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

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1 **Keywords:** Column study, Hydraulic conductivity, Reactive walls, Pumice, Zerovalent iron.

2

3 **1 Introduction**

4 Filter materials for water treatment are ideally used in small quantities. The high required affinity of
5 used aggregates for efficient water treatment is not always readily available in natural materials. On
6 the other hand, efficient filters should be designed to make the best use of these latter with the
7 minimum of processing (Smith et al., 2001). Alternatively, readily available natural materials (e.g.
8 anthracite, gravel, pumice, sand) may be mixed to low cost synthetic aggregates/materials (activated
9 carbon, blast furnace slag, metallic iron) for improving the performance of the resulting water
10 treatment systems. The key properties determining the permeability, the stability and the longevity
11 (sustainability) of granular filters include porosity/texture of used particles, particle size, particle
12 shape and particle size distribution or material sorting (Haarhoff and Vessal, 2010; Kubare and
13 Haarhoff, 2010; Miyajima, 2012; Btatkeu et al., 2013; Caré et al., 2013). Two key interrelated
14 properties required for a sustainable filter include: (i) high permeability combined with resistance to
15 internal erosion of fines and (ii) low susceptibility to chemical attack (prerequisite 1).

16 Granular metallic iron (Fe^0), as currently used in water treatment, is a reactive material and its
17 oxidative dissolution by water is a volumetric expansive process (Pilling and Bedworth, 1923; Caré
18 et al., 2008). This means that Fe^0 is highly susceptible to chemical attack and the products of this
19 chemical reaction are fines/precipitates (iron hydroxides and oxides). In other words, ‘prerequisite
20 1’ is not satisfied as the sustainability of Fe^0 filters is impaired by the same properties making Fe^0
21 an attractive material: the chemical reactivity of iron (Liu et al. 2013). However, without
22 considering these key properties, Fe^0 permeable reactive barriers (Fe^0 PRBs) have become an
23 established technology for the treatment of contaminated groundwater (O'Hannesin and Gillham,
24 1998; Li et al., 2006; Li and Benson, 2010; Comba et al., 2011; Gheju, 2011; Ruhl et al., 2012).
25 Currently, about 180 Fe^0 PRBs have been installed worldwide (ITRC, 2011).

1 The fundamental mechanisms of contaminant removal in Fe⁰ filtration systems are adsorption, co-
2 precipitation and adsorptive size-exclusion (Noubactep, 2008; 2010; 2011). Contaminant removal
3 also implies iron corrosion (Lavine et al., 2001; You et al., 2005; Jiao et al., 2009; Ghauch et al.,
4 2011; Gheju and Balcu 2011). Therefore, due to the volumetric expansive nature of this process
5 ('prerequisite 1'), the remediation of contaminated groundwater necessarily results in the gradual
6 clogging of the Fe⁰ PRB, and thus in the deterioration of the permeable barrier hydraulic
7 conductivity (permeability loss) over time (Zhang and Gillham, 2005; Courcelles et al., 2011;
8 Knowles et al., 2011; Jeen et al., 2012; Miyajima, 2012; Noubactep, 2013a).

9 The gradual clogging (permeability loss) of Fe⁰ filtration systems has several origins: (i) biological
10 activities like biofilm growth or biocorrosion, (ii) chemical processes like (hydr)oxide or calcite
11 precipitation, (iii) physical processes allowing the retention of fine particles in the PRB pores, and
12 (iv) production and accumulation of gases (mainly H₂). Pores clogging could generate a decrease in
13 treatment performance and the bypass of untreated contaminated groundwater (Courcelles et al.,
14 2011; Knowles et al., 2011; Jeen et al., 2012). Therefore, PRBs clogging issues will require cost-
15 intensive reactive material substitution, if satisfactory operational performance has to be
16 maintained. The present work is focused on the characterization of PRB clogging due to pore filling
17 by in-situ generated iron corrosion products neglecting the other possible phenomena that could
18 contribute to permeability reduction (i.e. gas retention, biocorrosion, biofouling) (Henderson and
19 Demond, 2011; Caré et al., 2012; Noubactep, 2013a).

20 The objective of the present work is to characterize the efficiency of Fe⁰/pumice granular
21 mixtures for contaminant removal in column experiments containing 0 to 100 % Fe⁰ (vol/vol). Fe⁰
22 is admixed to a well-characterized pumice specimen (Moraci and Calabrò, 2010; Calabrò et al.,
23 2011; Bilardi et al., 2013a), in different volumetric ratios. The model oxidic solution (about 8 mg/L
24 O₂) contained about 0.30 M of Cu^{II}, Ni^{II}, and Zn^{II}. The evolution of the systems is characterized by

1 determining the (i) extent of contaminant removal (or retention), and (ii) variation of hydraulic
2 conductivity.

3 **2 Materials and methods**

4 **2.1 Chemicals**

5 Copper(II) nitrate hydrate (purity 99.999), nickel(II) nitrate hexahydrate (purity 99.999) and zinc(II)
6 nitrate hexahydrate (purity 99.000) were obtained from Sigma-Aldrich. The three heavy metals are
7 used for their different affinity to iron oxides (Wang and Qin, 2007; Moreira and Alleoni, 2010;
8 Vodyanitskii, 2010). In addition, a survey of the electrode potential (E^0) of involved couples
9 indicated differential redox behaviours. In fact, Zn^{II} ($E^0 = -0.763$ V) can not be reduced by Fe^0 ($E^0 =$
10 -0.440 V) while Cu ($E^0 = 0.337$ V) is readily reduced. The electrode potential of Ni ($E^0 = -0.250$ V)
11 is relatively close to that of Fe ($\Delta E^0 = 0.19$ V) such that quantitative reduction can not be expected.

12 **2.2 Solid materials**

13 **Pumice:** the used pumice originates from Lipari (Aeolian Islands, Sicily – Italy); its mineralogical
14 composition was determined as follows: SiO_2 : 71.75 %; Al_2O_3 : 12.33 %; K_2O : 4.47 %; Na_2O : 3.59
15 %; Fe_2O_3 : 1.98 %; moreover it contains about 4 % of bound water (structural water) and traces of
16 other compounds (e.g. CaO, SO_3 , MgO, TiO_2 , FeO, MnO, P_2O_5). Although pumice exhibited a non
17 negligible removal capacity for heavy metals (Moraci and Calabrò, 2010; Calabrò et al., 2011), it
18 was used here as an operational inert material with the virtual capacity of storing corrosion products
19 in its pores and retarding clogging (Moraci and Calabrò, 2010; Noubactep and Caré, 2010;
20 Noubactep et al. 2012a; Noubactep et al. 2012b). The material is characterized by uniform grain
21 size distribution. The mean grain size (d_{50}) is about 0.3 mm and the coefficient of uniformity (U) is
22 1.4 (see Supporting Information).

23 **Metallic iron:** the used Fe^0 is of the type FERBLAST RI 850/3.5, distributed by Pometon S.p.A.,
24 Mestre - Italy. The material contents mainly iron (> 99.74 %). Identified impurities included mainly
25 Mn (0.26 %), O, S and C. The material is characterized by uniform grain size distribution. The

1 mean grain size (d_{50}) is about 0.5 mm and the coefficient of uniformity (U) is 2 (see Supporting
2 Information).

3 The microstructure of used Fe^0 and pumice was characterized using Mercury Intrusion Porosimetry
4 (MIP) measurements and by Scanning Electron Microscopy (SEM) observations (see Supporting
5 Information).

6 **2.3 Columns experiments**

7 The used solutions were obtained by dissolving copper nitrate, nickel nitrate and zinc nitrate in
8 distilled water. The molar concentration of the resulting solution was as follows: 0.27 M Cu, 0.29
9 M Ni and 0.37 M Zn. The corresponding mass concentrations are 17 mg/L Cu, 17 mg/L Ni, and 23
10 mg/L Zn.

11 No attempt was made to control the mass of dissolved oxygen (DO) present during the column
12 experiments. The main source of molecular oxygen is the air in the headspace of the PE bottles. It
13 can be assumed that the model solutions contained up to 8 mg/L DO. The role of dissolved oxygen
14 in accelerating the kinetics of aqueous iron corrosion is well-documented (e.g. Cohen, 1959;
15 Stratmann and Müller, 1994). Using an oxic solution is a tool to enable the characterization of
16 clogging under relevant conditions at reasonable experimental durations.

