

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

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## Abstract

Metallic iron ( $Fe^0$ ) is currently used in subsurface and above-ground water filtration systems on a pragmatic basis. Recent theoretical studies have indicated that, to be sustainable, such systems should not contain more than 60 %  $Fe^0$  (vol/vol). The prediction was already validated in a  $Fe^0$ /sand system using methylene blue as an operational tracer. The present work is the first attempt to experimentally verify the new concept using pumice particles. A well-characterized pumice sample is used as operational supporting material and is mixed with 200 g of a granular  $Fe^0$ , in volumetric proportions, varying from 0 to 100 %. The resulting column systems are characterized (i) by the time dependent evolution of their hydraulic conductivity and (ii) for their efficiency for the removal of  $Cu^{II}$ ,  $Ni^{II}$ , and  $Zn^{II}$  from a three-contaminants-solution (about 0.30 M of each metal). Test results showed a clear sustainability of the long term hydraulic conductivity with decreasing  $Fe^0$ /pumice ratio. In fact, the pure  $Fe^0$  system clogged after 17 days, while the 25 %  $Fe^0$  system could operate for 36 days. The experimental data confirmed the view that well-designed  $Fe^0$  PRBs may be successful at removing both reducible and irreducible metal species.

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

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### 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 p).

16 Granular metallic iron ( $\text{Fe}^0$ ), 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  $\text{Fe}^0$  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 p' is not satisfied as the sustainability of  $\text{Fe}^0$  filters is impaired by the same properties making  $\text{Fe}^0$   
21 an attractive material: the chemical reactivity of iron (Liu et al. 2013). However, without  
22 considering these key properties,  $\text{Fe}^0$  permeable reactive barriers ( $\text{Fe}^0$  PRBs) have become an  
23 established technology for the treatment of contaminated groundwater (O'Hannesin and Gillham,  
24 1998; Li et al., 2006; Bartzas and Komnitsas, 2010; Li and Benson, 2010; Comba et al., 2011;

1 Gheju, 2011; Giles et al., 2011; Hashim et al., 2011; Ruhl et al., 2012). Currently, about 180 Fe<sup>0</sup>  
2 PRBs have been installed worldwide (ITRC, 2011).

3 The fundamental mechanisms of contaminant removal in Fe<sup>0</sup> filtration systems are adsorption, co-  
4 precipitation and adsorptive size-exclusion (Noubactep, 2008; 2010; 2011). Contaminant removal  
5 also implies iron corrosion (Lavine et al., 2001; You et al., 2005; Jiao et al., 2009; Ghauch et al.,  
6 2011; Gheju and Balcu 2011). Therefore, due to the volumetric expansive nature of this process  
7 ('prerequisite p'), the remediation of contaminated groundwater necessarily results in the gradual  
8 clogging of the Fe<sup>0</sup> PRB, and thus in the deterioration of the permeable barrier hydraulic  
9 conductivity (permeability loss) over time (Zhang and Gillham, 2005; Courcelles et al., 2011;  
10 Knowles et al., 2011; Jeon et al., 2012; Miyajima, 2012; Noubactep, 2013a; 2013b; 2013c).

11 The gradual clogging (permeability loss) of Fe<sup>0</sup> filtration systems has several origins: (i) biological  
12 activities like biofilm growth or biocorrosion, (ii) chemical processes like (hydr)oxide or calcite  
13 precipitation, (iii) physical processes allowing the retention of fine particles in the PRB pores, and  
14 (iv) production and accumulation of gases (mainly H<sub>2</sub>). Pores clogging could generate a decrease in  
15 treatment performance and the bypass of untreated contaminated groundwater (Rangsivek and Jekel  
16 2005; Courcelles et al., 2011; Knowles et al., 2011; Jeon et al., 2012). Therefore, PRBs clogging  
17 issues will require cost-intensive reactive material substitution, if satisfactory operational  
18 performance has to be maintained. The present work is focused on the characterization of PRB  
19 clogging due to pore filling by in-situ generated iron corrosion products neglecting the other  
20 possible phenomena that could contribute to permeability reduction (i.e. gas retention, biocorrosion,  
21 biofouling) (Henderson and Demond, 2011; Caré et al., 2013; Noubactep, 2013a).

22 The objective of the present work is to characterize the efficiency of Fe<sup>0</sup>/pumice granular  
23 mixtures for contaminant removal in column experiments containing 0 to 100 % Fe<sup>0</sup> (vol/vol). Fe<sup>0</sup>  
24 is admixed to a well-characterized pumice specimen (Moraci and Calabrò, 2010; Calabrò et al.,  
25 2012; Bilardi et al., 2013a), in different volumetric ratios. The model oxidic solution (about 8 mg/L

1 O<sub>2</sub>) contained about 0.30 M of Cu<sup>II</sup>, Ni<sup>II</sup>, and Zn<sup>II</sup>. The evolution of the systems is characterized by  
2 determining the (i) extent of contaminant removal (or retention), and (ii) variation of hydraulic  
3 conductivity.

## 4 **2 Materials and methods**

### 5 **2.1 Chemicals**

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

### 13 **2.2 Solid materials**

14 **Pumice:** the used pumice originates from Lipari (Aeolian Islands, Sicily – Italy); its mineralogical  
15 composition was determined as follows: SiO<sub>2</sub>: 71.75 %; Al<sub>2</sub>O<sub>3</sub>: 12.33 %; K<sub>2</sub>O: 4.47 %; Na<sub>2</sub>O: 3.59  
16 %; Fe<sub>2</sub>O<sub>3</sub>: 1.98 %; moreover it contains about 4 % of bound water (structural water) and traces of  
17 other compounds (e.g. CaO, SO<sub>3</sub>, MgO, TiO<sub>2</sub>, FeO, MnO, P<sub>2</sub>O<sub>5</sub>). Although pumice exhibited a non  
18 negligible removal capacity for heavy metals (Moraci and Calabrò, 2010; Calabrò et al., 2012), it  
19 was used here as an operational inert material with the virtual capacity of storing corrosion products  
20 in its pores and retarding clogging (Moraci and Calabrò, 2010; Noubactep and Caré, 2010;  
21 Noubactep et al. 2012a; Noubactep et al. 2012b). The material is characterized by uniform grain  
22 size distribution. The mean grain size ( $d_{50}$ ) is about 0.3 mm and the coefficient of uniformity (U) is  
23 1.4 (see Supporting Information).

