Supplementary information

Improvement in arsenic adsorption and calcite dissolution kinetics through size reduction of a ferric hydroxide-calcite adsorbent

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1. Materials and methods: isotherm and kinetics modelling

Table S1. Initial solution characteristics, equilibrium phases and surface parameters in arsenic adsorption isotherm simulations. As(III) and As(V) simulations were run for different initial concentrations (0.0338-0.693 mol/L for As(III) and 0.0076-0.266 mol/L for As(V)) to reproduce the isotherm batch experiment, with the rest of parameters kept constant.

	As(III)		As(V)	
	OF-G	**OF-S**	**OF-G**	**OF-S**
Initial solution				
temp	25	25	25	25
pH	9.2	9.2	9.2	9.2
pe	4	4	4	4
redox	pe	pe	pe	pe
Water (kg)	0.05	0.05	0.05	0.05
Density (kg/dm^3)	1	1	1	1
As(III) (mmol/Kg)	0.0338-0.693	0.0364-0.693	-	-
As(V) (mmol/Kg)	-	-	0.0076-0.266	0.0080-0.266
Cl (mmol/Kg)	charge	charge	charge	charge
Na (mmol/Kg)	100	100	100	100
Equilibrium phases				
Ferrihydrite				
Reaction and Log K	$Fe(OH)_3 + 3H^+ = Fe^{+3} + 3H_2O$ Log K = 3.191			
Saturation index	0	0	0	0
Moles	0.000214	0.000214	0.000214	0.000214
Calcite				
Reaction and Log K	$CaCO_3 = Ca^{+2} + CO_3^{-2}$ Log K = -8.48			
Saturation index	0	0	0	0
Moles	0.0000213	0.0000213	0.0000213	0.0000213
Surface				
Hfo[a] equilibrium phase	Ferrihydrite	Ferrihydrite	Ferrihydrite	Ferrihydrite
Hfo area (m^2/mol)	22550	24901	22550	24901
Hfo_wOH[b] (sites mol/mol OF)	0.12	0.12	0.06	0.06
Hfo_sOH[c] (sites mol/mol OF)	0.007	0.007	0.001	0.001

a) Hfo = Hydrous ferric oxide, assimilated to ferryhydrite (Fe(OH)$_3$) with a molecular weight of 106.87 g/mol.
b) wOH = weak adsorption sites
c) sOH = strong adsorption sites

Table S2. Initial solution characteristics, kinetics, equilibrium phases and surface parameters in calcite dissolution simulations.

	As(III)				As(V)			
	OF-G		OF-S		OF-G		OF-S	
	Acid pH	Alkaline pH	Acid pH	Alkaline pH	Acid pH	Alkaline pH	Acid pH	Alkaline pH
Initial solution								
temp	25	25	25	25	25	25	25	25
pH	4	9.2	4	9.2	4	9.2	4	9.2
pe	4	4	4	4	4	4	4	4
redox	pe	pe	pe	pe	pe	pe	pe	pe
Water (kg)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Density (kg/dm^3)	1	1	1	1	1	1	1	1
As(III) (mmol/Kg)	0.33	0.33	0.33	0.33	-	-	-	-
As(V) (mmol/Kg)	-	-	-	-	0.33	0.33	0.33	0.33
Cl (mmol/Kg)	charge	charge	charge	charge	charge	charge	charge	charge
Na (mmol/Kg)	100	100	100	100	100	100	100	100
Kinetics-calcite[a]								
Current moles	2.13E-05	2.13E-05	2.13E-05	2.13E-05	2.13E-05	2.13E-05	2.13E-05	2.13E-05
Initial moles	2.13E-05	2.13E-05	2.13E-05	2.13E-05	2.13E-05	2.13E-05	2.13E-05	2.13E-05
Area (cm²/mol)	2.50E+05	2.50E+05	5.00E+05	5.00E+05	2.50E+05	2.50E+05	5.00E+05	5.00E+05
Exponential factor	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6