17 Simplified model solutions (no carbonates, bicarbonates and relevant cations) were used as this
18 work is a seminal one focused on the impact of molecular O_2 on the clogging process of Fe^0 PRBs
19 as influenced by pumice addition in various proportions. Testing more complex solutions relevant
20 to simulate natural situation could be built on the results from these simplified systems.

21 Laboratory scale polymethyl methacrylate (Plexiglas) columns were operated in up-flow mode. The
22 influent solution was pumped upwards from a single PE bottle using a precision peristaltic pump
23 (Ismatec, ISM930). In all the tests the flow rate was maintained constant at a value of 0.5 mL/min.
24 Tygon tubes were used to connect inlet reservoir, pump, columns and outlet. Six plexiglas columns
25 (50 cm long, 5.0 cm inner diameter) were used in the experiments (Fig. 1).

1 The ratio column diameter (D) to average material particle size (d) ensured the prevention of
2 channelling and wall effects. In fact, used D/d ratio (actually 100 to 165) is by far larger than the
3 threshold value of 50 (Badruzzaman and Westerhoff, 2005).

4 Six different systems were investigated (Systems A through F) (Tab. 1). System A was the
5 operational reference system containing only pumice (0 % Fe⁰) and system F was a pure iron
6 column (100 % Fe⁰). The volumetric proportion of Fe⁰ in the 4 other systems was 10, 25, 50 and
7 75 % following a procedure recently presented (Noubactep and Caré, 2011; Noubactep et al.
8 2012b). In systems B to F, the mass of iron was fixed to 200 g. This mass represented either 100 %
9 of the reactive zone (rz) or the relevant volumetric proportion of rz (Fig. 1, Tab. 1). Tab. 1
10 summarizes the theoretical (rz_{theor}, i.e. the height of the column occupied by the reactive medium if
11 Fe⁰ and pumice were used in series and not as a mixture) and measured (rz_{eff} i.e. the height of the
12 reactive zone in the column effectively measured) reactive zone for each individual systems.

13 The hydraulic conductivity was determined during the column tests, by either constant-head ($k >$
14 10^{-6} m/s) or variable-head ($k < 10^{-6}$ m/s) permeability methods (Head and Keeton, 2008), at given
15 times to assess the permeability of the systems. During hydraulic conductivity determinations, the
16 test was interrupted and a tank or a burette, filled with the same contaminated solution used during
17 the test, was connected to the column in order to carry out the appropriate procedure. At the end of
18 the permeability test the flow in the column was re-established with the operation mode illustrated
19 before. The duration of these procedures was very limited therefore the disturbance to the test was
20 fully acceptable. The column tests were performed at room temperature (21 ± 4 °C). Solution
21 specimens for analysis were collected from the columns outlet at periodic intervals and the
22 experiments were prolonged until contaminant breakthrough (system A) or a significant loss of the
23 hydraulic conductivity (systems C to F) was observed; only system B was voluntarily stopped after
24 90 days. Tab. SI summarizes the experimental research program (Supporting Information).

1 The aqueous concentrations of Cu, Ni and Zn were determined by Atomic Absorption
2 Spectrophotometry (AAS - Shimadzu AA – 6701F) using conventional Standard Methods (APHA
3 2005).

4 **2.4 Expression of the experimental results**

5 In order to characterize the magnitude of tested systems for contaminant removal, the removal
6 efficiency (E) and the specific removal (E_s) were calculated using Eq. 1 and Eq. 2 (Moraci and
7 Calabrò, 2010; Btatkeu et al., 2013).

$$8 \quad E = m_{\text{rem}}/m_{\text{in}}*100 \quad (1)$$

$$9 \quad E_s = m_{\text{rem}}/m_{\text{Fe}}*100 \quad (2)$$

10 where m_{in} is the mass of contaminant flowed into the column, m_{rem} is the mass of removed
11 contaminant, and m_{Fe} the mass of Fe^0 present in the column.

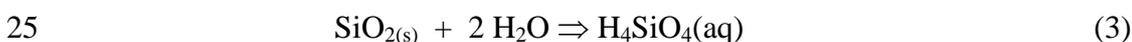
12 **3 Results and discussion**

13 **3.1 Contaminant removal**

14 The presentation is based on the concept that tested contaminants are removed in Fe^0 columns (at
15 $\text{pH} > 5$) by adsorption, co-precipitation and adsorptive size-exclusion (Noubactep, 2008; 2010;
16 2011). Given the importance of the pH value for this concept, the results of pH monitoring are
17 presented first.

18 **3.1.1 pH value**

19 Figure 2 summarizes the results of the evolution of the pH value in all investigated systems. It is
20 shown that in the reference system (100 % pumice), the initial pH (6.3) decreased to 5.8 and
21 remained constant for the entire column tests duration. The slight pH decrease could be attributed to
22 acidic sites at the pumice surface (Eq. 3). In all other systems, the pH value first increased to value
23 > 9.0 and progressively decreased to values close to 6.0 – 7.0. The observed pH increase is certainly
24 due to iron corrosion which consumes H^+ (Eq. 4).





The subsequent progressive decrease of the pH value is consistent with lowered kinetics of iron corrosion due to the formation of an oxide scale at the Fe^0 surface (Cohen, 1959; Evans, 1969; Aleksanyan et al., 2007; Nestic, 2007). The most important issue from Fig. 2 is that for all Fe^0 -containing systems, the effluent pH value is higher than 5.0. This suggests that contaminant removal by adsorption, co-precipitation and adsorptive size-exclusion (Noubactep, 2011) could be quantitative within these columns.

3.1.2 Iron release

Figure 3 summarizes the results of the evolution of dissolved iron concentration in the effluent. It is evident from Fig. 3a, that the highest iron release was observed in the system with the lowest Fe^0 ratio (B, 10 % Fe^0). The lowest Fe^0 ratio corresponds to the highest amount of pumice (243 g - Tab. 1), acidifying the system after Eq. 3. The transport of iron corrosion products is certainly favoured at low pH values and may be favoured by larger porosity (Nimmo, 2004; Woudberg and Du Plessis, 2008; Glover and Walker, 2009). In other words, in all other systems, even more iron could be dissolved but it is retained within the system by (i) adsorption onto available iron oxides or onto pumice, or (ii) precipitation as iron (hydr)oxides (Miyajima, 2012; Miyajima and Noubactep, 2013). It is very important to notice that the extent of iron release depends primarily on the intrinsic reactivity of used Fe^0 . Although data on iron release from column experiments are available in the literature (e.g. Westerhoff and James, 2003) it is impossible to make a quantitative comparison. In fact, a parameter (or an index) to characterize the intrinsic reactivity of Fe^0 is still lacking (Noubactep et al., 2009; Noubactep, 2012).

Fig. 3b shows that, apart from system B (10:90), in all other systems less than 1 mg/L iron was released in the effluent solution. It is interesting to note that, for the remaining systems, the two columns with the largest proportion of Fe^0 (50 and 100 %) exhibited the highest iron release.

3.1.3 Metal concentration

1 Table 2 summarizes the results of the removal of Cu^{II} , Ni^{II} and Zn^{II} in terms of removal efficiency
2 E , and of specific removal efficiency E_s for all the 5 systems containing Fe^0 . While, reading this
3 table, it should be kept in mind that the experimental duration was variable as most of the
4 experiments were stopped because of significant permeability loss (see Tab. 1). Nevertheless, it can
5 be seen that 367 to 2881 mg of individual contaminants flowed into the columns and were retained
6 with an efficiency $E > 90.0\%$. Moreover, the specific efficiency (E_s) varied from 1.7 to 13.6 mg
7 contaminant per g of Fe^0 .

8 An important feature from Tab. 2 regards the suitability of E_s values (Eq. 2) for the characterization
9 of processes occurring in $\text{Fe}^0/\text{H}_2\text{O}$ systems (Btatkeu et al., 2013; Miyajima and Noubactep, 2013).
10 Normalizing the extent of contaminant removal (m_{rev} - Eq. 2) by the available amount of Fe^0 (here
11 200 g) is only valid, if there is a clear linear relationship between iron corrosion and contaminant
12 removal. Such a relationship has not been demonstrated in the Fe^0 remediation literature despite
13 repeated reports on reaction orders. Moreover, an adequate argumentation for adsorptive processes
14 has been simply transposed to systems, where adsorption is only one (and not necessarily the
15 dominant) removal path.