24 **Metallic iron:** the used Fe<sup>0</sup> is of the type FERBLAST RI 850/3.5, distributed by Pometon S.p.A.,  
25 Mestre - Italy. The material contains mainly iron (> 99.74 %). Identified impurities included mainly

1 Mn (0.26 %), O, S and C. The material is characterized by uniform grain size distribution. The  
2 mean grain size ( $d_{50}$ ) is about 0.5 mm and the coefficient of uniformity (U) is 2 (see Supporting  
3 Information).

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

### 7 **2.3 Columns experiments**

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

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

18 Simplified model solutions (no carbonates, bicarbonates and relevant cations) were used as this  
19 work is a seminal one focused on the impact of molecular  $\text{O}_2$  on the clogging process of  $\text{Fe}^0$  PRBs  
20 as influenced by pumice addition in various proportions. Testing more complex solutions relevant  
21 to simulate natural situation could be built on the results from these simplified systems.

22 Laboratory scale polymethyl methacrylate (Plexiglas) columns were operated in up-flow mode. The  
23 influent solution was pumped upwards from a single PE bottle using a precision peristaltic pump  
24 (Ismatec, ISM930). In all the tests the flow rate was maintained constant at a value of 0.5 mL/min.

1 Tygon tubes were used to connect inlet reservoir, pump, columns and outlet. Six plexiglas columns  
2 (50 cm long, 5.0 cm inner diameter) were used in the experiments (Fig. 1).

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

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

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

1 hydraulic conductivity (systems C to F) was observed; only system B was voluntarily stopped after  
2 90 days. Tab. SI summarizes the experimental research program (Supporting Information).

3 The aqueous concentrations of Cu, Ni and Zn were determined by Atomic Absorption  
4 Spectrophotometry (AAS - Shimadzu AA – 6701F) using conventional Standard Methods (APHA  
5 2005).

## 6 **2.4 Expression of the experimental results**

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

$$10 \quad E = m_{\text{rem}}/m_{\text{in}}*100 \quad (1)$$

$$11 \quad E_s = m_{\text{rem}}/m_{\text{Fe}}*100 \quad (2)$$

12 where  $m_{\text{in}}$  is the mass of contaminant flowed into the column,  $m_{\text{rem}}$  is the mass of removed  
13 contaminant, and  $m_{\text{Fe}}$  the mass of  $\text{Fe}^0$  present in the column.

## 14 **3 Results and discussion**

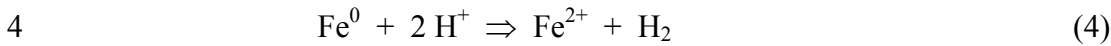
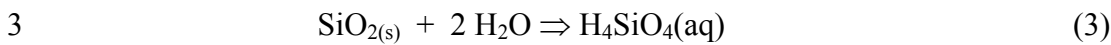
### 15 **3.1 Contaminant removal**

16 The presentation is based on the concept that tested contaminants are removed in  $\text{Fe}^0$  columns (at  
17  $\text{pH} > 5$ ) by adsorption, co-precipitation and adsorptive size-exclusion (Noubactep, 2008; 2010;  
18 2011; 2013a). Given the importance of the pH value for this concept, the results of pH monitoring  
19 are presented first.

#### 20 **3.1.1 pH value**

21 Figure 2 summarizes the results of the evolution of the pH value in all investigated systems. It is  
22 shown that in the reference system (100 % pumice), the initial pH (6.3) decreased to 5.8 and  
23 remained constant for the entire column tests duration. The slight pH decrease could be attributed to  
24 acidic sites at the pumice surface (Eq. 3). In all other systems, the pH value first increased to value

1 > 9.0 and progressively decreased to values close to 6.0 – 7.0. The observed pH increase is certainly  
2 due to iron corrosion which consumes H<sup>+</sup> (Eq. 4).



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

### 11 **3.1.2 Iron release**

12 Figure 3 summarizes the results of the evolution of dissolved iron concentration in the effluent. It is  
13 evident from Fig. 3a, that the highest iron release was observed in the system with the lowest Fe<sup>0</sup>  
14 ratio (B, 10 % Fe<sup>0</sup>). The lowest Fe<sup>0</sup> ratio corresponds to the highest amount of pumice (243 g - Tab.  
15 1), acidifying the system after Eq. 3. The transport of iron corrosion products is certainly favoured  
16 at low pH values and may be favoured by larger porosity (Nimmo, 2004; Woudberg and Du Plessis,  
17 2008; Glover and Walker, 2009). In other words, in all other systems, even more iron could be  
18 dissolved but it is retained within the system by (i) adsorption onto available iron oxides or onto  
19 pumice, or (ii) precipitation as iron (hydr)oxides (Miyajima, 2012; Miyajima and Noubactep, 2013).  
20 It is very important to notice that the extent of iron release depends primarily on the intrinsic  
21 reactivity of used Fe<sup>0</sup>. Although data on iron release from column experiments are available in the  
22 literature (e.g. Westerhoff and James, 2003) it is impossible to make a quantitative comparison. In  
23 fact, a parameter (or an index) to characterize the intrinsic reactivity of Fe<sup>0</sup> is still lacking  
24 (Noubactep et al., 2009; Noubactep, 2012).



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

### 4 **3.1.3 Metal concentration**

5 Table 2 summarizes the results of the removal of Cu<sup>II</sup>, Ni<sup>II</sup> and Zn<sup>II</sup> in terms of removal efficiency  
6 E, and of specific removal efficiency E<sub>s</sub> for all the 5 systems containing Fe<sup>0</sup>. It should be kept in  
7 mind that the experimental duration was variable as most of the experiments were stopped because  
8 of significant permeability loss (see Tab. 1). Nevertheless, it can be seen that 367 to 2881 mg of  
9 individual contaminants flowed into the columns and retained with an efficiency E > 90.0 %.  
10 Moreover, the specific efficiency (E<sub>s</sub>) varied from 1.7 to 13.6 mg contaminant per g of Fe<sup>0</sup>.

11 An important feature from Tab. 2 regards the suitability of E<sub>s</sub> values (Eq. 2) for the characterization  
12 of processes occurring in Fe<sup>0</sup>/H<sub>2</sub>O systems (Btatkeu et al., 2013; Miyajima and Noubactep, 2013).  
13 Normalizing the extent of contaminant removal (m<sub>rev</sub> - Eq. 2) by the available amount of Fe<sup>0</sup> (here  
14 200 g) is only valid, if there is a clear linear relationship between iron corrosion and contaminant  
15 removal. Such a relationship has not been demonstrated in the Fe<sup>0</sup> remediation literature despite  
16 repeated reports on reaction orders. Moreover, an adequate argumentation for adsorptive processes  
17 has been simply transposed to systems, where adsorption is only one (and not necessarily the  
18 dominant) removal mechanism.

