



Short Communication

Designing laboratory metallic iron columns for better result comparability

C. Noubactep^{a,c,*}, S. Caré^b^a *Angewandte Geologie, Universität Göttingen, Goldschmidtstraße 3, D-37077 Göttingen, Germany*^b *Université Paris-Est, Laboratoire Navier, (ENPC/IFSTTAR/CNRS), 2 allée Kepler, 77420 Champs sur Marne, France*^c *Kultur und Nachhaltige Entwicklung CDD e.V., Postfach 1502, D-37005 Göttingen, Germany*

ARTICLE INFO

Article history:

Received 13 December 2010

Received in revised form 6 March 2011

Accepted 8 March 2011

Available online 12 March 2011

Keywords:

Deep bed filtration
Operational parameters
Results comparability
Water filtration
Zerovalent iron

ABSTRACT

Despite the amount of data available on investigating the process of aqueous contaminant removal by metallic iron (Fe^0), there is still a significant amount of uncertainty surrounding the design of Fe^0 beds for laboratory testing to determine the suitability of Fe^0 materials for field applications. Available data were obtained under various operating conditions (e.g., column characteristics, Fe^0 characteristics, contaminant characteristics, oxygen availability, solution pH) and are hardly comparable to each other. The volumetric expansive nature of iron corrosion has been univocally reported as major drawback for Fe^0 beds. Mixing Fe^0 with inert materials has been discussed as an efficient tool to improve sustainability of Fe^0 beds. This paper discusses some problems associated with the design of Fe^0 beds and proposes a general approach for the characterization of Fe^0 beds. Each Fe^0 column should be characterized by its initial porosity, the composition of the steady phase and the volumetric proportion of individual materials. Used materials should be characterized by their density, porosity, and particle size. This work has introduced simple and reliable mathematical equations for column design, which include the normalisation of raw experimental data prior to any data treatment.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Metallic iron (Fe^0) as reactive medium for aqueous contaminant removal has been intensively investigated during the last two decades [1–6]. These studies have demonstrated the potential of Fe^0 for use in (i) subsurface permeable reactive barriers [1], (ii) above ground wastewater treatment [3,5], (iii) household water filters [7–10], and (iv) drinking water treatment plants [11–13]. The fundamental mechanisms of contaminant removal in Fe^0 beds are adsorptive size-exclusion and co-precipitation [5,6,13–19].

Data for pilot- and full-scale remediation scheme are mostly obtained from laboratory columns [20–22]. Laboratory column studies are in turn conventionally designed based on batch treatability studies [21,23,24]. A major problem of available data from batch studies is the poor comparability of results from different laboratories using different conditions. Most experimental conditions are not relevant for field situations [25,26]. For example, only shaking intensity lower than 50 m^{-1} could enable the formation of a universal oxide-scale in the vicinity of the Fe^0 surface as observed in column studies and in full-scale barriers [25]. A careful look behind published data on laboratory column experi-

ments ([27–32]; see Table 1) also demonstrates large variability in the experimental design. General design procedures are not available. Differences in design procedures may cloud interpretations of reported data. Therefore, any effort to ensure the comparability of laboratory results over time and space would accelerate the development of the Fe^0 remediation technology.

The objective of the present communication is to improve the comparability of laboratory column results by offering the scientific community tools for a common basis for the design of Fe^0 beds. Previous theoretical works [9,31,32] have demonstrated that mixing Fe^0 and other materials (gravel, pumice, sand, quartz) is the prerequisite for long service life. This mixture should be characterized by the volumetric proportion of Fe^0 (Fig. 1) and other materials (additives) and the initial porosity [32]. The specific objective of this communication is to establish equations for the evaluation of the mass of the materials to be used.

2. Basis for comparable results

Cylindrical columns usually used for laboratory experiments primarily differ in their size (diameter \times length). For example, columns with 5 cm internal diameters exist with lengths varying from 30 to 100 cm (Table 1). Completely filling the six different columns from Table 1 with reactive materials (e.g., Fe^0) will yield 0.2–9.8 kg of Fe^0 for the experiment. The question is how to objectively compare results obtained with various amount of the same

* Corresponding author at: Angewandte Geologie, Universität Göttingen, Goldschmidtstraße 3, D-37077 Göttingen, Germany. Tel.: +49 551 39 3191, fax: +49 551 399379.