16 In pure adsorption systems (e.g. activated carbon, iron oxide, clay), the whole mass of adsorbing
17 material is present at the start of the removal process (t_0 or $t = 0$), its adsorption capacity can be
18 exhausted with the time. In a Fe^0 system on the contrary, adsorbing species are generated in situ
19 after the start of the experiment ($t > t_0$). Accordingly the extent of contaminant removal depends on
20 the kinetics of iron corrosion and the affinity of contaminants for corrosion products as far as pure
21 adsorption is concerned. Additionally, contaminants are also removed by co-precipitation and size-
22 exclusion. In other words, normalizing the extent of contaminant removal by the Fe^0 amount
23 requires at least the knowledge of the intrinsic reactivity of used Fe^0 and the impact of operational
24 parameters thereon. The most relevant operational parameter in the present work is the volumetric
25 Fe^0 :pumice ratio.

1 Figure 4 shows that the influence of the volumetric Fe⁰:pumice ratio on the removal efficiency of
2 Cu²⁺, Ni²⁺, Zn²⁺ is very similar to the influence of the adsorbent amount on adsorption of Mn²⁺ by
3 clay minerals (Goldani et al., 2013). These authors reported on a decreasing trend of the adsorption
4 capacity (q_e value / mg g⁻¹) for Mn²⁺ with increasing adsorbent amount (50 to 500 mg). This
5 observation was mainly rationalized by the fact that a large adsorbent amount reduces the
6 unsaturation of the adsorption sites. Correspondingly, the number of such sites per unit mass comes
7 down resulting in comparatively less adsorption at higher adsorbent amount. In the present work,
8 the Fe⁰ amount is constant (200 g), only its volumetric ratio in the mixture to pumice varies.
9 Moreover, a higher Fe⁰ ratio is coupled to a shorter reactive zone (e.g. 2.6 cm for 100 % Fe⁰ and
10 26.2 cm for 10 % Fe⁰). Thus, a higher Fe⁰ volumetric ratio may create particle aggregation
11 (cementation), decreasing the total number of adsorption sites, decreasing the porosity of the
12 reactive zone, and increasing the diffusion path to adsorption sites. Altogether, these factors
13 contribute to the decrease of the amount of contaminant adsorbed, assuming that the same amount
14 of adsorbent is generated in all systems. As summarized in Tab. 2, except system B (10 % Fe⁰),
15 metal removal was quantitative in all other systems.

16 Contaminant breakthrough was observed in other systems only short before the experiment was
17 stopped and was mainly attributed to transport through preferential flow paths (Miyajima and
18 Noubactep, 2013a and ref. cited therein). Even under such conditions the concentration of Cu and
19 Zn remained below 1 mg/L whereas the concentration of Ni exceeded 4 mg/L for system F (100 %
20 Fe⁰) and system D (50 % Fe⁰) but not for system E (75 % Fe⁰). This anomaly in the sequence D/E/F
21 confirms that the process responsible for metal breakthrough near system clogging is probably a
22 meta-stable one (preferential flow).

23 **3.2.4 Mechanism of contaminant removal**

24 The experimental data previously described has shown that contaminants are quantitatively
25 removed in columns with volumetric Fe⁰ ratio higher than 10 % until the system is almost clogged.

1 In the system with 10 % Fe^0 , quantitative iron release is observed (Fig. 5). Quantitative iron release
2 coincided with minimal contaminant removal (or contaminant breakthrough) as discussed above.
3 This section further discusses the behaviour of system B (Fig. 5a).
4 The ionic radii of the investigated cations increase in the order $\text{Ni}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+}$. The metallic
5 ions are removed by four different mechanisms (Herbert, 1996; Wang and Qin, 2007; Vodyanitskii,
6 2010): (i) co-precipitation with iron hydroxides, (ii) adsorption onto the (hydr)oxide surfaces, (iii)
7 isomorphic substitution for Fe in the iron oxide structure, or adsorptive size-exclusion. In multi-
8 element systems, the most common reported affinity sequence for iron oxides and soils is $\text{Cu} > \text{Zn}$
9 $> \text{Ni}$ (Moreira and Alleoni, 2010). This trend is confirmed by Fig. 5b.
10 Fig. 5a illustrates the fact that contaminants breakthrough occurs when increased iron release is
11 observed. For example, no significant breakthrough was observed in system B until $t=30$ days
12 although up to 8 mg/L Fe was released into the outlet solution. For $t > 30$ days Zn and Ni
13 breakthrough occurs and the breakthrough magnitude is in agreement with the affinity sequence for
14 iron oxides ($\text{Cu} > \text{Zn} > \text{Ni}$). Accordingly, breakthrough is first observed for less bounded Ni
15 followed by Zn. As concerning Cu no breakthrough was observed through the end of the
16 experiment. At first glance, this observation could be attributed to Cu^{II} cementation at the surface of
17 Fe^0 in the column. In fact, Cu reduction to elemental Cu (Cu^0), as mentioned above, is very
18 favourable and is used in many hydrometallurgical processes (Gros et al., 2011a; 2011b). However,
19 because Cu removal in this study occurred at $\text{pH} > 5$ (section 3.2.1), the Fe^0 surface was necessarily
20 covered by iron (hydr)oxides (Aleksanyan et al., 2007; Nestic, 2007) and was not directly accessible
21 to Cu^{II} (Ni^{II} and Zn^{II}). More detailed discussion on the removal of metallic ions by Fe^0 in multi-
22 elements system is given for instance by Cantrell et al.(1995), Qiu et al. (2000), Bartzas et al.
23 (2006), Komnitsas et al. (2006; 2007) and Scott et al. (2011).
24 It should be recalled that in a $\text{Fe}^0/\text{H}_2\text{O}$ system, so-called structural Fe^{II} (adsorbed Fe^{II}) is available
25 and is, in some circumstances, a more efficient reducing agent than Fe^0 (White & Peterson, 1996).

1 Accordingly, Cu^{II} might be quantitatively removed within the oxide scale on iron. Even if Cu^{II} is
2 reduced at the surface of Fe^0 , it will be enmeshed within the matrix of iron oxides as corrosion
3 proceeds. In conclusion, aqueous Cu^{II} is also permanently removed by the process of iron corrosion
4 (enmeshment or co-precipitation). It should be also remembered that the stronger affinity of Cu^{II} for
5 iron oxides (adsorption) is sufficient to rationalize the absence of Cu breakthrough for 90 days (Fig.
6 5b).

7 **3.3 Hydraulic conductivity**

8 The results presented in Fig. 6 clearly demonstrate that granular Fe^0 /pumice mixtures are more
9 sustainable in terms of long term permeability than the pure Fe^0 PRB for the decontamination of
10 used model solution. Fig. 6a shows that the pure pumice systems exhibited an initial porosity of
11 72.6 % while the porosity of the pure Fe^0 system was 49.6 % (Tab. 1). Fig. 6b shows that the 100 %
12 Fe^0 system was clogged after 17 days; the 25 % Fe^0 system after 37 days and the 10 % Fe^0 system
13 was still highly permeable after 90 days. Even though the 10 % Fe^0 system was not efficient at
14 removing Ni and Zn, such systems could be used to generate dissolved Fe for other purposes
15 including: (i) in-situ generation of Fe for contaminant removal (Khan et al., 2000; Pokhrel and
16 Viraraghavan, 2009) and (ii) oxygen scavenger to sink the O_2 concentrations in above-ground
17 devices (Mackenzie et al., 1999; Noubactep and Schöner, 2010; Noubactep et al., 2010).