19 In pure adsorption systems (e.g. activated carbon, iron oxide, clay) were the whole mass of  
20 adsorbing material is present at the start of the removal process (t<sub>0</sub> or t = 0), its adsorption capacity  
21 can be exhausted with time. In a Fe<sup>0</sup> system on the contrary, adsorbing species are generated in situ  
22 after the start of the experiment (t > t<sub>0</sub>). Accordingly the extent of contaminant removal depends on  
23 the kinetics of iron corrosion and the affinity of contaminants for corrosion products as far as only  
24 adsorption is concerned. Additionally, contaminants are also removed by co-precipitation and size-  
25 exclusion. In other words, normalizing the extent of contaminant removal by the Fe<sup>0</sup> amount

1 requires at least the knowledge of the intrinsic reactivity of used  $\text{Fe}^0$  and the impact of operational  
2 parameters thereon. The most relevant operational parameter in the present work is the volumetric  
3  $\text{Fe}^0$ :pumice ratio.

4 Figure 4 shows that the influence of the volumetric  $\text{Fe}^0$ :pumice ratio on the removal efficiency of  
5  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  is very similar to the influence of the adsorbent amount on adsorption of  $\text{Mn}^{2+}$  by  
6 clay minerals (Goldani et al., 2013). These authors reported a decreasing trend of the adsorption  
7 capacity ( $q_e$  value /  $\text{mg g}^{-1}$ ) for  $\text{Mn}^{2+}$  with increasing adsorbent amount (50 to 500 mg). This  
8 observation was mainly rationalized by the fact that a large adsorbent amount reduces the  
9 unsaturation of the adsorption sites. Correspondingly, the number of such sites per unit mass  
10 decreases resulting in comparatively less adsorption at higher adsorbent amount. In the present  
11 work, the  $\text{Fe}^0$  amount is constant (200 g) and only its volumetric ratio in the mixture to pumice  
12 varies. Moreover, a higher  $\text{Fe}^0$  ratio is coupled to a shorter reactive zone (e.g. 2.6 cm for 100 %  $\text{Fe}^0$   
13 and 26.2 cm for 10 %  $\text{Fe}^0$ ). Thus, a higher  $\text{Fe}^0$  volumetric ratio may create particle aggregation  
14 (cementation), decreasing the total number of adsorption sites, decreasing the porosity of the  
15 reactive zone, and increasing the diffusion path to adsorption sites. Altogether, these factors  
16 contribute to the decrease of the amount of contaminant adsorbed, assuming that the same amount  
17 of adsorbent is generated in all systems. As summarized in Tab. 2, except system B (10 %  $\text{Fe}^0$ ),  
18 metal removal was quantitative in all other systems.

19 Contaminant breakthrough was observed in other systems only short before the experiment was  
20 stopped and was mainly attributed to transport through preferential flow paths (Miyajima and  
21 Noubactep, 2013 and ref. cited therein). Even under such conditions the concentration of Cu and Zn  
22 remained below 1 mg/L whereas the concentration of Ni exceeded 4 mg/L for system F (100 %  $\text{Fe}^0$ )  
23 and system D (50 %  $\text{Fe}^0$ ) but not for system E (75 %  $\text{Fe}^0$ ). This anomaly in the sequence D/E/F  
24 confirms that the process responsible for metal breakthrough near system clogging is probably a  
25 meta-stable one (preferential flow).

### 1 **3.2.4 Mechanism of contaminant removal**

2 The experimental data previously described has shown that contaminants are quantitatively  
3 removed in columns with volumetric Fe<sup>0</sup> ratio higher than 10 % until the system is almost clogged.  
4 In the system with 10 % Fe<sup>0</sup>, quantitative iron release is observed (Fig. 5). Quantitative iron release  
5 coincided with minimal contaminant removal (or contaminant breakthrough) as discussed above.  
6 This section further discusses the behaviour of system B (Fig. 5a).

7 The ionic radii of the investigated cations increase in the order Ni<sup>2+</sup> < Cu<sup>2+</sup> < Zn<sup>2+</sup>. The metallic  
8 ions are removed by four different mechanisms (Herbert, 1996; Wang and Qin, 2007; Vodyanitskii,  
9 2010): (i) co-precipitation with iron hydroxides, (ii) adsorption onto the (hydr)oxide surfaces, (iii)  
10 isomorphic substitution for Fe in the iron oxide structure, or adsorptive size-exclusion. In multi-  
11 element systems, the most common reported affinity sequence for iron oxides and soils is Cu > Zn  
12 > Ni (Moreira and Alleoni, 2010). This trend is confirmed by Fig. 5b.

13 Fig. 5a illustrates the fact that contaminants breakthrough occurs when increased iron release is  
14 observed. For example, no significant breakthrough was observed in system B until t=30 days  
15 although up to 8 mg/L Fe was released into the outlet solution. For t > 30 days Zn and Ni  
16 breakthrough occurs and the breakthrough magnitude is in agreement with the affinity sequence for  
17 iron oxides (Cu > Zn > Ni). Accordingly, breakthrough is first observed for less bounded Ni  
18 followed by Zn. As concerning Cu no breakthrough was observed through the end of the  
19 experiment. At first glance, this observation could be attributed to Cu<sup>II</sup> cementation at the surface of  
20 Fe<sup>0</sup> in the column. In fact, Cu reduction to elemental Cu (Cu<sup>0</sup>), as mentioned above, is very  
21 favourable and is used in many hydrometallurgical processes (Gros et al., 2011a; 2011b). However,  
22 because Cu removal in this study occurred at pH > 5 (section 3.2.1), the Fe<sup>0</sup> surface was necessarily  
23 covered by iron (hydr)oxides (Aleksanyan et al., 2007; Nestic, 2007) and was not directly accessible  
24 to Cu<sup>II</sup> (Ni<sup>II</sup> and Zn<sup>II</sup>). More detailed discussion on the removal of metallic ions by Fe<sup>0</sup> in multi-

1 elements system is given for instance by Cantrell et al.(1995), Qiu et al. (2000), Bartzas et al.  
2 (2006), Komnitsas et al. (2006; 2007) and Scott et al. (2011).

