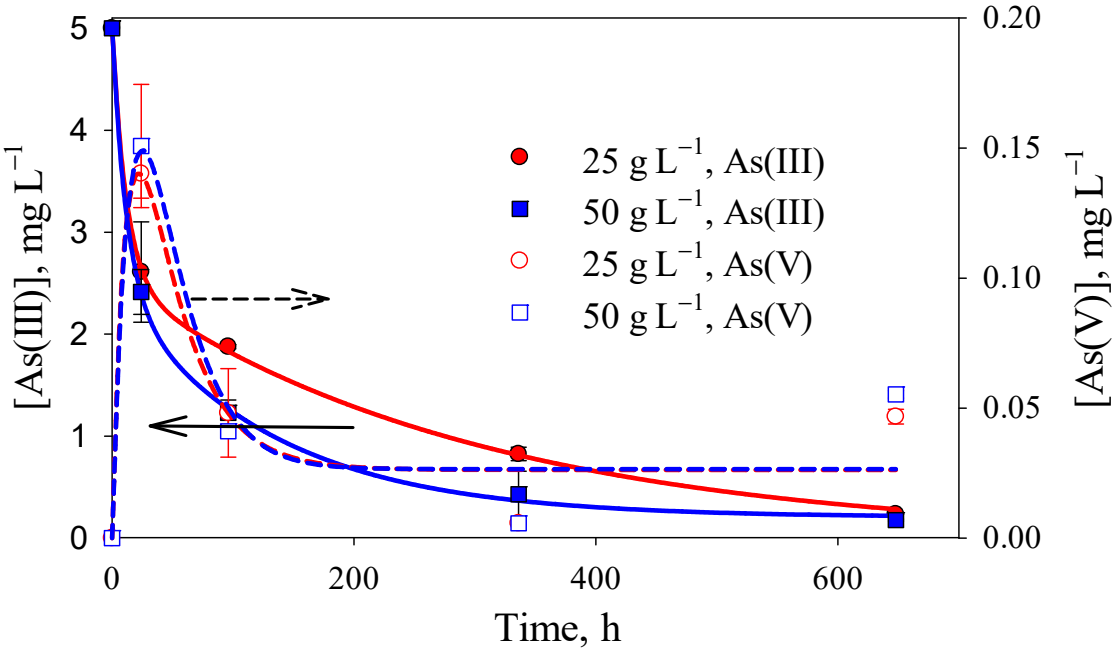

Figure S1. Kinetics of adsorption of As(III) and formation and adsorption of As(V) in the clay system. Conditions: [As(III)] = 5 mg L^{-1}, pH 7, [clay] = 25 or 50 g L^{-1}, RT, EC = 0.03 mS cm^{-1}. Full lines correspond to the adjustment to Equation.(6) of the main text, with [As(III)] calculated from Equation (4) of the main text. Dashed lines are only for better visualization and do not correspond to any fitting equation.

S5. Comparison of technologies

Table S3 shows the kinetic parameters of the experimental results of As(III) removal extracted from Figure 9 with Eq. (3) of the main text, with μFe(0) and with or without the addition of clay.

Table S3. Kinetic parameters of the experimental results of As(III) removal extracted from Figure 8 with Eq. (3) of the main text, with μFe(0) and with or without the addition of clay.

Experiment	A, mg L^{-1}	$k \times 10^3$, h^{-1}	$[As(V)]_\infty$, mg L^{-1}	R^2
μFe(0)	5.00 ± 0.05	30 ± 2	0.05 ± 0.01	1
clay (25 g L^{-1}) + μFe(0)	4.90 ± 0.10	25 ± 2	0.08 ± 0.05	1
clay (50 g L^{-1}) + μFe(0)	4.90 ± 0.06	30 ± 2	0.10 ± 0.03	1

References

1. Leupin, S.J. Hug, Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zero-valent iron, Water Res. 39 (2005) 1729–1740, doi: 10.1016/j.watres.2005.02.012.
2. H. Sun, L. Wang, R. Zhang, J. Sui, G. Xu, Treatment of groundwater polluted by arsenic compounds by zero valent iron, J. Hazard Mater. 129 (2006) 297–303, doi: 10.1016/j.jhazmat.2005.08.026.
3. I.A. Katsoyiannis, T. Ruettimann, S.J. Hug, pH Dependence of Fenton Reagent Generation and As(III) Oxidation and Removal by Corrosion of Zero Valent Iron in Aerated Water, Environ. Sci. Technol. 42 (2008) 7424–7430, doi:

10.1021/es800649p.

4. S.R. Kanel, B. Manning, L. Charlet, H. Choi, Removal of Arsenic(III) from Groundwater by Nanoscale Zero-Valent Iron, Environ. Sci. Technol. 39 (2005) 1291–1298, doi: 10.1021/es048991u.
5. J.M. Meichtry, M.D. Castiglia, F. Mugrabi, L.E. Lan, F.D. Reina, G.E. De Seta, A.R. López, E. Domingo, Removal of arsenic in water by low-cost materials and safe final disposal, Proyecciones, 13 (2015) 47–58, http://hdl.handle.net/11336/114271.
6. A. Agazzi, C. Pirola, Fundamentals method and future trends of environmental microwave sample preparation, Microchem. J. 67 (2000) 337–341, doi: 10.1016/S0026-265X(00)00085-0.
7. C. Su, R. Puls, Arsenate and arsenite removal by zero valent iron: kinetics, redox transformation and implications for in situ groundwater remediation, Environ. Sci. Technol. 35 (2001) 1487–1492, doi: 10.1021/es001607i.
8. S. Bang, G.P. Korfiatis, X.J. Meng. Removal of arsenic from water by zero-valent iron, J. Hazard Mater. 121 (2005) 61-67, doi: 10.1016/j.jhazmat.2005.01.030.
9. C. Trois, A. Cibati, South African sands as an alternative to zero valent iron for arsenic removal from an industrial effluent: Batch experiments, J. Environ. Chem. Eng. 3 (2015) 488–498, doi.org/10.1016/j.jece.2014.12.019.
10. S.R. Kanel, H. Choi, Removal of Arsenic from Groundwater by Industrial Byproducts and Its Comparison with Zero-Valent Iron, J. Hazard. Toxic Radioact. Waste 21 (2017) 04016028, doi: 10.1061/(ASCE)HZ.2153-5515.0000349.

11. H.-L. Lien, R. T. Wilkin, High-level arsenite removal from groundwater by zero-valent iron, Chemosphere 59 (2005) 377–386, doi: 10.1016/j.chemosphere.2004.10.055.
12. A. F. Rusydi, Correlation between conductivity and total dissolved solid in various type of water: A review, IOP Conf. Series: Earth and Environmental Science 118 (2018) 012019, doi :10.1088/1755-1315/118/1/012019.