18 A fundamental feature from Fig. 6a is that it combines contaminant removal (here E_s value for Zn)
19 and initial porosity. The initial porosity decreases linearly with increasing Fe^0 ratio. This behaviour
20 is rationalized by the fact that a compact material (Fe^0) is admixed to a porous one (pumice). The
21 initial pore volume will be progressively filled by in situ generated iron corrosion products (Caré et
22 al., 2013) which adsorb and co-precipitate metal ions. Reduced pore volume increases size-
23 exclusion efficiency while decreasing permeability. The challenge of designing hybrid Fe^0 /material
24 systems is to find out the optimal system concealing sustained permeability and efficient

1 contaminant removal. Fig. 6a confirms/shows unambiguously that such a system should contain as
 2 less Fe⁰ (volumetric proportion) as possible (Caré et al., 2013; Miyajima and Noubactep, 2013).
 3 Considering the factor of 65 times to account for the differential kinetics of Fe⁰ oxidation under
 4 oxic (8 mg/L O₂) and anoxic (0 mg/L O₂) conditions (Cohen, 1959), it can be argued that the
 5 shortest experimental duration (17 days) reported here could corresponds to about 1105 days under
 6 anoxic conditions. These are more than 3 years necessary to observe clogging under the
 7 experimental conditions of this work after 17 days. This result justifies the use of oxic conditions to
 8 investigate target processes under laboratory conditions. By performing parallel experiments with
 9 various amounts of molecular O₂ (Vidic and Suidan, 1991) a better characterization of the impact of
 10 the availability of molecular O₂ is possible. This effort is even urgently needed as Fe⁰ beds have
 11 been proposed for an array of applications varying from pure anoxic (groundwater remediation) to
 12 oxic (household filter) systems.

13 Fig. 7 depicts the evolution of the experimental duration and the residual porosity (modelled, see
 14 below) as a function of the initial porosity of the columns containing Fe⁰. The lowest porosity (49.6
 15 %) corresponds to system F (100 % Fe⁰) and the largest (70.5 %) to system B (10 % Fe⁰). It is seen
 16 that the experimental duration (system sustainability) increases almost linearly with decreasing Fe⁰
 17 proportion from 100 to 25 %. From 25 to 10 % Fe⁰ an abrupt increase of the experimental duration
 18 is observed. These results are qualitatively confirmed by the evolution of the residual porosity for
 19 $\eta = 6.4$ (Fig. 7a) where η is the coefficient of volumetric expansion of rust specimens (Caré et al.,
 20 2008).

21 The residual porosity ($\Phi(t)/\Phi_0$) is defined as the ratio of the porosity at time t $\Phi(t)$ to the initial
 22 porosity Φ_0 induced by the formation of rust leading to porosity loss according to:

$$23 \quad \frac{\Phi(t)}{\Phi_0} = 1 - \frac{\Delta V}{\Phi_0 \cdot V} \quad (5)$$

24 Where $\Delta V = (\eta - 1) \cdot V$ is the effective volumetric expansion of the initial volume V of Fe⁰.

1 The residual porosity which, acting as an indicator of the hydraulic conductivity, is given for all
2 systems in Fig. 7. The observed time-dependant decrease of the hydraulic conductivity is attributed
3 to two different factors: (i) the decrease of the effective pore-size as concentric layers of iron oxides
4 are formed on Fe^0 , and (ii) the filling of pores by precipitated Fe species that escaped out of the
5 oxide scale. Permeability loss due to in-situ generated particles is retarded when larger particle sizes
6 are used. Accordingly, as the grain-size increases, the loss of hydraulic conductivity should follow
7 the inverse trend. In other words, the kinetics of the occupation of the voids depends on the grain-
8 size of used particles (effective pore-size).

9 Theoretically, for spherical grains of uniform size (monosized), the grain diameter will not impact
10 initial porosity but only the void diameter. However, the total porosity generally increases with
11 increasing sorting (grain size distribution), decreases with increasing sphericity and roundness of
12 particles, decreases with the increasing of relative density (closer packing) (Gibb et al., 1984). All
13 these aspects have to be considered to discuss literature results as well.

14 It appears from Fig. 7a that the residual porosity tends to zero ($\Phi(t)/\Phi_0 = 0$ or permeability loss) for
15 clogged systems ($\% \text{Fe}^0 \geq 25$ – clogging precedes Fe^0 depletion). For $\text{Fe}^0 < 25\%$, $\Phi(t)/\Phi_0 \neq 0$ at Fe^0
16 depletion in accordance with the evolution of the hydraulic conductivity and the test duration. At
17 first glance, this observation could be misinterpreted as the confirmation of the proposed model. But
18 under the experimental conditions, Fe^0 was not completely depleted. Accordingly, this experimental
19 evidence rather suggests that the entrance zone of the column could have been rapidly clogged due
20 to elevated O_2 levels (Mackenzie et al., 1999). The presence of O_2 leads to iron (hydr)oxides with
21 higher expansion coefficient (η) implying a more rapid decrease of the residual porosity (Fig. 7b).

22 Fig. 7b depicts the modelled variation of the residual porosity for 3 different values of η (2.08, 3.03
23 and 6.4). It is seen that under ideal conditions (uniform corrosion), the sustainability of a Fe^0 filter
24 depends on the availability of O_2 . Accordingly the most sustainable systems is the one operating
25 under conditions where Fe_3O_4 ($\eta = 2.08$) is the major iron corrosion product (anoxic conditions).

1 These conditions could be obtained in a second column in series with a first one acting as O₂
2 scavenger.

3 The fact that observed preservation of permeability with time is coupled with a decrease of
4 contaminant removal efficiency suggests that for any Fe⁰/additive couple, an increase of filter
5 sustainability with decreasing Fe⁰ proportion down to a threshold value (here 25 % Fe⁰) would be
6 observed.

7 This study has traceably demonstrated that admixing non expansive material with Fe⁰ is a tool to
8 increase permeable reactive barriers sustainability. In other words, an efficient but not sustainable
9 system (100 % Fe⁰) is transformed into an efficient and more sustainable one by admixing a certain
10 volumetric proportion of pumice (here ≥ 75 %). The admixing material (here pumice) should
11 necessarily be less expensive than Fe⁰; thus, cost savings could be regarded as a positive side effect
12 of increased performance.

13 **3.4 Significance for future works**

14 This study is a continuation of a broad-based work aiming at designing non-site-specific Fe⁰
15 filtration systems for water treatment and environmental remediation in its third step.

16 The first step consisted in identifying the common underlying mechanisms for contaminant removal
17 (Noubactep, 2007; 2008; 2010; 2011). Adsorption, co-precipitation and size-exclusion were
18 identified as fundamental paths for water treatment in Fe⁰ packed beds (Noubactep, 2011). This
19 result belittled the importance of chemical reduction in the process of contaminant removal in
20 Fe⁰/H₂O systems and clearly demonstrated that Fe⁰ is not a relevant reducing agent under
21 environmental conditions. The strong fact that Fe⁰ is the parent of all reducing species (e.g. Fe^{II},
22 Fe₃O₄, green rust, H/H₂) should never be misinterpreted as ‘contaminant reduction coupled with
23 electrochemical iron corrosion’ (Noubactep, 2013b).

24 The second step consisted in writing the dimensionless equation of a Fe⁰ packed beds (Noubactep
25 and Caré, 2010; Noubactep et al., 2010; Noubactep and Caré, 2011; Noubactep et al., 2012a;

1 Noubactep et al., 2012b; Caré et al., 2013). It is important to notice, that the equation is based on
2 the volumetric fraction of the packed beds available for ‘storing’ corrosion products (total porosity)
3 (Noubactep and Caré, 2011). This theoretical work has shown that the volumetric ratio of Fe⁰ in a
4 granular mixture should ideally not exceed 60 %. The basics for a systematic research for non-site-
5 specific Fe⁰ filtration systems were established. In particular each Fe⁰ material should be
6 characterized for its intrinsic reactivity; all used materials should be characterized for their form,
7 homogeneity and shape (Crane and Noubactep, 2012; Noubactep et al., 2012a; Caré et al., 2013).
8 The current third step consists in validation the equation of the column (Calabrò et al., 2011;
9 Biliardi et al., 2013a; Biliardi et al., 2013b). In this effort methylene blue (MB) was positively
10 tested as an operational tracer (Miyajima, 2012; Btatkeu et al., 2013; Miyajima and Noubactep,
11 2013). Experiments with MB confirmed theoretical predictions that a pure Fe⁰ bed is not
12 sustainable. Moreover, it could be shown that the optimal volumetric Fe⁰ ratio for sustainable filters
13 is lower 50 %. Given the large density difference between Fe⁰ (7.8 g cm³) and commonly tested
14 additives (e.g. anthracite, gravel, pumice, sand) (< 3.0 g cm³), this results clearly shows that the
15 commonly used 1:1 weight ratio is not optimal as well. Experiments with MB suggested that the
16 optimal Fe⁰ volumetric ratio in a dual Fe⁰/sand system is comprised between 30 and 50 %.