3 It should be recalled that in a  $\text{Fe}^0/\text{H}_2\text{O}$  system, so-called structural  $\text{Fe}^{\text{II}}$  (adsorbed  $\text{Fe}^{\text{II}}$ ) is available  
4 and is, in some circumstances, a more efficient reducing agent than  $\text{Fe}^0$  (White & Peterson, 1996).  
5 Accordingly,  $\text{Cu}^{\text{II}}$  might be quantitatively removed within the oxide scale on iron. Even if  $\text{Cu}^{\text{II}}$  is  
6 reduced at the surface of  $\text{Fe}^0$ , it will be enmeshed within the matrix of iron oxides as corrosion  
7 proceeds. In conclusion, aqueous  $\text{Cu}^{\text{II}}$  is also permanently removed by the process of iron corrosion  
8 (enmeshment or co-precipitation). It should be also remembered that the stronger affinity of  $\text{Cu}^{\text{II}}$  for  
9 iron oxides (adsorption) is sufficient to rationalize the absence of Cu breakthrough for 90 days (Fig.  
10 5b).

### 11 **3.3 Hydraulic conductivity**

12 The results presented in Fig. 6 clearly demonstrate that granular  $\text{Fe}^0$ /pumice mixtures are more  
13 sustainable in terms of long term permeability than the pure  $\text{Fe}^0$  PRB for the decontamination of  
14 used model solution. Fig. 6a shows that the pure pumice systems exhibited an initial porosity of  
15 72.6 % while the porosity of the pure  $\text{Fe}^0$  system was 49.6 % (Tab. 1). Fig. 6b shows that the 100 %  
16  $\text{Fe}^0$  system was clogged after 17 days; the 25 %  $\text{Fe}^0$  system after 37 days and the 10 %  $\text{Fe}^0$  system  
17 was still highly permeable after 90 days. Even though the 10 %  $\text{Fe}^0$  system was not efficient at  
18 removing Ni and Zn, such systems could be used to generate dissolved Fe for other purposes  
19 including: (i) in-situ generation of Fe for contaminant removal (Khan et al., 2000; Pokhrel and  
20 Viraraghavan, 2009) and (ii) oxygen scavenger to sink the  $\text{O}_2$  concentrations in above-ground  
21 devices (Mackenzie et al., 1999; Noubactep and Schöner, 2010; Noubactep et al., 2010).

22 A fundamental feature from Fig. 6a is that it combines contaminant removal (here  $E_s$  value for Zn)  
23 and initial porosity. The initial porosity decreases linearly with increasing  $\text{Fe}^0$  ratio. This behaviour  
24 is rationalized by the fact that a compact material ( $\text{Fe}^0$ ) is admixed to a porous one (pumice). The  
25 initial pore volume will be progressively filled by in situ generated iron corrosion products (Caré et

1 al., 2013) which adsorb and co-precipitate metal ions. Reduced pore volume increases size-  
2 exclusion efficiency while decreasing permeability. The challenge of designing hybrid Fe<sup>0</sup>/material  
3 systems is to find out the optimal system concealing sustained permeability and efficient  
4 contaminant removal. Fig. 6a confirms/shows unambiguously that such a system should contain as  
5 less Fe<sup>0</sup> (volumetric proportion) as possible (Caré et al., 2013; Miyajima and Noubactep, 2013).  
6 Considering the factor of 65 times to account for the differential kinetics of Fe<sup>0</sup> oxidation under  
7 oxic (8 mg/L O<sub>2</sub>) and anoxic (0 mg/L O<sub>2</sub>) conditions (Cohen, 1959), it can be argued that the  
8 shortest experimental duration (17 days) reported here could corresponds to about 1105 days under  
9 anoxic conditions. These are more than 3 years necessary to observe clogging under the  
10 experimental conditions of this work after 17 days. This result justifies the use of oxic conditions to  
11 investigate target processes under laboratory conditions. By performing parallel experiments with  
12 various amounts of molecular O<sub>2</sub> (Vidic and Suidan, 1991) a better characterization of the impact of  
13 the availability of molecular O<sub>2</sub> is possible. This effort is even urgently needed as Fe<sup>0</sup> beds have  
14 been proposed for an array of applications varying from pure anoxic (groundwater remediation) to  
15 oxic (household filter) systems.

16 Fig. 7 depicts the evolution of the experimental duration and the residual porosity (modelled, see  
17 below) as a function of the initial porosity of the columns containing Fe<sup>0</sup>. The lowest porosity (49.6  
18 %) corresponds to system F (100 % Fe<sup>0</sup>) and the largest (70.5 %) to system B (10 % Fe<sup>0</sup>). It is seen  
19 that the experimental duration (system sustainability) increases almost linearly with decreasing Fe<sup>0</sup>  
20 proportion from 100 to 25 %. From 25 to 10 % Fe<sup>0</sup> an abrupt increase of the experimental duration  
21 is observed. These results are qualitatively confirmed by the evolution of the residual porosity for  
22  $\eta = 6.4$  (Fig. 7a) where  $\eta$  is the coefficient of volumetric expansion of rust specimens (Caré et al.,  
23 2008).

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

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

1  
2 Where  $\Delta V = (\eta - 1) \cdot V$  is the effective volumetric expansion of the initial volume  $V$  of  $\text{Fe}^0$ .  
3 The residual porosity which is an indicator of the hydraulic conductivity, is given for all systems in  
4 Fig. 7. The observed time-dependant decrease of the hydraulic conductivity is attributed to two  
5 different factors: (i) the decrease of the effective pore-size as concentric layers of iron oxides are  
6 formed on  $\text{Fe}^0$ , and (ii) the filling of pores by precipitated Fe species that escaped out of the oxide  
7 scale. Permeability loss due to in-situ generated particles is retarded when larger particle sizes are  
8 used. Accordingly, as the grain-size increases, the loss of hydraulic conductivity should follow the  
9 inverse trend. In other words, the kinetics of the occupation of the voids depends on the grain-size  
10 of used particles (effective pore-size).  
11 Theoretically, for spherical grains of uniform size (monosized), the grain diameter will not impact  
12 initial porosity but only the void diameter. However, the total porosity generally increases with  
13 increasing sorting (grain size distribution), decreases with increasing sphericity and roundness of  
14 particles, decreases with the increasing of relative density (closer packing) (Gibb et al., 1984). All  
15 these aspects have to be considered to discuss literature results as well.  
16 It appears from Fig. 7a that the residual porosity tends to zero ( $\Phi(t)/\Phi_0 = 0$  or permeability loss) for  
17 clogged systems ( $\% \text{Fe}^0 \geq 25$  – clogging precedes  $\text{Fe}^0$  depletion). For  $\text{Fe}^0 < 25 \%$ ,  $\Phi(t)/\Phi_0 \neq 0$  at  $\text{Fe}^0$   
18 depletion in accordance with the evolution of the hydraulic conductivity and the test duration. At  
19 first glance, this observation could be misinterpreted as the confirmation of the proposed model. But  
20 under the experimental conditions,  $\text{Fe}^0$  was not completely depleted. Accordingly, this experimental  
21 evidence rather suggests that the entrance zone of the column could have been rapidly clogged due  
22 to elevated  $\text{O}_2$  levels (Mackenzie et al., 1999). The presence of  $\text{O}_2$  leads to iron (hydr)oxides with  
23 higher expansion coefficient ( $\eta$ ) implying a more rapid decrease of the residual porosity (Fig. 7b).