E-mail address: cnoubac@gwdg.de (C. Noubactep).

Table 1
Variability of the operational conditions for column experiments as illustrated by material masses likely to be used in six different columns. D is the internal diameter of the column and L its length. It is assumed that the entire column volume is filled by spherical particle of Fe^0 , sand or pumice in an ideal cubic packing ($C=0.64$).

D (cm)	L (cm)	V_{column} (cm^3)	V_{solid} (cm^3)	m_{Fe} (kg)	m_{sand} (kg)	m_{pumice} (kg)	Ref.
2.0	12	37.7	24.1	0.19	0.06	0.015	[27]
2.6	40	212.5	136.0	1.06	0.34	0.087	[28]
4.1	25	330.0	211.0	1.60	0.60	0.135	[29]
5.0	30	589.3	377.1	2.94	0.94	0.241	[30]
5.0	50	982.1	628.6	4.90	1.57	0.402	[31]
5.0	100	1964.3	1257.1	9.81	3.14	0.805	[32]

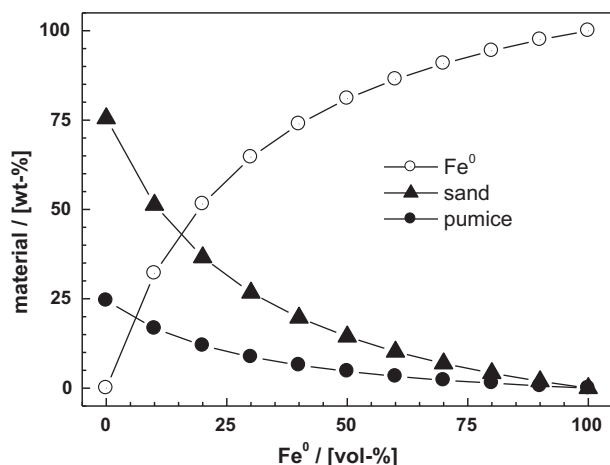


Fig. 1. Evolution of the material weight percent in a ternary system Fe^0 /sand/pumice as the initial 50:50 sand:pumice mixture (vol) is progressively amended with Fe^0 . The sand:pumice volumetric ratio is kept constant during the whole simulation. It is evident that due to difference in densities the weight percent variation is different for individual materials.

materials? The situation is exacerbated when the materials are different (particle size, shape, chemical composition or generally intrinsic reactivity). When material mixture should be performed, the rationale for purposeful mixing should be developed.

Using the material apparent specific weight tabulated by Noubactep and Caré [9], Table 1 clearly shows that a given volume (e.g., V_{solid} in the same column) is occupied by a mass m of pumice, $4.14m$ of sand, and $12.19m$ of Fe^0 . The coefficients are the ratios of the apparent specific weights (ρ_i/ρ_j). This observation confirms that the volumetric ratio is the sole appropriate approach to design column studies. Accordingly, an approach to have comparable results could be to fix the Fe^0 volume. A given Fe^0 volume corresponds to various heights depending on the column internal diameter. Accordingly, beside used Fe^0 mass (corresponding to a volumetric fraction of solid), the column dimensions should always be specified. Three examples are given below for illustration.

In the laboratory, the Fe^0 amount is commonly given in weight (g or kg). Therefore, a practical approach is to fix a mass of Fe^0 (m_0) which is likely to enable observable effects within a reasonable time (e.g., 6 weeks).

- An experiment is designed to compare the reactivity of different Fe^0 materials. Parallel column experiments have to be conducted in which Fe^0 is the sole variable and the same mass (m_0) is used in individual columns.
- An experiment is designed to compare the impacts of chloride (Cl^-) and sulphates (SO_4^{2-}) on the efficient of a Fe^0 for methylene blue (MB) discoloration. The three following parallel experiments could be conducted with the mass m_0 of a Fe^0 sample: (i) MB in deionised water, (ii) MB in a Cl^- solution, and (iii) MB in a SO_4^{2-} solution. The MB concentration is the same in all experiments, Cl^- and SO_4^{2-} solutions have the same equivalent concentration.