17 The present work has systematically tested the Fe⁰/pumice system for the first time using Cu, Ni
18 and Zn as model contaminants. The results showed that the optimal Fe⁰ ratio for a sustainable filter
19 is 25 %. This result could be regarded as close to 30 % as determined by Miyajima and Noubactep
20 (2013). However, under their experimental conditions, these authors could not experimentally
21 document permeability loss. Accordingly, the present work has provided the most reliable optimal
22 Fe⁰ ratio for sustainable Fe⁰ filtration systems. In other words, this work provide the following rule
23 of thumb for further research (including pilot plant studies): “mix one volume of Fe⁰ and 3 volumes
24 of the additive(s)”. The universal validity of this rule of thumb relies on the evidence that it is based
25 on a dimensionless equation. Thus, if a filter has to contain 1 kg Fe⁰, the volume occupied by this

1 Fe⁰ mass is used as unit and three units volume of the additives of comparable size (and shape) are
2 to be added and homogenized.

3 **4. Concluding remarks**

4 Environmental remediation and water treatment using metallic iron (Fe⁰) in packed beds is an
5 established technology. Despite two decades of active research, this technology is still mostly
6 regarded as an innovative one or has been simply declared a developed one. However, a developed
7 technology is a technology that has established the scientific basis of the involved processes. This
8 work has clearly confirmed theoretical predictions that: (i) pure Fe⁰ beds are not sustainable as a
9 rule, (ii) a bed made up of 25 % Fe⁰ (vol/vol) and 75 % pumice is probably the most efficient
10 system concealing sustained permeability and increased efficiency for contaminant removal, (iii)
11 the specificity of contaminant removal in Fe⁰ filters fundamentally depends on the adsorptive
12 affinity to iron oxides (and not on the redox affinity).

13 The knowledge that the most sustainable filter is made up of more than 70 % (vol/vol) of pumice
14 corroborates the view that sustainable Fe⁰/aggregate filters are Fe⁰-amended aggregate filters (e.g.
15 Fe⁰-amended pumice filter or Fe⁰-amended sand filter). Most common natural aggregates are
16 anthracite, sand, gravel, pumice or crushed rock. However, manufactured aggregates (e.g. blast
17 furnace slag) can also be used as well. Basically there is an infinite number of Fe⁰-amended filters
18 as relevant aggregates may include activated carbon and biomaterial (e.g. wood and coconut shell).
19 A Fe⁰-amended filter can be regarded as a size-exclusion system in which size exclusion is
20 improved by in situ generated iron corrosion products. This is a typical case of self-filtration. The
21 challenge for future works is the proper design of these filters.

22 Further research at laboratory scale is needed to develop methodologies for the Fe⁰ filter design.
23 This effort should be accompanied by numerical modelling. Pilot scale installations are needed
24 afterwards to fine tune determine the practicality of several aspects optimised at lab scale.

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7

8

1 **Table 1:** Main characteristics of the studied columns. “Volume” is the apparent volume of granular
 2 medium. “ $r_{z_{theor}}$ ” is sum of the volumes occupied by the two media separately. “ $r_{z_{eff}}$ ” is the
 3 measured reactive zone. The estimated porosity and the duration of the experiment are also given.

4
5

System	Volume		Mass		Column			
	Fe ⁰ (%)	Pumice (%)	Fe ⁰ (g)	Pumice (g)	$r_{z_{theor}}$ (cm)	$r_{z_{eff}}$ (cm)	Porosity* (%)	Duration (day)
A	0	100	0.0	269.7	29.69	30.0	72.6	45
B	10	90	200.0	242.7	26.72	26.2	70.5	90
C	25	75	200.0	80.9	10.48	9.8	64.9	36**
D	50	50	200.0	27.0	5.24	5.0	59.5	28**
E	75	25	200.0	9.0	3.49	3.4	54.8	22**
F	100	0	200.0	0.0	2.62	2.6	49.6	17**

6 * in this values the internal porosity of the pumice is also included

7 ** stopped because of excessive permeability loss

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- 1 **Table 2:** Magnitude of contaminant removal in investigated systems. m_{in} is the mass of contaminant
 2 flowed into the column, E is the removal efficiency and E_s the specific removal.

System	m_{in}			E			E_s		
	Ni	Cu	Zn	Ni	Cu	Zn	Ni	Cu	Zn
	(mg)			(%)			(mg/g)		
B	2130	2130	2881	90.1	99.8	94.2	9.58	10.6	13.6
C	881.3	881.3	1192	98.7	99.9	99.9	4.53	4.40	5.96
D	612	612	828	93.3	99.9	99.6	2.86	3.06	4.12
E	514.1	514.1	695.5	97.9	99.9	99.9	2.52	2.57	3.47
F	367.2	367.2	496.8	94.7	99.9	99.8	1.74	1.83	2.48

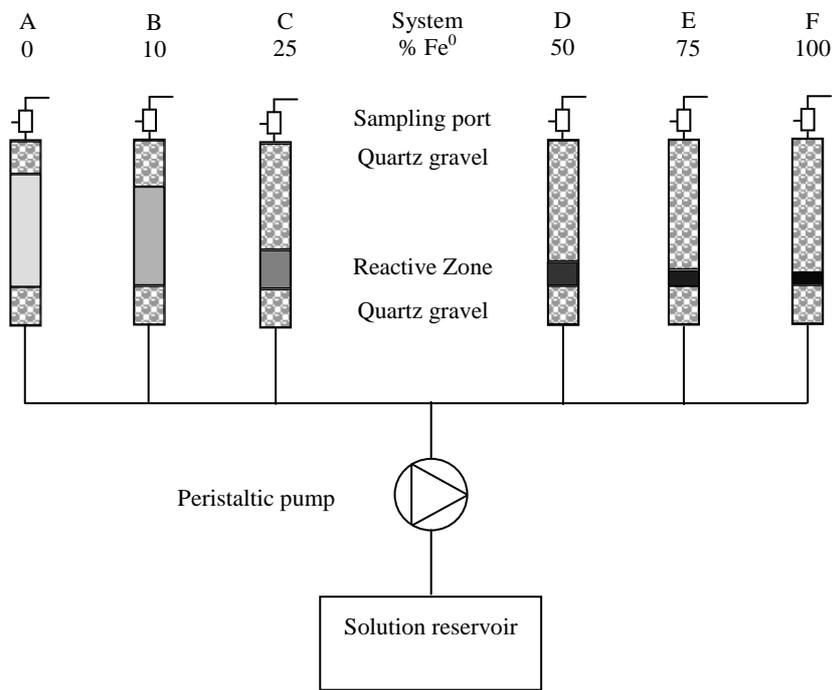
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1 **Figure 1**

2

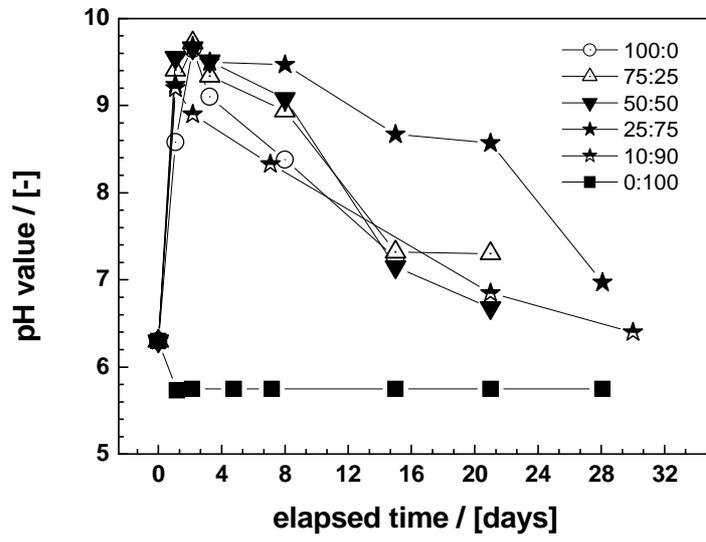


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1 **Figure 2**

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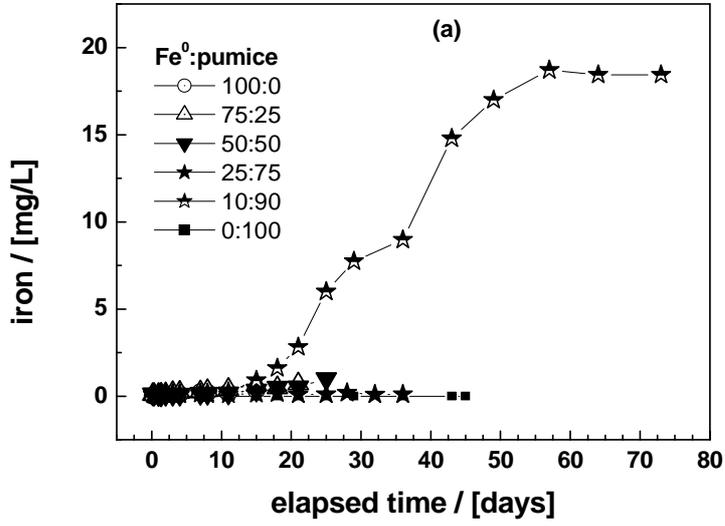