1 Fig. 7b depicts the modelled variation of the residual porosity for 3 different values of  $\eta$  (2.08, 3.03  
2 and 6.4). It is seen that under ideal conditions (uniform corrosion), the sustainability of a  $\text{Fe}^0$  filter  
3 depends on the availability of  $\text{O}_2$ . Accordingly the most sustainable system is the one operating  
4 under conditions where  $\text{Fe}_3\text{O}_4$  ( $\eta = 2.08$ ) is the major iron corrosion product (anoxic conditions).  
5 These conditions could be obtained in a second column in series with a first one acting as  $\text{O}_2$   
6 scavenger.

7 The fact that observed preservation of permeability with time is coupled with a decrease of  
8 contaminant removal efficiency suggests that for any  $\text{Fe}^0$ /additive couple, an increase of filter  
9 sustainability with decreasing  $\text{Fe}^0$  proportion down to a threshold value (here 25 %  $\text{Fe}^0$ ) would be  
10 observed.

11 This study has traceably demonstrated that admixing non expansive material with  $\text{Fe}^0$  is a tool to  
12 increase permeable reactive barriers sustainability. In other words, an efficient but not sustainable  
13 system (100 %  $\text{Fe}^0$ ) is transformed into an efficient and more sustainable one by admixing a certain  
14 volumetric proportion of pumice (here  $\geq 75$  %). The admixing material (here pumice) should  
15 necessarily be less expensive than  $\text{Fe}^0$ ; thus, cost savings could be regarded as a positive side effect  
16 of increased performance.

### 17 **3.4 Significance for future works**

18 This study is a continuation of a broad-based work aiming at designing non-site-specific  $\text{Fe}^0$   
19 filtration systems for water treatment and environmental remediation in its third step.

20 The first step consisted in identifying the common underlying mechanisms for contaminant removal  
21 (Noubactep, 2007; 2008; 2010; 2011). Adsorption, co-precipitation and size-exclusion were  
22 identified as fundamental paths for water treatment in  $\text{Fe}^0$  packed beds (Noubactep, 2011). This  
23 result belittled the importance of chemical reduction in the process of contaminant removal in  
24  $\text{Fe}^0/\text{H}_2\text{O}$  systems and clearly demonstrated that  $\text{Fe}^0$  is not a relevant reducing agent under  
25 environmental conditions. The strong fact that  $\text{Fe}^0$  is the parent of all reducing species (e.g.  $\text{Fe}^{\text{II}}$ ,

1  $\text{Fe}_3\text{O}_4$ , green rust,  $\text{H}/\text{H}_2$ ) should never be misinterpreted as ‘contaminant reduction coupled with  
2 electrochemical iron corrosion’ (Noubactep, 2013b; 2013c).

3 The second step consisted in writing the dimensionless equation of a  $\text{Fe}^0$  packed beds (Noubactep  
4 and Caré, 2010; Noubactep et al., 2010; Noubactep and Caré, 2011; Noubactep et al., 2012a;  
5 Noubactep et al., 2012b; Caré et al., 2013). It is important to notice, that the equation is based on  
6 the volumetric fraction of the packed beds available for ‘storing’ corrosion products (total porosity)  
7 (Noubactep and Caré, 2011). This theoretical work has shown that the volumetric ratio of  $\text{Fe}^0$  in a  
8 granular mixture should ideally not exceed 60 %. The basics for a systematic research for non-site-  
9 specific  $\text{Fe}^0$  filtration systems were established. In particular each  $\text{Fe}^0$  material should be  
10 characterized for its intrinsic reactivity; all used materials should be characterized for their form,  
11 homogeneity and shape (Crane and Noubactep, 2012; Noubactep et al., 2012a; Caré et al., 2013).

12 The current third step consists in validation the equation of the column (Calabrò et al., 2012; Bilardi  
13 et al., 2013a; Bilardi et al., 2013b). In this effort methylene blue (MB) was positively tested as an  
14 operational tracer (Miyajima, 2012; Btatkeu et al., 2013; Miyajima and Noubactep, 2013).  
15 Experiments with MB confirmed theoretical predictions that a pure  $\text{Fe}^0$  bed is not sustainable.  
16 Moreover, it could be shown that the optimal volumetric  $\text{Fe}^0$  ratio for sustainable filters is lower 50  
17 %. Given the large density difference between  $\text{Fe}^0$  ( $7.8 \text{ g cm}^3$ ) and commonly tested additives (e.g.  
18 anthracite, gravel, pumice, sand) ( $< 3.0 \text{ g cm}^3$ ), this results clearly shows that the commonly used  
19 1:1 weight ratio is not optimal as well. Experiments with MB suggested that the optimal  $\text{Fe}^0$   
20 volumetric ratio in a dual  $\text{Fe}^0$ /sand system is comprised between 30 and 50 %.

21 The present work has systematically tested the  $\text{Fe}^0$ /pumice system for the first time using Cu, Ni  
22 and Zn as model contaminants. The results showed that the optimal  $\text{Fe}^0$  ratio for a sustainable filter  
23 is 25 %. This result could be regarded as close to 30 % as determined by Miyajima and Noubactep  
24 (2013). However, under their experimental conditions, these authors could not experimentally  
25 document permeability loss. Accordingly, the present work has provided the most reliable optimal



1 Fe<sup>0</sup> ratio for sustainable Fe<sup>0</sup> filtration systems. In other words, this work proposes (provides) the  
2 following rule of thumb for further research (including pilot plant studies): “mix one volume of Fe<sup>0</sup>  
3 and 3 volumes of the additive(s)”. The universal validity of this rule of thumb relies on the evidence  
4 that it is based on a dimensionless equation. Thus, if a filter has to contain 1 kg Fe<sup>0</sup>, the volume  
5 occupied by this Fe<sup>0</sup> mass is used as unit and three units volume of the additives of comparable size  
6 (and shape) are to be added and homogenized.

