

Supplementary Materials

Improvement of As(V) Adsorption by reduction of Granular to Micro-sized Ferric Hydroxide

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1. Preliminary information of groundwater samples from Nitrastur site

Figure S1 shows a simplified plot with the position of the samples N1 and CW3 (in orange color) that were separated 6.2 m. Figure S1 also shows other wells (blue color) that were used in finished European projects and that surround the studied samples. All the numbers of figure S1 are expressed in meters taking as a reference the position of N1. Blue arrow shows the groundwater direction and black arrow the orientation to North. The figure has been adapted from[1][2].

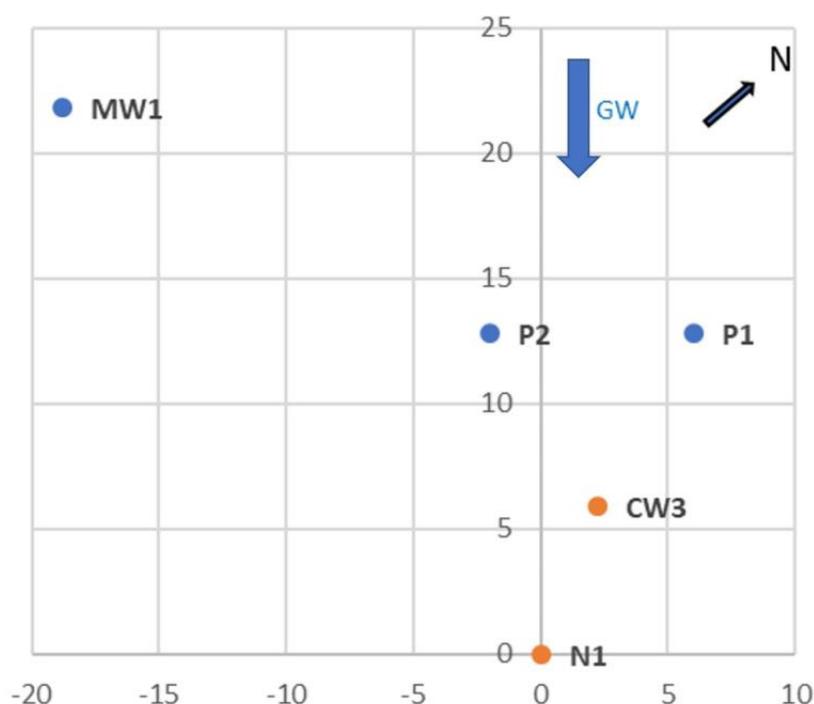


Figure S1. Simplified plot of groundwater samples around N1 and CW3 wells.

Table S1 shows results of characterization of contaminated groundwater present in the zone of Figure S1 (older analysis of N1 and analysis of surrounding wells at different dates) that have been published recently in literature. All these characterization data are

from contaminated groundwater before remediation tests performed in European projects. The well N1 was already present in the site before the sampling of the present paper and its groundwater was very well characterized in March, June, September and December 2015 [3].

Table S1. Preliminary information about contaminated groundwater samples from the Nitrastur site.

		N1	MW1	P1&P2	X
Sampling date		All seasons 2015	Winter 2016	Spring 2017	Between 2016 and 2018
N of samples		4	1	2	1
Reference		[3]	[4]	[5]	[6]
EU project		I+DARTS	NANOREM	Reground	Reground
pH	(-)	2.5	6.6	6-6.5	7.4
Oxid.-Reduct. Potential (ORP)	(mV)	+400	+96.44	+400	nr
Chloride	(mg/L)	8.7	nr	nr	8.1
Sulphate	(mg/L)	566	460	nr	471
Nitrate	(mg/L)	nd	1.1	nr	nr
Phosphate	(mg/L)	nd	0.4	nr	nr
Sodium	(mg/L)	36.3	nr	nr	12.1
Calcium	(mg/L)	113	nr	nr	240
Magnesium	(mg/L)	14.3	nr	nr	19.1
Arsenic	($\mu\text{g/L}$)	2265-8327	1796	nr	3320
Lead	($\mu\text{g/L}$)	0.3-1.1	16.3	100-600	7.5
Zinc	($\mu\text{g/L}$)	93-385	199	0-1000	300
Copper	($\mu\text{g/L}$)	3-17	42.8	0-1000	6.6
Cadmium	($\mu\text{g/L}$)	0.1-0.9	1.5	25-300	Nd
Nickel	($\mu\text{g/L}$)	3-13	11.8	0-200	38.0