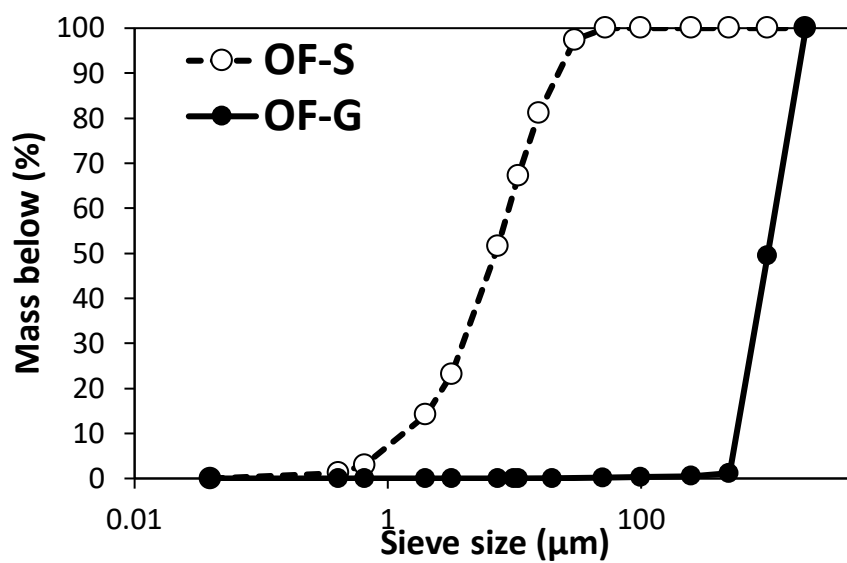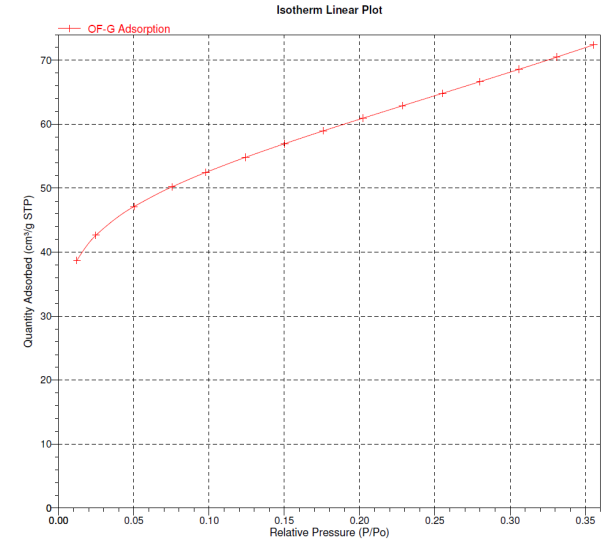a) Rate equation defined by Plummer *et al.* (1978)

2. Adsorbent characterization

*Figure S1. Particle Size Distribution of OF-G and OF-S.*

a)OF-G

BET Surface Area Report

BET Surface Area: 217.9597 ± 0.3397 m²/g
Slope: 0.019847 ± 0.000031 g/cm³ STP
Y-Intercept: 0.000125 ± 0.000004 g/cm³ STP
C: 159.779465
Qm: 50.0689 cm³/g STP
Correlation Coefficient: 0.9999952
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (P/Po)	Quantity Adsorbed (cm³/g STP)	1/[Q(Po/P - 1)]
0.050128697	47.1285	0.001120
0.075283446	50.1969	0.001622
0.097877120	52.4743	0.002068
0.124169580	54.8218	0.002586
0.150138824	56.9534	0.003102
0.175869166	58.9600	0.003619