- An experiment is designed to compare the impact of mixing Fe^0 with additives. The reference system should be the mass m_0 of Fe^0 , and volumetric proportions of Fe^0 have to be replaced by appropriated additives. Table 1 shows that each column is characterized by a constant pore volume which is the external or inter-granular porosity. For porous materials the internal porosity or intra-granular porosity has been discussed as a storage room for in situ generated corrosion products and thus a tool to sustain Fe^0 reactivity [9,10,32]. Similarly, mixing Fe^0 and non-porous inert additives is beneficial for the system because inert material will not contribute to pore filling or filter clogging.

The next section will establish some general equations to support design operations.

3. Mathematical equations for column design

A hypothetical cylindrical filter having an inner diameter D , a length L , and a reactive zone h_{rz} is considered. The reactive zone is the fraction of L ($L > h_{\text{rz}}$) containing the reactive material, possibly mixed with selected additives. The filter is filled by spherical particles (reactive materials and non-reactive additives) having a constant diameter d . Considering the granular material as composed of mono-dispersed spheres subjected to soft vibrations, the column compactness (or packing density) C ranges between 0.60 and 0.64 for a random close packing but it is generally considered to be equal to 0.64 (limit value). It can be noticed that the value of the compactness depends on various parameters as the distribution size of particles, their shape [33–35]. The theoretical value of $C=0.64$ is strictly valid for particles with spherical shape and similar sizes. It is assumed in this study that ratio of cylinder diameter ($D=2R$) to particle diameter (d), $\beta=2R/d$ is optimal for axial hydrodynamic dispersion [36,37].

The volume of the reactive zone (V_{rz}), the volume of solid (V_{solid}), the volume of inter-granular pores (V_{pore}), the volume of individual solids (V_i) with the apparent specific weight ρ_i , and the thickness of the reactive zone (h_{rz}) are given by Eq. (1) through Eq. (6):

$$V_{\text{rz}} = \frac{\pi D^2 h_{\text{rz}}}{4} \quad (1)$$

$$V_{\text{rz}} = V_{\text{solid}} + V_{\text{pore}} \quad (2)$$

$$V_{\text{solid}} = C V_{\text{rz}} \quad (3a)$$

$$V_{\text{pore}} = (1 - C) V_{\text{rz}} \quad (3b)$$

$$V_{\text{solid}} = \sum V_i = V_{\text{solid}1} + V_{\text{solid}2} + V_{\text{solid}3} + \dots \quad (4)$$

$$V_i = \frac{m_i}{\rho_i} \quad (5)$$

$$h_{\text{rz}} = \frac{4V_{\text{rz}}}{\pi D^2} = \frac{4V_{\text{solid}}}{C\pi D^2} \quad (6)$$

3.1. Volumetric solid fractions in the reactive zone

Replacing V_{solid} in Eq. (2) by its expression from Eq. (4) yields:

$$V_{\text{rz}} = V_{\text{solid}} + V_{\text{pore}} = V_{\text{pore}} + \sum V_i \Rightarrow \alpha_{\text{pore}} + \sum \alpha_i = 1 \quad (7)$$

where α_{pore} and α_i are the volumetric fractions of the inter-granular pores and of the individual solid phase “i” in the column respectively. The fractions are related to the volume of the reactive zone V_{rz} ($\alpha_{\text{pore}} = V_{\text{pore}}/V_{\text{rz}}$ and $\alpha_i = V_{\text{solid } i}/V_{\text{rz}}$).