#### 7 **4. Concluding remarks**

8 Environmental remediation and water treatment using metallic iron (Fe<sup>0</sup>) in packed beds is an  
9 established technology. Despite two decades of active research, this technology is still mostly  
10 regarded as an innovative one or has been simply declared a developed one. However, a developed  
11 technology is a technology that has established the scientific basis of the involved processes. This  
12 work has clearly confirmed theoretical predictions that: (i) pure Fe<sup>0</sup> beds are not sustainable, (ii) a  
13 bed made up of 25 % Fe<sup>0</sup> (vol/vol) and 75 % pumice is probably the most efficient system  
14 concealing sustained permeability and increased efficiency for contaminant removal, (iii) the  
15 specificity of contaminant removal in Fe<sup>0</sup> filters fundamentally depends on the adsorptive affinity to  
16 iron oxides (and not on the redox affinity).

17 The knowledge that the most sustainable filter is made up of more than 70 % (vol/vol) of pumice  
18 corroborates the view that sustainable Fe<sup>0</sup>/aggregate filters are Fe<sup>0</sup>-amended aggregate filters (e.g.  
19 Fe<sup>0</sup>-amended pumice filter or Fe<sup>0</sup>-amended sand filter). Most common natural aggregates are  
20 anthracite, sand, gravel, pumice or crushed rock. However, manufactured aggregates (e.g. blast  
21 furnace slag) can also be used as well. Basically there is an infinite number of Fe<sup>0</sup>-amended filters  
22 as relevant aggregates may include activated carbon and biomaterial (e.g. wood and coconut shell).  
23 A Fe<sup>0</sup>-amended filter can be regarded as a size-exclusion system in which size exclusion is  
24 improved by in situ generated iron corrosion products. This is a typical case of self-filtration. The  
25 challenge for future works is the proper design of these filters.

1 Further research at laboratory scale is needed to develop methodologies for the Fe<sup>0</sup> filter design.  
2 This effort should be accompanied by numerical modelling. Pilot scale installations are needed  
3 afterwards to fine tune determine the practicality of several aspects optimised at lab scale.

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1 **Table 1:** Main characteristics of the studied columns. “Volume” is the apparent volume of granular  
 2 medium. “ $r_{z_{theor}}$ ” is the 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.

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

6 \* 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>B</b> | 2130     | 2130  | 2881  | 90.1 | 99.8 | 94.2 | 9.58   | 10.6 | 13.6 |
| <b>C</b> | 881.3    | 881.3 | 1192  | 98.7 | 99.9 | 99.9 | 4.53   | 4.40 | 5.96 |
| <b>D</b> | 612      | 612   | 828   | 93.3 | 99.9 | 99.6 | 2.86   | 3.06 | 4.12 |
| <b>E</b> | 514.1    | 514.1 | 695.5 | 97.9 | 99.9 | 99.9 | 2.52   | 2.57 | 3.47 |
| <b>F</b> | 367.2    | 367.2 | 496.8 | 94.7 | 99.9 | 99.8 | 1.74   | 1.83 | 2.48 |

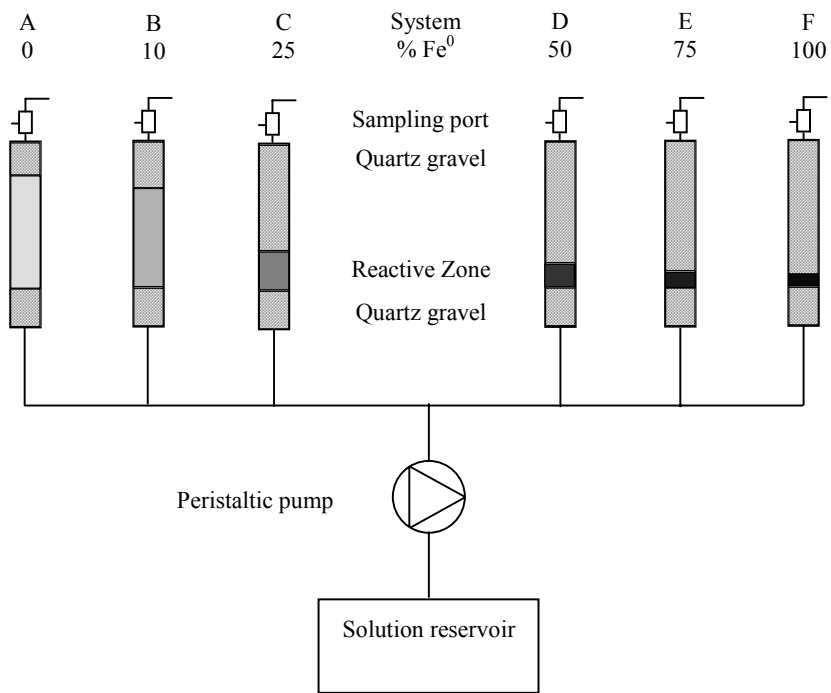
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1 **Figure 1**

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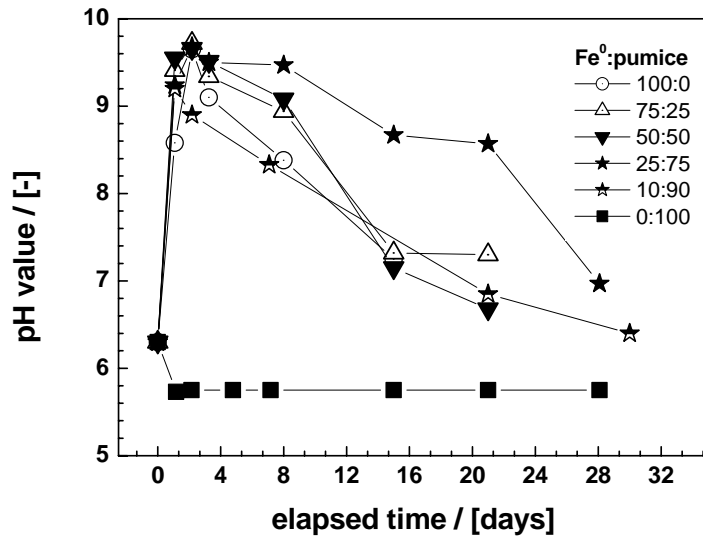