b) OF-S
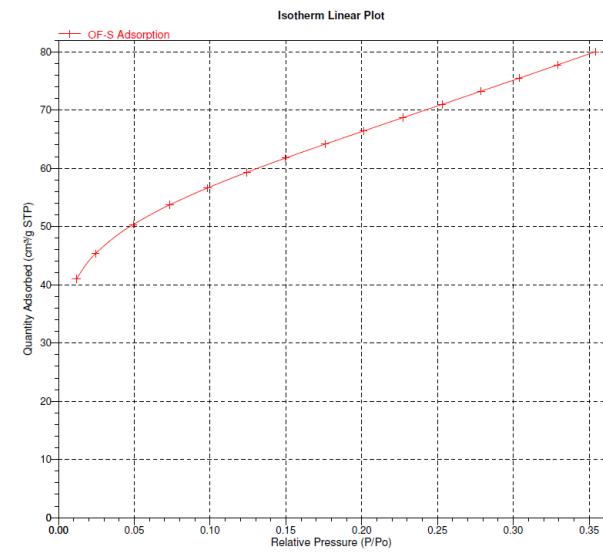
BET Surface Area Report

BET Surface Area: 233.4484 ± 1.3524 m²/g
Slope: 0.018556 ± 0.000106 g/cm³ STP
Y-Intercept: 0.000092 ± 0.000021 g/cm³ STP
C: 203.506954
Qm: 53.6269 cm³/g STP
Correlation Coefficient: 0.9998530
Molecular Cross-Sectional Area: 0.1620 nm²

| Relative Pressure (P/Po)	Quantity Adsorbed (cm³/g STP)	1/[Q(Po/P - 1)]
0.049335465	50.3437	0.001031
0.073410528	53.7244	0.001475
0.098252962	56.6146	0.001925
0.124294770	59.3082	0.002393
0.149732375	61.7507	0.002852
0.175753265	64.1264	0.003325
0.201308672	66.4018	0.003796
0.227167052	68.6846	0.004280
0.252957022	70.9552	0.004772
0.278667338	73.2230	0.005276
0.303913502	75.4625	0.005786

Figure S2. BET isotherms and surface area reports for a) OF-G and b) OF-S.

