Supplementary Information: Material characterization

Improving the sustainability of granular iron/pumice systems for water treatment

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SI Material characterization

SI1 Experimental Section

The microstructure of used Fe^0 and pumice was characterized using mercury intrusion porosimetry (MIP) measurements and by scanning electron microscopy (SEM) observations.

Moreover grain size distribution and the geotechnical parameters (i.e. coefficient of uniformity and mean grain size) derived from it have been determined.

SI1.1 MIP

MIP is performed by injecting mercury into a desaturated porous material. The in-pore invasion process is supposed to be governed by the Washburn-Laplace equation in which the size of intruded pore accessed, assimilated to cylindrical pores are inversely proportional to the applied pressure according to Eq. 5 (Washburn, 1921):

$$P = -\frac{2\gamma \cos\theta}{R_p} \qquad \text{(SI1)}$$

where P is the mercury injection pressure (Pa), γ is the surface tension of mercury (0.485 N/m), θ is the contact angle between solid and mercury ($\theta = 130°$) and R_p is the pore access radius for cylindrical pores (m). MIP measurements have been carried out using a Micromeritics instrument apparatus type (AutoPore IV 9500). The instrument is capable of a minimum intruding pressure of 3.4 kPa and a maximum pressure of 227 MPa, so that the pore radius ranges from 2.7 nm to 180 μm.

For pumice particles the measured pore data allow determining the inter-particular and intra-particular porosities of the pumice particles, the apparent specific weight ρ_{as} (defined as the ratio of the mass and the apparent volume of the pumice particles) and the specific weight ρ_s (defined as the ratio of the mass and the volume of the solid phase of the pumice particles).

SI1.2 SEM

During SEM (Hitachi, type: s3400N) observations, secondary electron mode was used. Pumice particles were coated with carbon. The observations enable a characterization of the morphology of both materials and of the inner pore structure of pumice.

SI2 Results and Discussion

SI2.1 SEM Observations of Fe^0 and pumice particles

SEM images detailing the microstructures of, respectively, Fe^0 and pumice particles are shown in Fig. SI1. These observations show that the Fe^0 and pumice particles are irregular. It can be observed that the pumice particles (grains) are porous with oval shaped and fibrous cavities (or pores). The diameter of these cavities at the surface is lower than about 40 μm (radius 20 μm).

SI2.2 MIP measurements of pumice particle*s*

As shown in Fig. SI2, where for graphical convenience the pore size distribution is as usual expressed as $\frac{dV_i}{d(\log r)}(\log r)$ where V_i is the volume intruded by mercury and R is the pore equivalent radius, pumice exhibits a well defined peak around 70 μm and pores with equivalent radius inferior to 20 μm. According to the SEM observations, these results show that the pores with radius inferior to 20 μm can be attributed to the inner porosity of the pumice particles, so that the pores with equivalent radius superior to 20 μm can be attributed to the inter-particular porosity. The total porosity of the pumice medium Φ_0 (%)in the conditions used in MIP tests, is defined as:

$$\Phi_0 = V_{\text{mercury intruded}} * M / V \qquad \text{(SI3)}$$

Where $V_{\text{mercury intruded}}$ is the total intrusion volume (mL/g), M the mass of pumice (g) and V the volume of the pumice medium (mL).

The volume of the inter-particular volume Φ_{inter} (%) is given by:

$$\Phi_{inter} = V_{R>20\mu m} / V \qquad \text{(SI4)}$$

Where $V_{R>20\mu m}$ (mL) is the volume of intruded mercury in pores with radius superior to 20 µm.

It can be noticed that the compactness C_{pumice} (-) of the pumice particles, defined as the ratio of the apparent volume of the particles to the total packing volume (V = volume of the medium), is given by:

$$C_{pumice} = 1 - \Phi_{inter}. \qquad \text{(SI5)}$$

Furthermore, the volume of the intra-particular φ_{pp} is given by:

$$\varphi_{pp=} = V_{R<40\mu m} / V / C_{pumice} \qquad \text{(SI6)}$$

Where $V_{R<20\mu m}$ (mL) is the volume of intruded mercury in pores with radius inferior to 20 µm.

The results are given in Tab. SI2. The total porosity of the pumice medium has been estimated to be 73.3 % and the inner porosity of the pumice to be 41.0 %.