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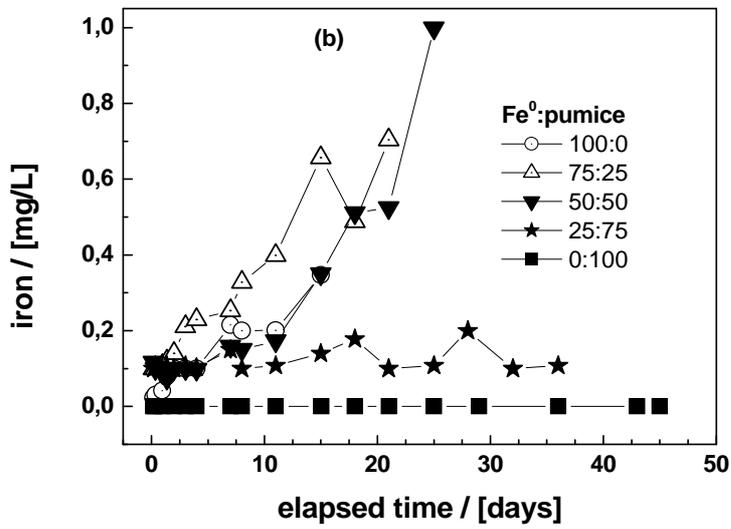
1 **Figure 3**

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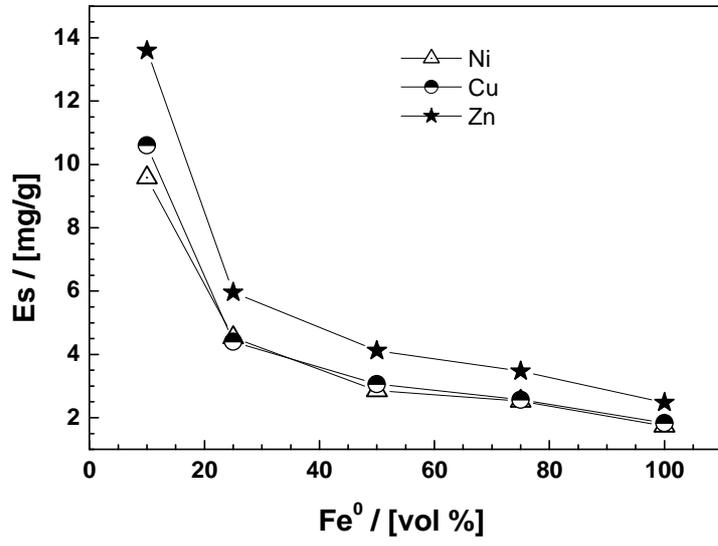
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1 Figure 4

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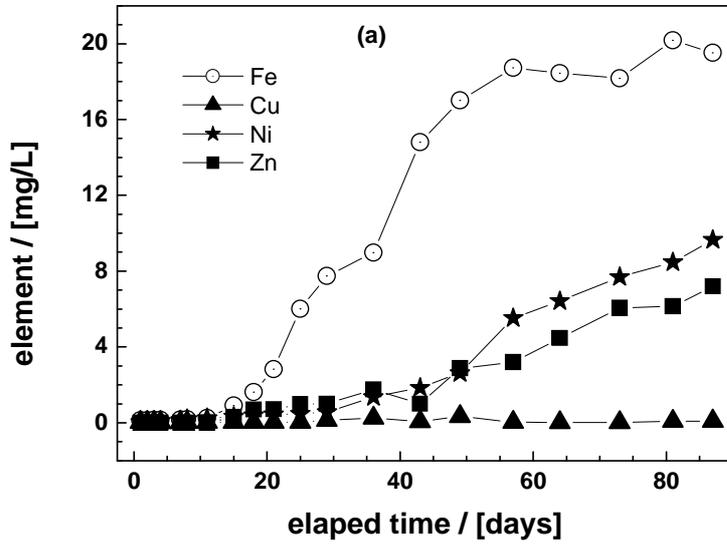
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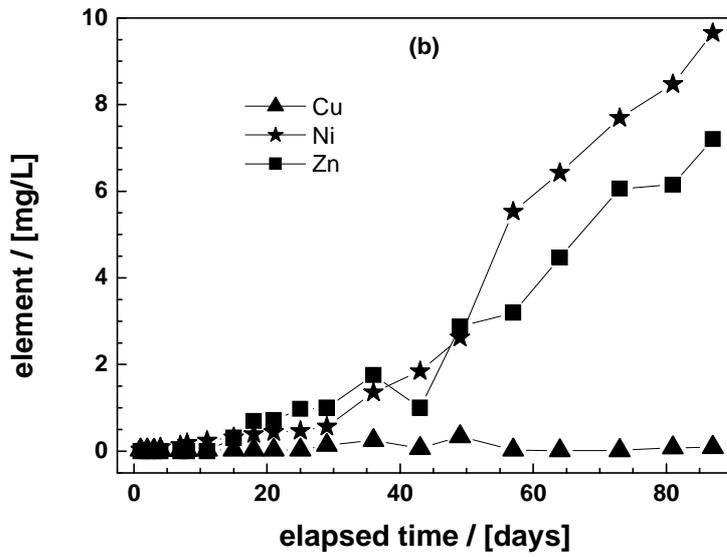
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1 **Figure 5**

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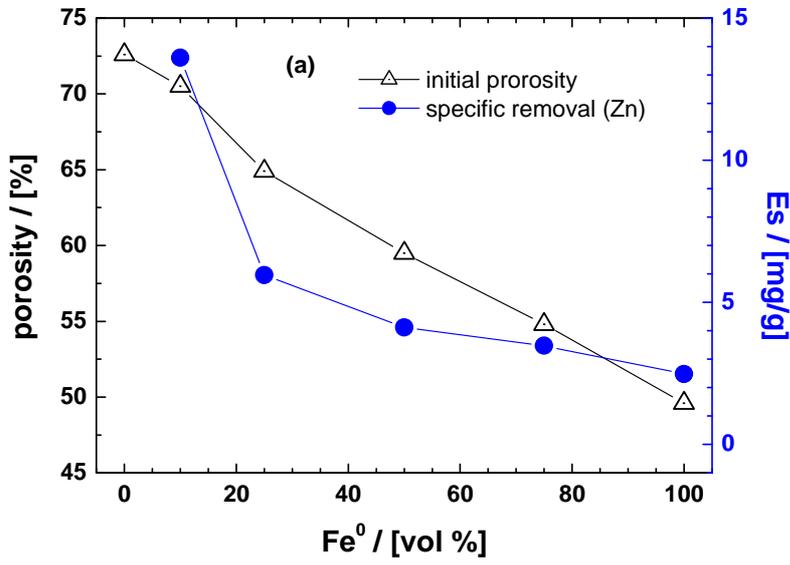
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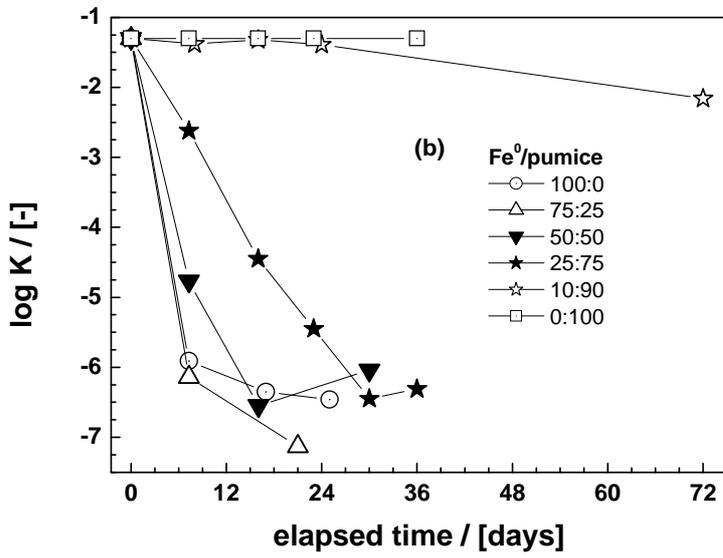
1 **Figure 6**