OF-G
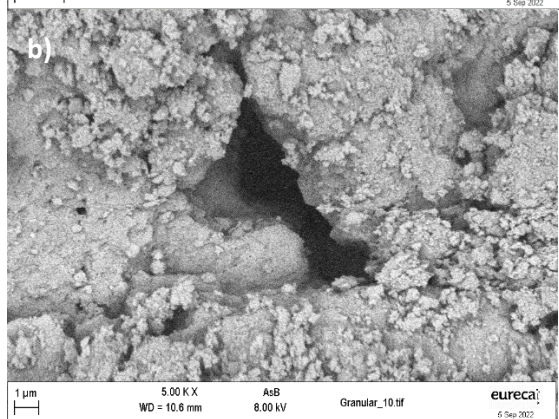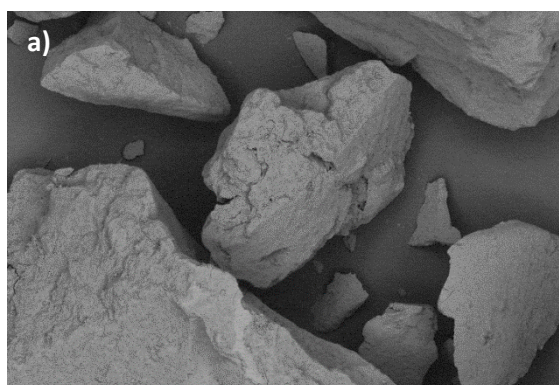
OF-S
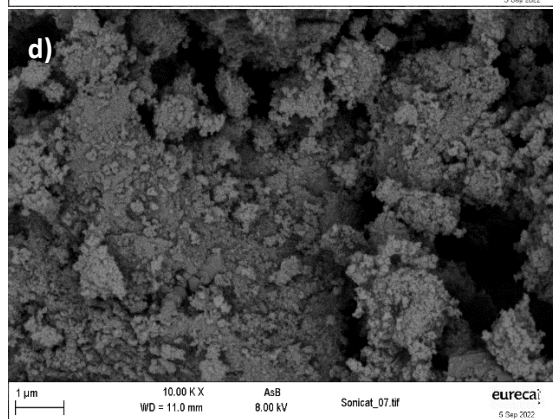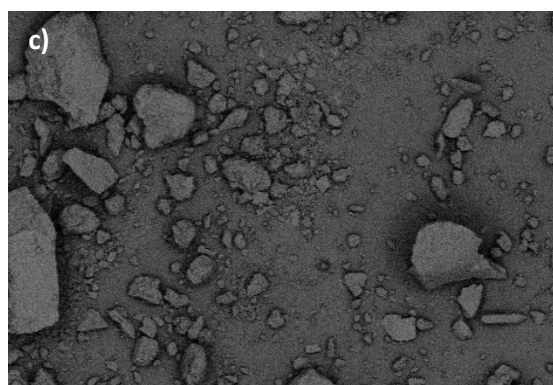
Figure S3. SEM images of a,b) OF-G and c,d) OF-S at different magnifications.
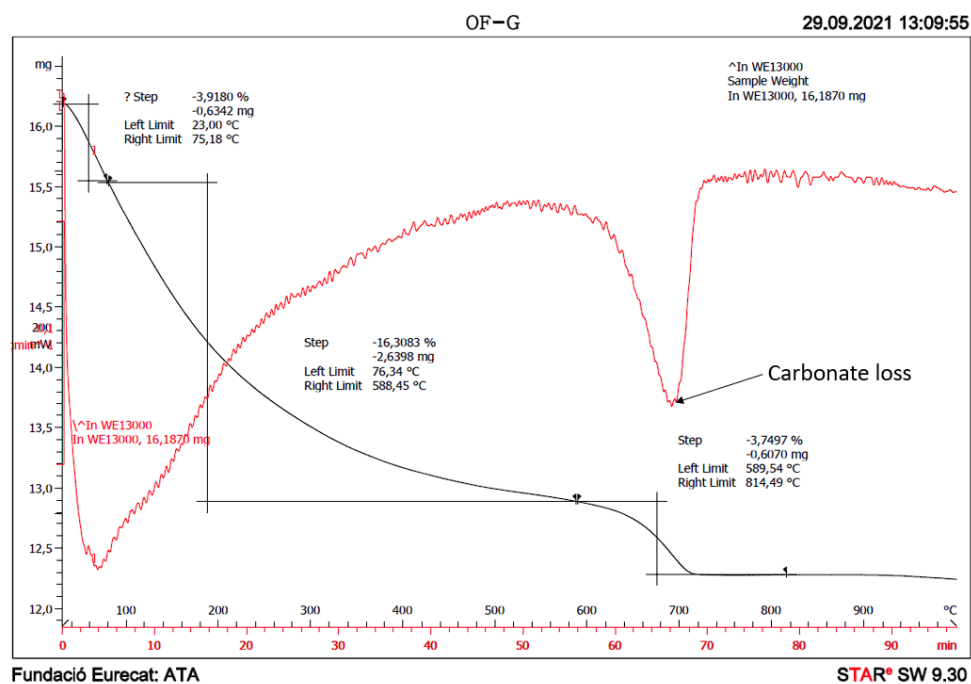
Figure S4. Thermogravimetric analysis of OF-G.
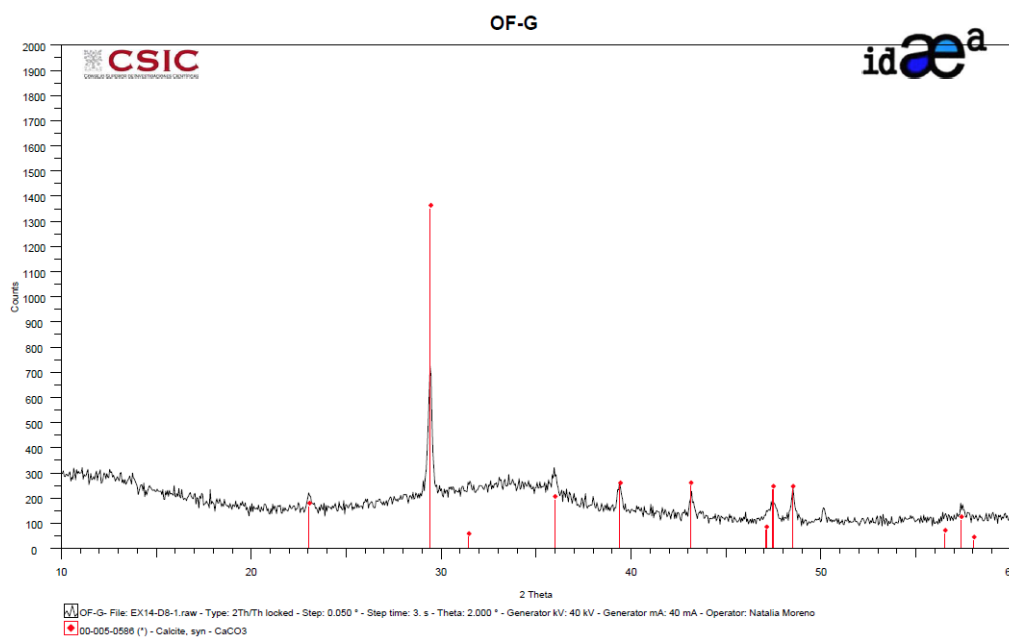