SI2.3 Grain size distributions of Fe^0 and pumice particles

The grain size distributions of Fe^0 and pumice particles are shown in Fig. SI3.

The main geotechnical parameters derived by the grain size distributions are the coefficient of uniformity $U = d_{60}/d_{10}$ (i.e. ratio between the diameters corresponding to 60 and 10 % finer in the grain size distribution) and the mean grain size d_{50}(i.e. the diameters corresponding to 50 % finer in the grain size distribution).

The mean grain size (d_{50}) is about 0.5 mm and 0.3 mm for ZVI and Pumice respectively, their coefficients of uniformity (U) are, respectively 2 and 1.4 and therefore both materials are characterised by a uniform grain size distribution.

SI2.4 Porosity of the columns

Under the hypothesis that the relative density (packing) of granular mixtures are the same in the columns and in the MIP tests, the estimated porosity of the reactive zone can be given for systems A through E (Tab. 1, main text) according to:

$$\Phi_0 = \Phi_{inter} + \varphi_{pp}.f_{pp} \quad \text{(SI7)}$$

where f_{pp} (-) is the pumice particle volume fraction determined by $f_{pp} = V_{pp}/V$ with V_{pp} the volume of the pumice particles and the V the volume of the reactive zone.

References

Washburn E.W., 1921. The dynamics of capillary flow, Phys. Rev. 17, 273–283.

Table SI1: Composition and experimental duration of the studied columns. *-marked systems were stopped because of excessive permeability loss.

System	**Composition** (Fe^0:pumice)	**Duration** (day)
A	0:100	45
B	10:90	90
C	25:75	36*
D	50:50	28*
E	75:25	22*
F	100:0	17*

Table SI2: Characteristics of Fe^0 and pumice particles tested by MIP.

	Fe^0	Pumice
Specific weight ρ_s (g/cm^3)	7.78	1.92
Apparent specific weight ρ_{as} (g/cm^3)	7.78	1.14
Compactness C (-)	0.51	0.45
Inter particular porosity Φ_{inter} (%)	49.6	54.8
Intra particular porosity φ_{pp} (%)	-	41.0
Porosity Φ_0 (%)	49.6	73.3

Figure SI1: SEM images of the Fe^0 particles (A) and of the pumice particles (B).