nd, non detected; nr, not reported

The pH of N1 groundwater was very acidic in 2015 during different climatic conditions (heavy rain, wet and dry weather), but increased the following years [7]. The Oxidation-Reduction Potential (ORP) showed oxidant conditions in the groundwater for all the samples. The analysis of predominant anions in N1 showed high amount of sulphates, high amount of arsenic and moderate amount of metals. These results (acidic pH, sulphates, arsenic and metals) show an important leaching of the surface pyrite ashes in a similar way than in the formation of acid mine drainage. These results were very similar to an unspecified sample from the site (named as X in the table) used in Reground project, with the exception of pH that increased as cited by [7]. From the anionic and cationic composition showed in table S1 an Ionic Strength of $2.5 \cdot 10^{-2}$ M was estimated for N1 and X samples. The sample MW1 was very close in time (few months) with the sampling of contaminated groundwater of the present paper. Again, sulphate and arsenic were high, pH was higher than in 2015 and presence of metals was moderate. This sample also shows that other anions as phosphate are not important. Samples P1 and P2 from the project reground analyzed one year later than our samples show also pH of 6-6.5 and moderate presence of metals.

As a conclusion, in the matrix of real sample is expected a pH around 6-7.4, oxidative conditions, and a minimum ionic strength around $2.5 \cdot 10^{-2}$ M and high amounts of arsenic and sulphate (around 500 mg/L).

2. Speciation of arsenic in the samples

Table S2 shows the pH, redox and Ionic Strength conditions at the beginning and at the end of equilibrium studies. These conditions allow to perform the predominance equilibrium diagram for arsenic shown un Figure S2.

Table S2. pH, redox conditions and Ionic Strength of the studied samples.

Samples	Initial conditions	Equilibrium conditions
DI	As(V) standard diluted background of nitric acid, pH=5. I=1·10 ⁻⁵ M	Dissolutions equilibrated with air at pH=8.6-9.4
S	Same as DI with aprox 5.2·10 ⁻³ M sulfate (500 mg/L). I=2.3·10 ⁻² M	Dissolutions equilibrated with air at pH=8.6-9.4
N1	Measured pH=6.9. I=0.1 M and ORP 100-400 mV estimated from the site (Table S1)	Dissolutions equilibrated with air at pH=8.6-9.4
CW3	Measured pH=6.6. I=0.1 M and ORP 100-400 mV estimated from the site (Table S1)	Dissolutions equilibrated with air at pH=8.6-9.4

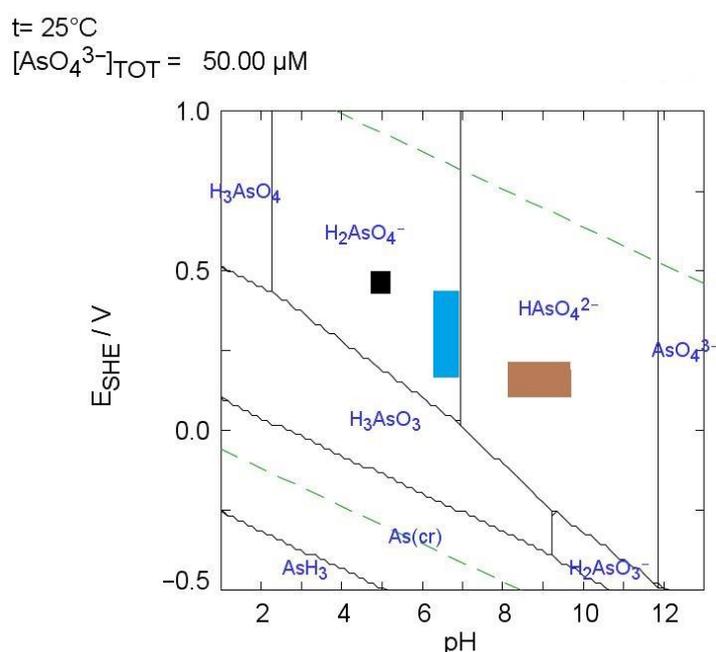


Figure S2. Theoretical speciation of the studied samples.