Figure S5. XRD diffractogram of OF-G sample.

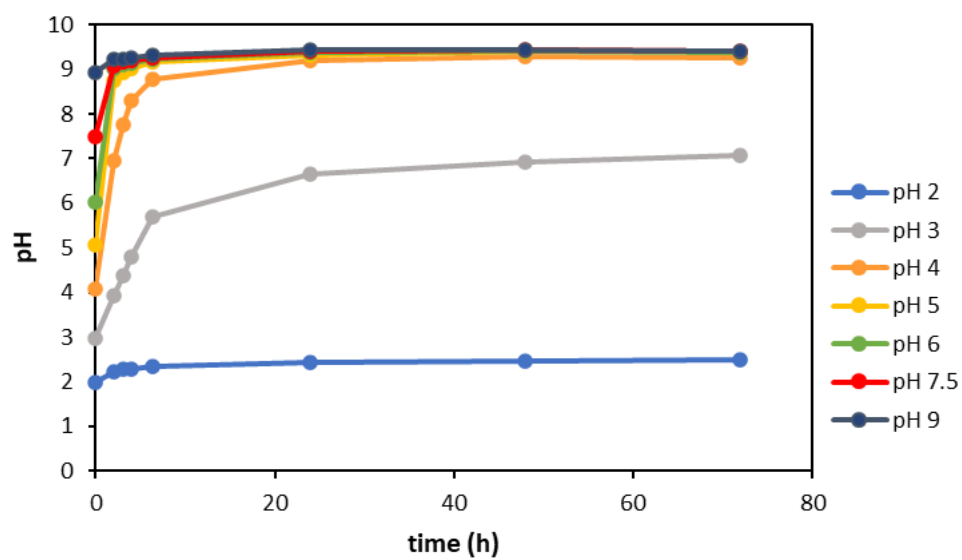## 3. pH evolution due to calcite dissolution

Figure S6. pH variation in batch experiment with OF-G sample and a synthetic water at initial pH from 2 to 9.
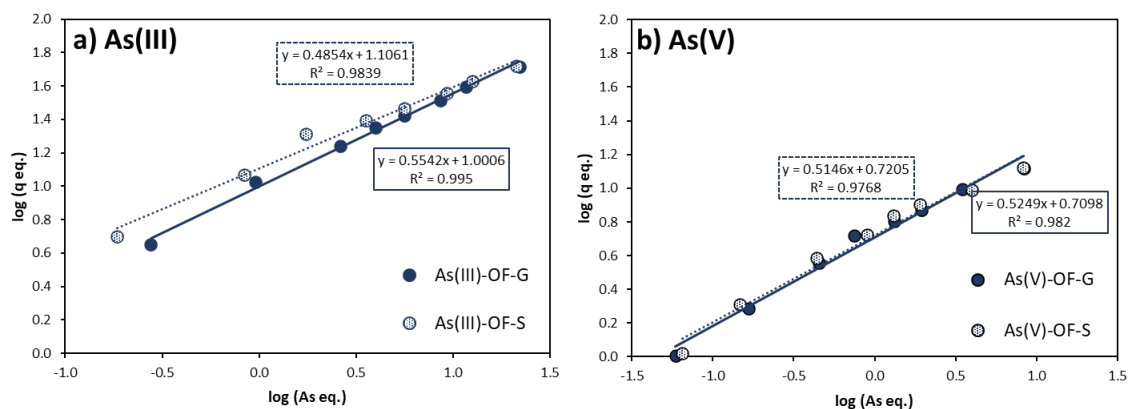
4. Arsenic adsorption equilibrium