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1 **Figure 2**

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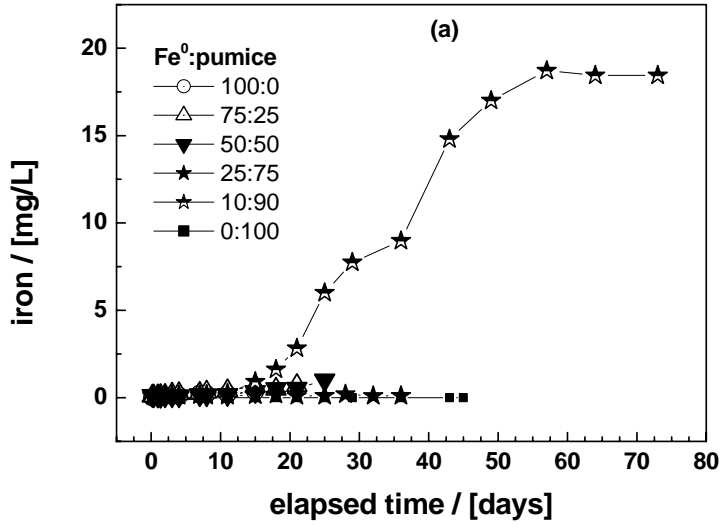


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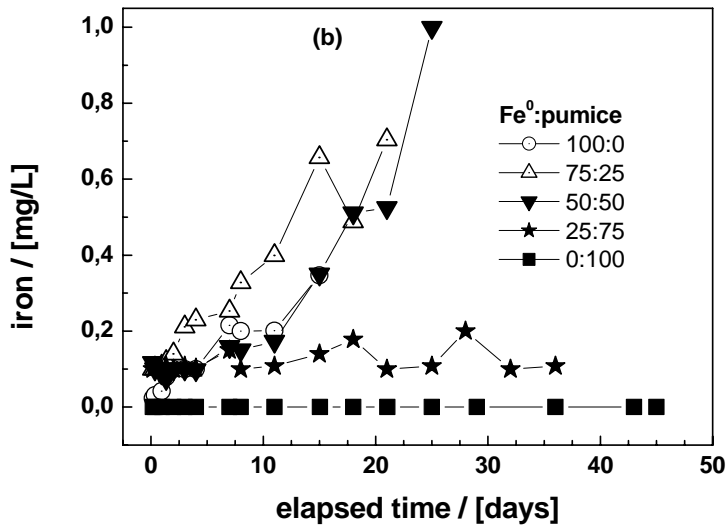
1 **Figure 3**

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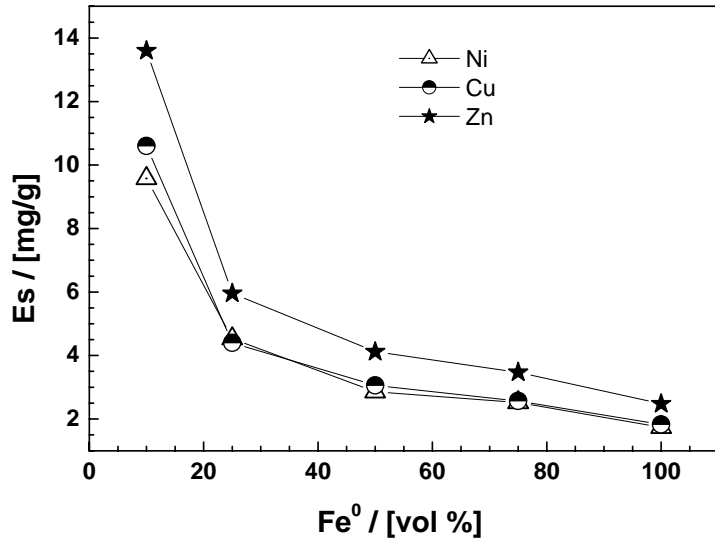
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1 Figure 4

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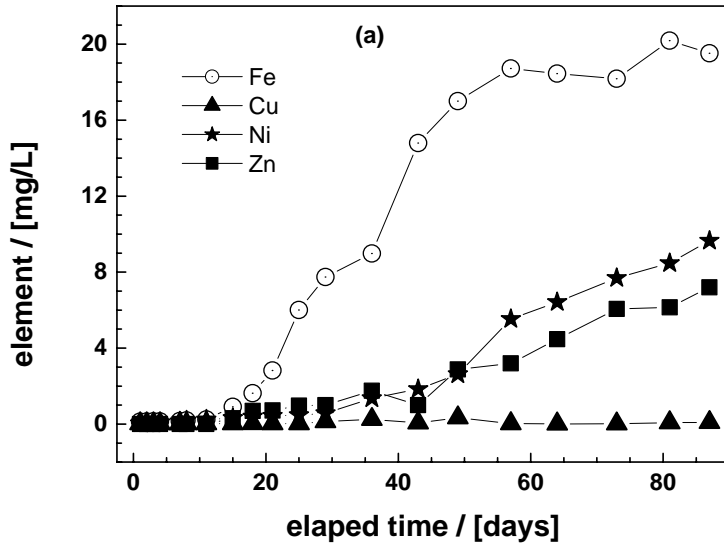
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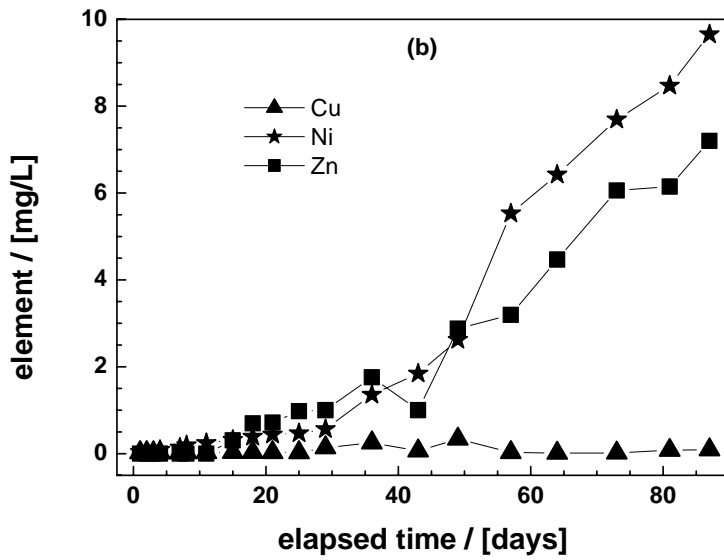
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1 **Figure 5**