Speciation with equilibrium diagrams has been performed using SPANA software [8] to study the arsenic species in the aqueous medium under equilibrium conditions. This software allows the selection species and includes a database for arsenic equilibrium constants. The concentration of As has been set to 5·10⁻⁵ M and the Ionic Strength has been set as variable. The following Figure shows the speciation of initial synthetic samples (black square) assuming 400-500 mV of ORP, initial groundwater samples (blue) with ORP from table S1 and equilibrium samples (in brown) assuming 100-200 mV ORP for dissolutions in contact with air.

3. Characterization of the adsorbents

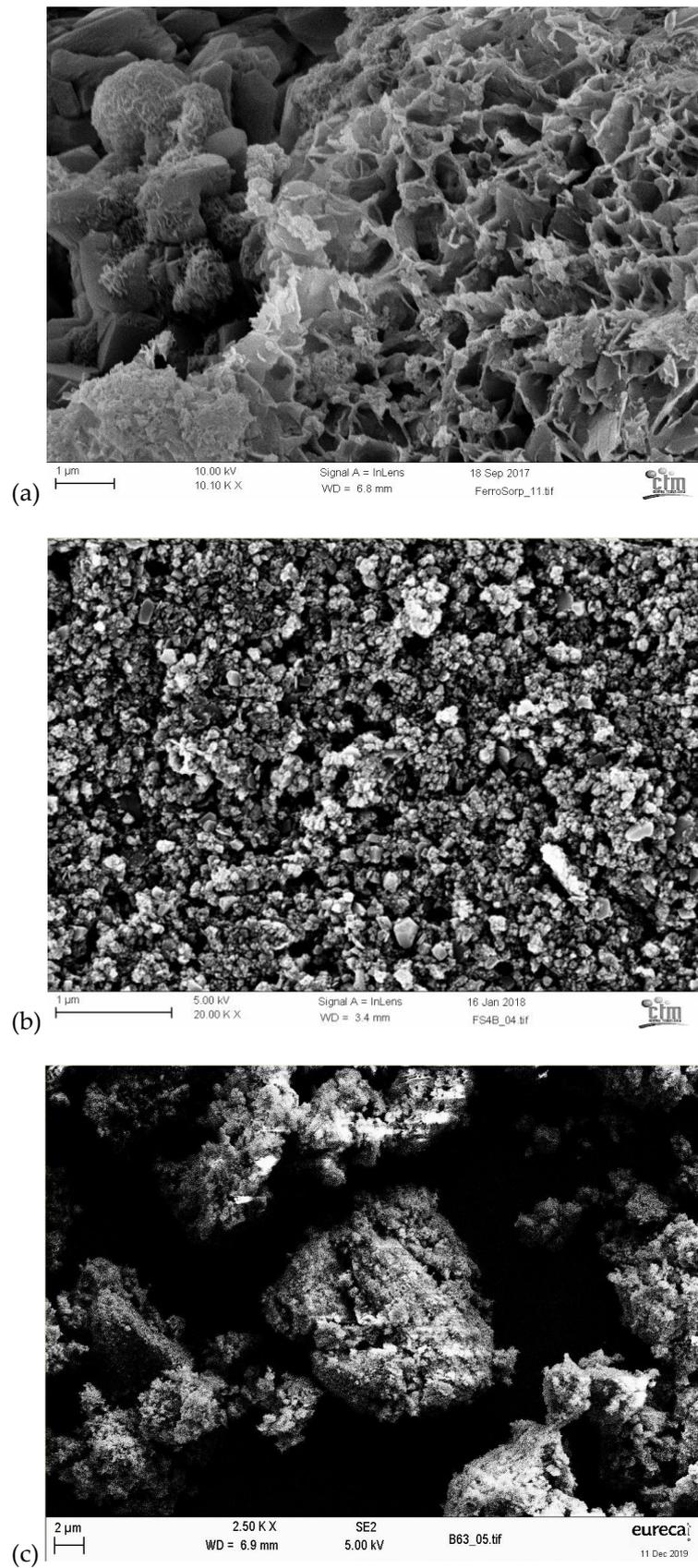


Figure S3. SEM microphotographs (a) OF-G (initial GFH), (b) OF-M (milled), (c) OF-U (ultra-sonicated).

Table S3. Size, BET area and zeta potential at equilibrium pH [9].

	OF-G	OF-M	OF-U
Size ¹ (μm)	500-2000 ²	0.1-2	1.9-50.3
BET Surface Area (m^2/g)	199.7	98.4	160.2
Zeta potential ³ (mV)	-8.4 \pm 2,8	-9.5 \pm 1,0	-8.4 \pm 1,9
Equilibrium pH	8.6	9.4	9.4

¹ Range p10 to p90 in volume, ² Manufacturer information, ³ Average \pm Standard deviation.

Detailed information from this table is available at Supplementary Materials of ref [9].

4. Fitting parameters of equilibrium isotherms (stirred tubes)

Table S4. 95% Confidence Interval (CI) for q_{max} fitting parameters.

		OF-G	OF-M	OF-U
		Langmuir isotherm (q_{max} fitting)		
d.f. (degrees of freedom)		21	13	14
Slope	(g/mg)	0,152398	0,192785	0,123457
Standard error	(g/mg)	0,005894	0,008334	0,004134