Figure S7. Fitting of experimental data with the linearization of Freundlich equation for a) As(III) and b) As(V).
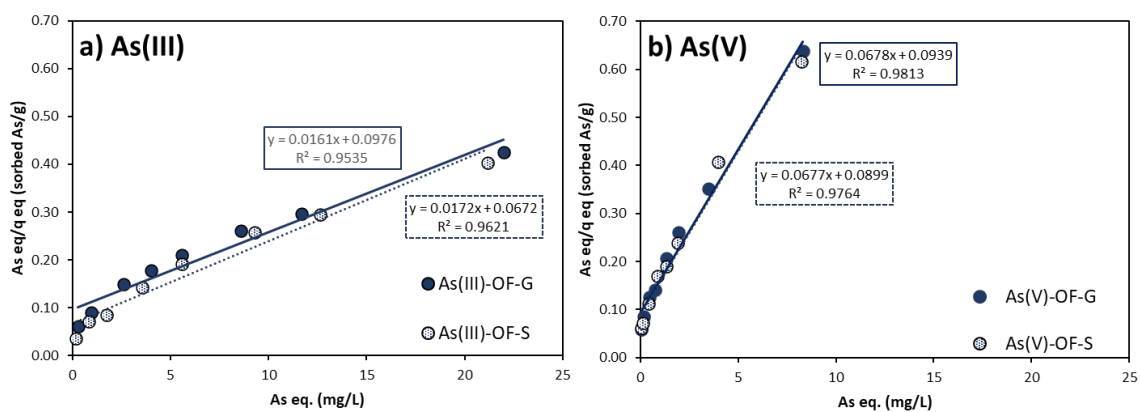

Figure S8. Fitting of experimental data with the linearization of Langmuir equation for a) As(III) and b) As(V).
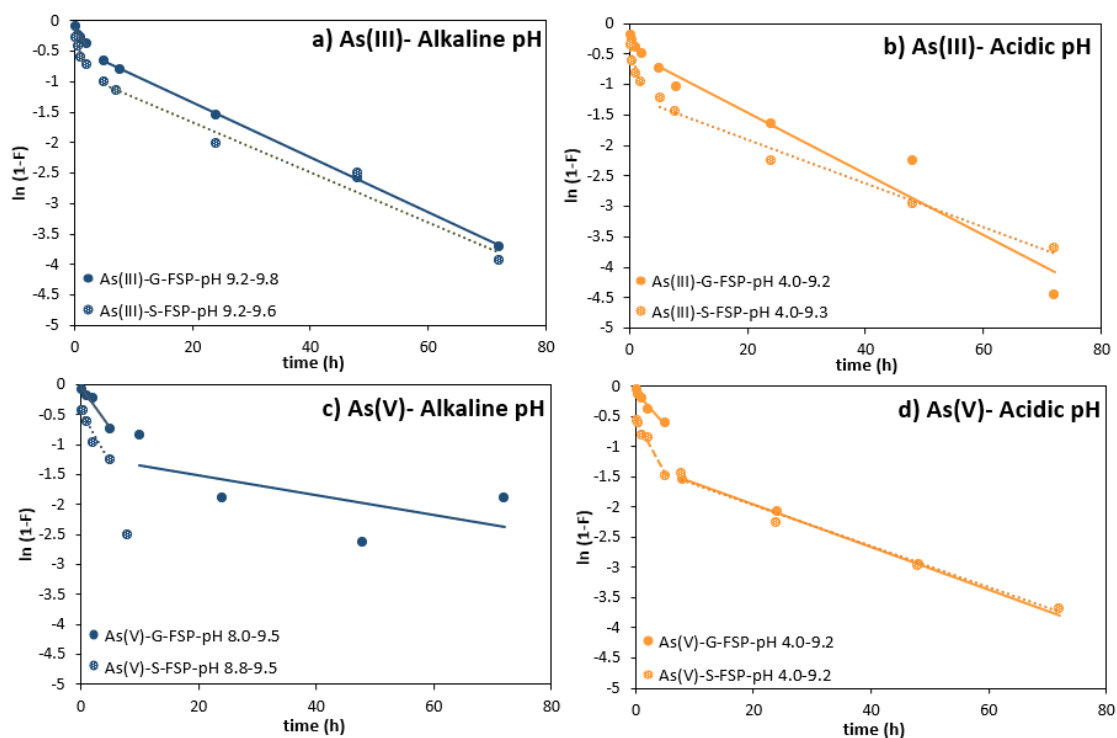
5. Arsenic adsorption kinetics