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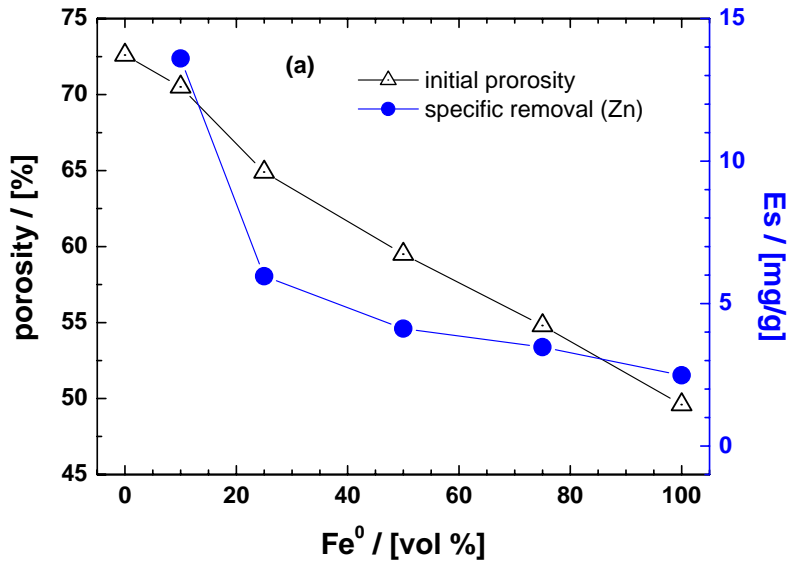
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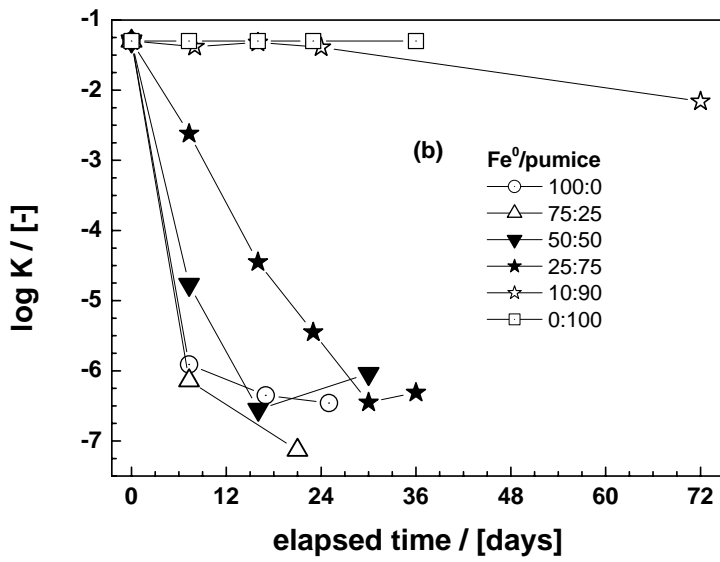
1 **Figure 6**

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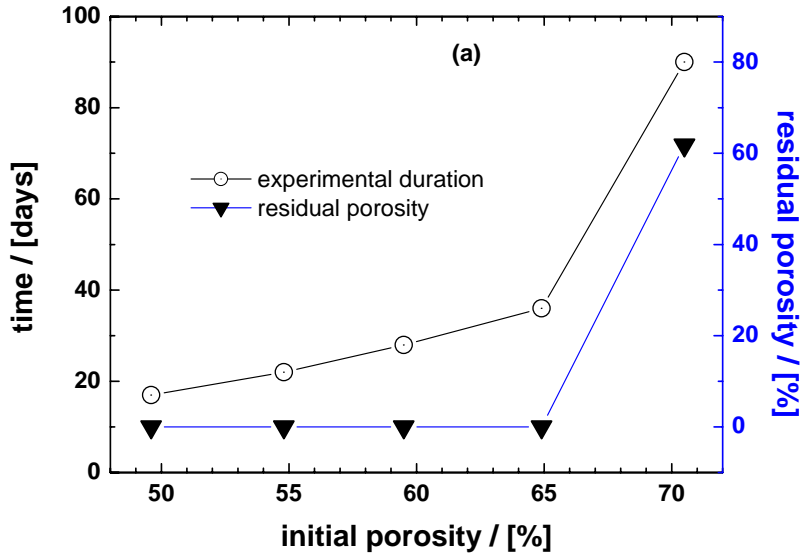
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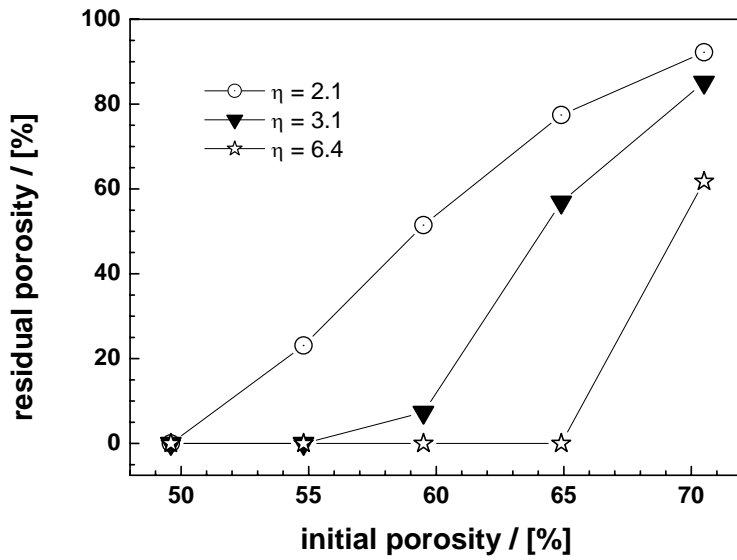
1 **Figure 7**

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1 **Figure captions**

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3 **Figure 1:** Schematic diagram of the experimental design. Used materials were (i)  $\text{Fe}^0$  (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). The black colour represents  $\text{Fe}^0$  and the grey colour pumice. The darker a reactive zone,  
6 the higher the  $\text{Fe}^0$  ratio.

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

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

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

15 **Figure 5:** Magnitude of Cu, Fe, Ni and Zn release from the column with 10 %  $\text{Fe}^0$ . The lines are not fitting  
16 functions, they simply connect points to facilitate visualization.

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

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

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