Eq. (7) suggests that $\sum \alpha_i$ is necessarily equal to C. Thus, Eq. (2) should be written:

$$V_{\text{rz}} = V_{\text{solid}} + V_{\text{pore}} = V_{\text{rz}} (\alpha_{\text{pore}} + \sum \alpha_i) \quad (8)$$

For instance, for a system containing a mixture of four solid phases, Eq. (7) should read:

$$\alpha_{\text{pore}} + \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 = 1 \quad (8a)$$

or

$$\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 = 1 - \alpha_{\text{pore}} = C \quad (8b)$$

Eq. (8) is very important for the calculations of the amounts of individual additives to achieve wished material mixtures as it will be discussed in the next section. Eq. (8b) suggests that α_i is necessarily a fraction of C. Thus, a simple rule of proportion can be established to calculate α_i for each proportion P_i of the solid phase. C necessarily corresponds to 100% solid. The relation between α_i and P_i is given by Eq. (9):

$$\alpha_i = \frac{CP_i}{100} \quad (9)$$

Table 2 gives some values of α_i for selected relevant P_i values. For example, if a quaternary system should be made up of 40% of material A, 30% material B, 20% material C and 10% material D, the coefficients to be used are: 0.256, 0.192, 0.128 and 0.064 respectively. A quaternary system seems to be strange or complicated. However, such a system could comprise Fe^0 as basic reactive material, MnO_2 to sustain Fe^0 reactivity, pumice as storage solid and quartz as non-porous inert filling material.

3.2. Initial porosity of reactive the zone

In the case of non porous spherical particles, the initial porosity of the reactive zone Φ_0 is the inter-granular porosity α_{pore} and is given by Eq. (10) [32].

$$\Phi_0 = 1 - C \quad (10)$$

If individual particles are porous, the intra-granular porosity should be considered [32]. In this case the initial porosity should read:

$$\Phi_0 = (1 - C) + \sum \alpha_i \phi_i \quad (11)$$

where C is the compactness of the reactive zone, α_i the volumetric fraction of the solid i (Table 2) and ϕ_i its internal porosity.

Eqs. (1)–(11) are the basis for purposeful experimental design as will be discussed below for selected cases.

4. Designing some Fe^0 systems

4.1. A four component system

For the design of a quaternary system of Fe^0 , sand, pumice and MnO_2 , Eq. (8) can be used:

$$V_{\text{rz}} = V_{\text{rz}}(\alpha_{\text{pore}} + \alpha_{\text{Fe}} + \alpha_{\text{sand}} + \alpha_{\text{pumice}} + \alpha_{\text{MnO}_2})$$

$$V_{\text{rz}} = \alpha_{\text{pore}}V_{\text{rz}} + \alpha_{\text{Fe}}V_{\text{rz}} + \alpha_{\text{sand}}V_{\text{rz}} + \alpha_{\text{pumice}}V_{\text{rz}} + \alpha_{\text{MnO}_2}V_{\text{rz}}$$

$$V_{\text{rz}} = V_{\text{pore}} + V_{\text{Fe}} + V_{\text{sand}} + V_{\text{pumice}} + V_{\text{MnO}_2}$$

Assuming $V_{\text{rz}} = 1000$ mL, $\alpha_{\text{Fe}} = 0.192$ ($P_{\text{Fe}} = 30\%$), $\alpha_{\text{sand}} = 0.256$ ($P_{\text{sand}} = 40\%$), $\alpha_{\text{pumice}} = 0.128$ ($P_{\text{pumice}} = 20\%$), and $\alpha_{\text{MnO}_2} = 0.064$ ($P_{\text{MnO}_2} = 10\%$), the volume of the materials are 192, 256, 128 and 64 mL respectively and $V_{\text{pore}} = 360$ mL.

Using Eq. (5) ($m_i = \rho_i V_i$), the needed mass of each material can be calculated. Results showed that 1498 g of Fe, 678 g of sand, 82 g of pumice and 224 g of MnO_2 will be used and homogeneously mixed to design the desired column.

The initial porosity of the resulted column is given by Eq. (11)

$$\Phi_0 = (1 - C) + \alpha_{\text{Fe}}\phi_{\text{Fe}} + \alpha_{\text{sand}}\phi_{\text{sand}} + \alpha_{\text{pumice}}\phi_{\text{pumice}} + \alpha_{\text{MnO}_2}\phi_{\text{MnO}_2}$$

But Fe and sand (quartz) are non-porous, therefore Φ_0 is given by:

$$\Phi_0 = (1 - C) + \alpha_{\text{pumice}}\phi_{\text{pumice}} + \alpha_{\text{MnO}_2}\phi_{\text{MnO}_2}$$

Using values above ($\alpha_{\text{pumice}} = 0.128$ and $\alpha_{\text{MnO}_2} = 0.064$), $\phi = 0.80$ (80%) for pumice, and $\phi = 0.25$ (25%) for MnO_2 , give an initial porosity of 0.48 (vs. 0.36 in a pure Fe^0 column).