Figure S9. Film diffusion mass transfer models and linear adjustments for As(III) and As(V) experiments. Solid lines correspond to OF-G and dotted lines to OF-S linear adjustments. a) As(III) adsorption at alkaline pH, b) As(III) adsorption at acidic pH, c) As(V) adsorption at alkaline pH, d) As(V) adsorption at acidic pH.

Table S3. Absolute values of constants of the adjusted film-diffusion mass transfer models.

		As(III)		As(V)	
		OF-G	**OF-S**	**OF-G**	**OF-S**
Alkaline pH	K_{fd1} (1/h)	0.1386	0.2357	0.1375	0.1777
	R^2	0.88	0.91	0.96	0.92
	K_{fd2} (1/h)	0.045	0.0411	0.0166	-*
	R^2	0.99	0.97	0.38	-
Acid pH	K_{fd1} (1/h)	0.1489	0.3127	0.1091	0.1838
	R^2	0.94	0.87	0.94	0.98
	K_{fd2} (1/h)	0.0503	0.0359	0.0354	0.0339
	R^2	0.94	0.98	0.99	0.99

K_{fd1}: film diffusion constant
K_{fd2}: pore diffusion constant
R^2: coefficient of determination
*This constant could not be calculated since q_e was lower than the adsorbed As in intermediate points

6. Calcite dissolution kinetics

Table S4. Measured calcium release rates in the medium for the first 5 h (data from Fig. 3).

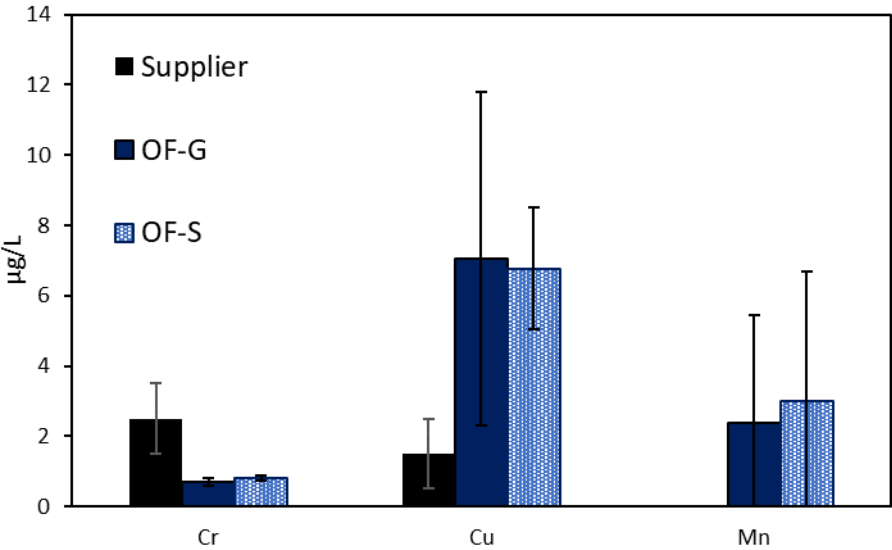|	As(III)		As(V)	
	OF-G	**OF-S**	**OF-G**	**OF-S**
Alkaline pH (mg/L/s × 10^{-3})	0.8 ± 0.4	2 ± 3	0.5 ± 0.5	2 ± 2
Acid pH (mg/L/s × 10^{-3})	0.8 ± 0.6	2 ± 3	1.0 ± 0.8	3 ± 5

7. Environmental significance

Figure S10. Traces released during the arsenic adsorption experiments.