t-Student _{0,025}	-	2,080	2,160	2,145
UCL	(g/mg)	0,164655	0,210790	0,132323
LCL	(g/mg)	0,140141	0,174779	0,114591

5. Fitting parameters of kinetic experiments (stirred bakers)

Table S5. Fitting parameters for the pseudo first- and pseudo second- order adsorption kinetics models for OF-G adsorbent.

		OF-G1	OF-G2	OF-G3	OF-G1bis
q_0	(mg/g)	0	3.043	5.230	0
q_e Langmuir	(mg/g)	3.858	6.033	6.387	3.767
n	Exp. points	7	6	5	19
Pseudo first-order (linear)					
R^2		nf	0.99913	0.99998	0.97336
q_e	(mg/g)	nf	5.388	10.177	3.331
k_1	(h^{-1})	nf	0.1512	0.0237	0.0790
Pseudo second-order (linear)					
R^2		0.98004	0.92747	0.98004	0.98074
q_e	(mg/g)	3.543	6.353	13.703	3.793
k_2	(g/mg.h)	0.0684	0.0241	0.0017	0.0286
Pseudo second-order (non-linear)					
q_e	(mg/g)	3.587	6.471	14.508	3.932
k_2	(g/mg.h)	0.0612	0.0213	0.0014	0.0233
SS_{err}		0.190	0.011	<0.001	0.237

nf-could not be fitted satisfactory

Table S6. Fitting parameters for the pseudo first- and pseudo second- order adsorption kinetics models for OF-U sorbent.

		OF-U1	OF-U2	OF-U3
q_0	(mg/g)	0	4.470	7.170
q_e Langmuir	(mg/g)	4.443	6.878	7.803

n	Exp. points	16	6	6
Pseudo first-order (linear)				
R ²		nf	nf	nf
q _e	(Ln(mg/g))	nf	nf	nf
K ₁	(h ⁻¹)	nf	nf	nf
Pseudo second-order (linear)				
R ²		0.99987	0.99986	0.99946
q _e	(mg/g)	4.483	7.229	9.750
k ₂	(g/mg.h)	0.441	0.668	0.846
Pseudo second-order (non-linear)				
q _e	(mg/g)	4.337	7.135	9.722
k ₂	(g/mg.h)	0.793	0.909	0.931
SS _{err}	(mg ² /g ²)	0.217	0.022	0.002

nf-could not be fitted satisfactory

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