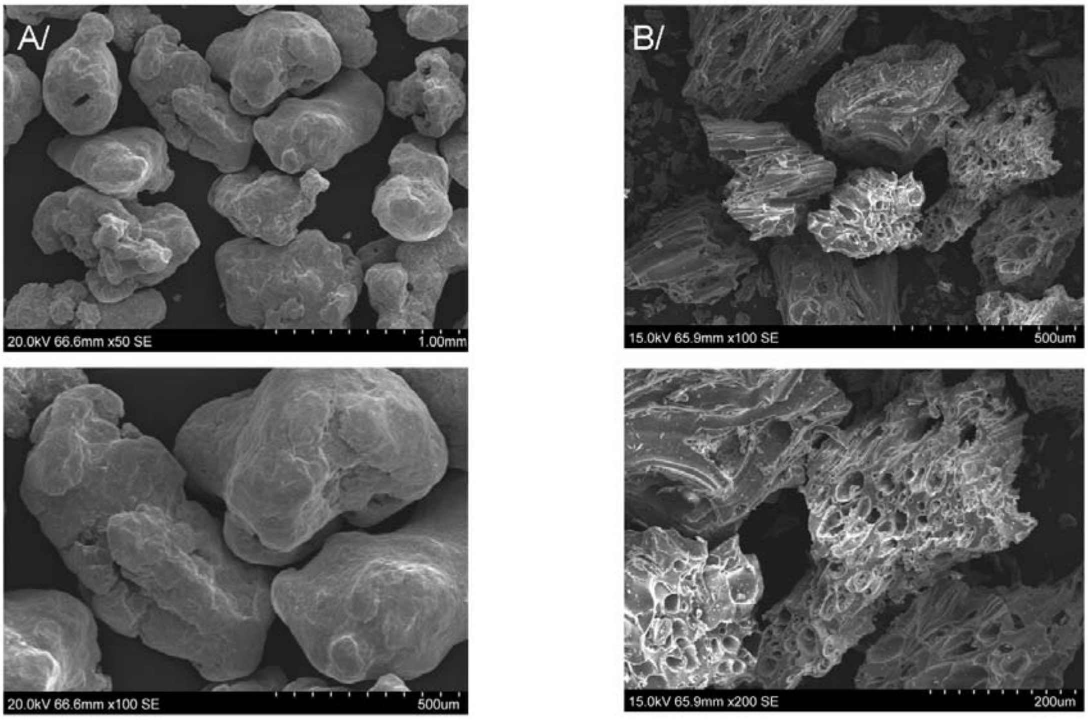

Figure SI2: Cumulative volume intruded (mL/g) and pore size distribution of the pumice particles. Two types of porosity are observed: inter particular porosity Φ_{inter} (R > 20μm) and intra particular porosity φ_{pp} (R < 20μm).

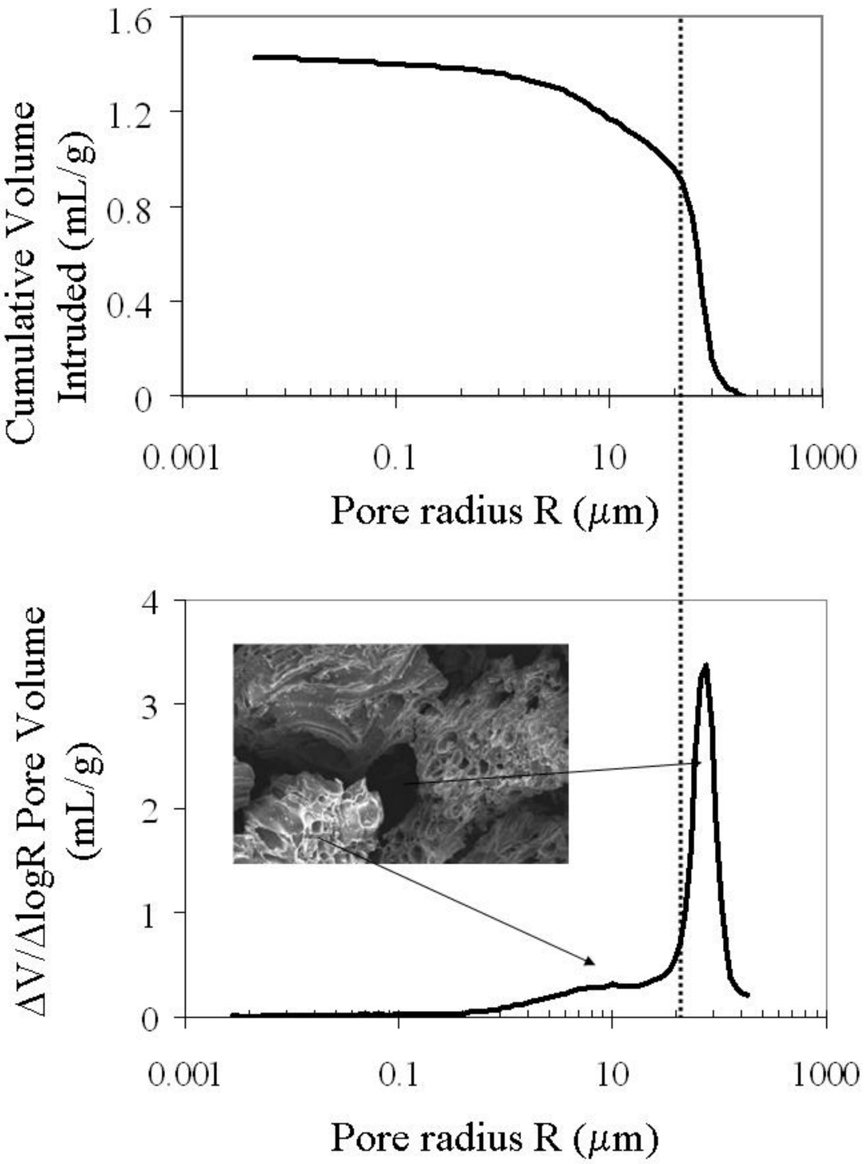

Figure SI3: Grain size distributions of used materials: Fe^0 (a) and pumice (b).