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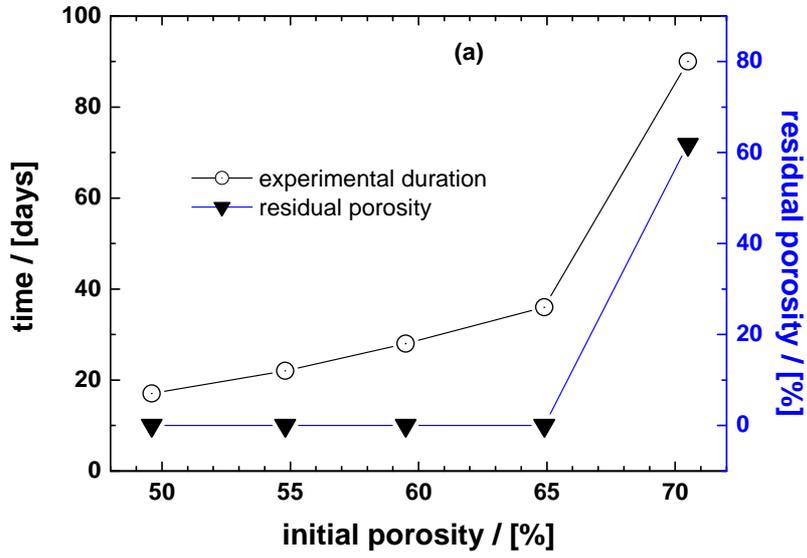
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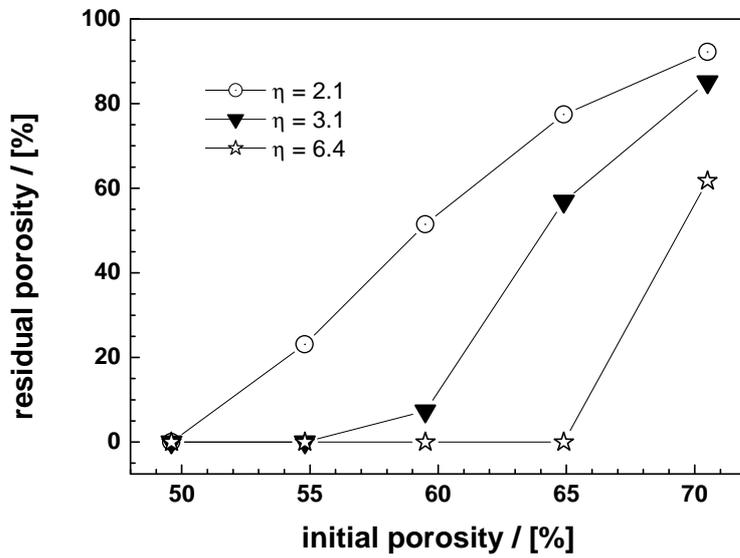
1 **Figure 7**

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1 **Figure captions**

2

3 **Figure 1:** Schematic diagram of the experimental design. Used materials were (i) Fe⁰ (0 or 200 g),
4 (ii) pumice (0 to 270 g), and (iii) quartz gravel (10 cm at the inlet and balance to fill the column at
5 the outlet).

6 **Figure 2:** Time-dependant evolution of the pH value of column effluent. The lines are not fitting
7 functions, they simply connect points to facilitate visualization.

8 **Figure 3:** Time-dependant evolution of the iron concentration of column effluent for a) all
9 experimental duration and b) the first 50 days. The lines are not fitting functions, they simply
10 connect points to facilitate visualization.

11 **Figure 4:** Influence of the Fe:pumice volumetric ratio on the removal efficiency of Cu^{II}, Ni^{II} and Zn^{II} as
12 reflected by the Es (mg/g) values. The lines are not fitting functions, they simply connect points to
13 facilitate visualization.

14 **Figure 5:** Magnitude of Cu, Fe, Ni and Zn release from the column with 10 % Fe⁰. The lines are not fitting
15 functions, they simply connect points to facilitate visualization.

16 **Figure 6:** (a) Comparison of the initial porosity and the specific efficiency (Es value for Zn) as
17 influenced by the Fe:pumice volumetric ratio, (b) Time-dependant evolution of the hydraulic
18 conductivity in all six systems. The lines are not fitting functions, they simply connect points to
19 facilitate visualization.

20 **Figure 7:** (a) Time-dependant evolution of the residual porosity in all six systems and (b) residual
21 porosity $\Phi(t)/\Phi_0$ for three values of the expansion coefficient η . The residual porosity is $\Phi(t)/\Phi_0 = 0$
22 for systems with clogging before Fe⁰ depletion and $\Phi(t)/\Phi_0 \neq 0$ at Fe⁰ depletion. The lines are not
23 fitting functions, they simply connect points to facilitate visualization.

24

Supplementary Information: Material characterization

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

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1 **SI Material characterization**

2 **SII Experimental Section**

3 The microstructure of used Fe⁰ and pumice was characterized using mercury intrusion porosimetry
4 (MIP) measurements and by scanning electron microscopy (SEM) observations.

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

7 **SII.1 MIP**

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

12
$$P = -\frac{2\gamma\cos\theta}{R_p} \quad (\text{SII})$$

13 where P is the mercury injection pressure (Pa), γ is the surface tension of mercury (0.485 N/m), θ is
14 the contact angle between solid and mercury ($\theta = 130^\circ$) and R_p is the pore access radius for
15 cylindrical pores (m). MIP measurements have been carried out using a Micromeritics instrument
16 apparatus type (AutoPore IV 9500). The instrument is capable of a minimum intruding pressure of
17 3.4 kPa and a maximum pressure of 227 MPa, so that the pore radius ranges from 2.7 nm to 180
18 μm .

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

1 **SI1.2 SEM**

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

5 **SI2 Results and Discussion**

6 **SI2.1 SEM Observations of Fe⁰ and pumice particles**

7 SEM images detailing the microstructures of, respectively, Fe⁰ and pumice particles are shown in
8 Fig. SI1. These observations show that the Fe⁰ and pumice particles are irregular. It can be observed
9 that the pumice particles (grains) are porous with oval shaped and fibrous cavities (or pores). The
10 diameter of these cavities at the surface is lower than about 40 μm (radius 20 μm).

11

12 **SI2.2 MIP measurements of pumice particles**

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

$$20 \quad \Phi_0 = V_{\text{mercury intruded}} * M / V \quad (\text{SI3})$$

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

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

$$24 \quad \Phi_{\text{inter}} = V_{R>20\mu\text{m}} / V \quad (\text{SI4})$$

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

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

$$5 \quad C_{\text{pumice}} = 1 - \Phi_{\text{inter}}. \quad (\text{SI5})$$

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

$$7 \quad \phi_{\text{pp}} = V_{R<40\mu\text{m}} / V / C_{\text{pumice}} \quad (\text{SI6})$$

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

9 The results are given in Tab. SI2. The total porosity of the pumice medium has been estimated to be
10 73.3 % and the inner porosity of the pumice to be 41.0 %.

11

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

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

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

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

21

22 **SI2.4 Porosity of the columns**

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

1
$$\Phi_0 = \Phi_{inter} + \Phi_{pp} \cdot f_{pp} \quad (SI7)$$

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

4

5 **References**

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

7

8

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

3

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*

4

5

1 **Table SI2:** Characteristics of Fe⁰ and pumice particles tested by MIP.

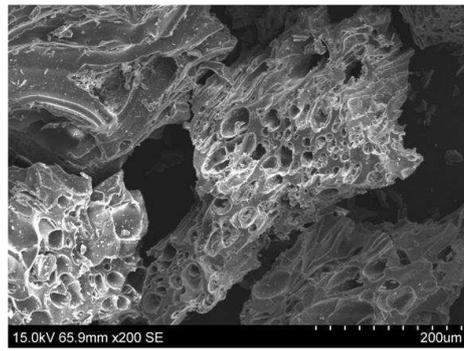
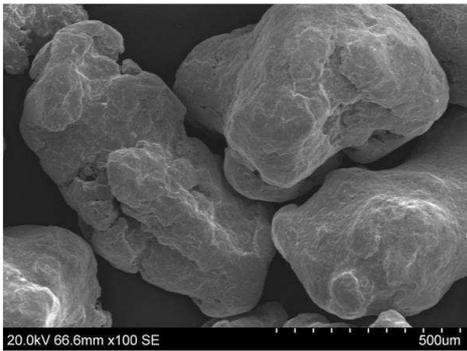
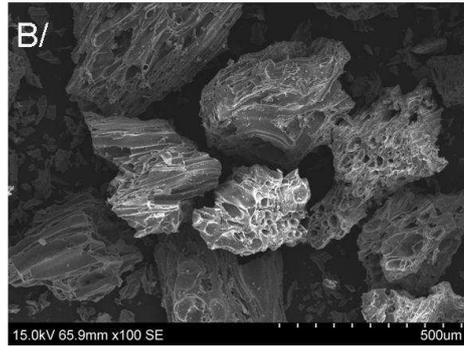
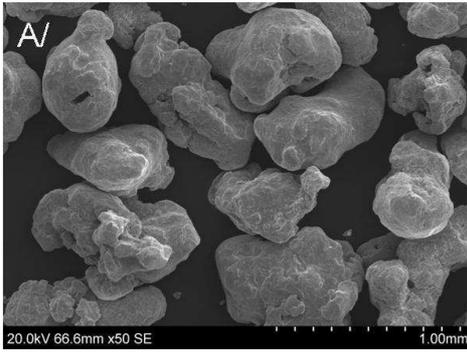
2

	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

3

4

1 **Figure S11:** SEM images of the Fe⁰ particles (A) and of the pumice particles (B).

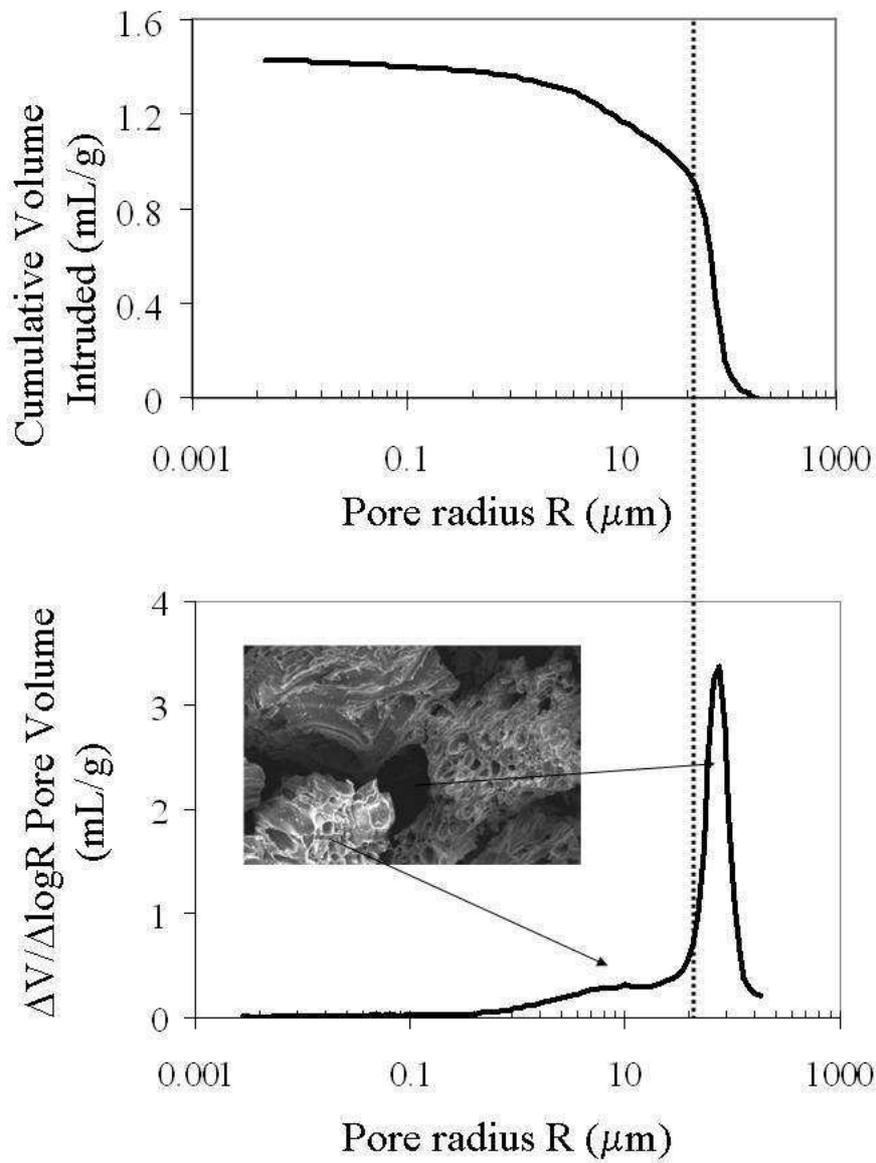


2

3

4

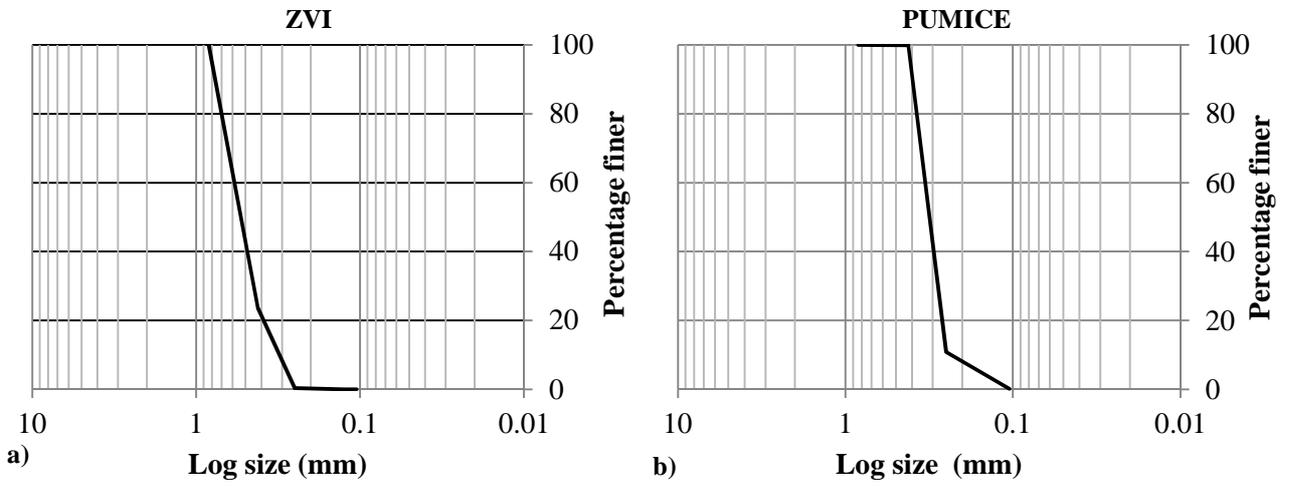
1 **Figure SI2:** Cumulative volume intruded (mL/g) and pore size distribution of the pumice particles.
2 Two types of porosity are observed: inter particular porosity Φ_{inter} ($R > 20\mu\text{m}$) and intra particular
3 porosity ϕ_{pp} ($R < 20\mu\text{m}$).
4
5



6
7
8

1 **Figure SI3:** Grain size distributions of used materials: Fe⁰ (a) and pumice (b).

2



3

4