This example shows an increase of the initial porosity by 33% for the given mixture.

4.2. Working with a constant Fe^0 mass

To work with a constant Fe^0 mass, the volume (V_{Fe}) occupied by the given Fe mass is calculated using Eq. (5). This volume represents a certain fraction of solid in the filter (α_{Fe} in Eq. (8a)). Knowing V_{solid} , the volume of the reactive zone V_{rz} and its thickness h_{rz} can be deduced using Eq. (3a) and Eq. (6).

It is obvious, that h_{rz} depends on the inner diameter of the filter. Accordingly, the simplest way to investigate the effect of bed thickness on the efficiency of Fe^0 beds is to work with a constant Fe^0 mass, representing a fix volumetric percentage of solid and using columns of various internal diameters (D_i).

Working with a constant Fe^0 mass can be regarded as the most powerful tool to achieve comparable results. For example, laboratory column experiments could be routinely performed with 100 g of Fe^0 representing 30 vol.% of the solid in the reactive zone. Calculations show that the reactive zone will occupy a volume of 20 mL. To have such a volume using columns with inner diameters D_1 (2.0 cm), D_2 (2.6 cm) and D_3 (5.0 cm), the column length should be 6.37, 3.77, and 1.02 cm respectively. All columns of Table 1 satisfy this basic condition. However building an homogeneous 1.02 cm layer of “ Fe^0 + additive” could be a difficult task. While repeating the calculations above with 250 g Fe^0 results show that needed column lengths are 15.93, 9.43, and 2.55 cm respectively. While column 1 ($D = 2$ cm, $L = 12$ cm) is no more applicable, filling column 3 ($D = 5$ cm) with only 2.55 cm of homogeneous mixture could still be difficult to achieve. Therefore an objective could be a minimum reactive zone length of 5 cm. To achieve this thickness, a Fe^0 of 500 g is needed for column 3. This is necessarily coupled with longer experimental duration. As a result, it is suggested that columns with more than 3 cm internal diameter are not suitable for short term laboratory experiments. This suggestion is coupled with the desire to save Fe^0 costs in columns and to shorten experimental durations.

4.3. Working with a constant initial porosity

For column experiments performed with a constant Fe^0 mass (e.g., 100 g), using various additives could enable a constant initial porosity (Φ_0). The aim could be for example to experimentally quantify the impact of MnO_2 on Fe^0 bed’s hydraulic permeability.

Table 2
Relation between the volumetric fraction (α_i) of solid materials in the column ($\alpha_{\text{pore}} = 0.36$) and their volumetric percent (P_i) as solid. α_i is obtained by a rule of proportion relative to ($\alpha_{\text{max}} = 0.64$ corresponding to 100% solid). α values are very useful for multi-solid system designs (see text).

P_i	0	10	20	30	40	50	60	70	80	90	100
α_i	0.00	0.064	0.128	0.192	0.256	0.320	0.384	0.448	0.512	0.576	0.640

Table 3
Selected appropriate solutions for Eq. (11b).

α_{quartz}	0.08	0.13	0.16	0.19	0.22
α_{pumice}	0.24	0.19	0.16	0.13	0.1
ϕ_{pumice}	0.33	0.42	0.50	0.62	0.80

The length of the reactive zone will vary as a function of the porosity of the tested additive. Eq. (11) ($\Phi_0 = (1 - C) + \sum \alpha_i \phi_i$) should be solved while fixing one or two variables.

For example, the reference system uses Fe⁰ (100 g representing 50 vol.%) and a limestone with $\phi_{\text{lime}} = 25\%$. A second system having the same initial porosity (Φ_0) and been made up of Fe ($\phi_{\text{Fe}} = 0\%$), quartz ($\phi_{\text{quartz}} = 0\%$) and pumice should be designed. Which pumice amount should be used?

For the reference system, $\alpha_{\text{Fe}} = 0.32$; $\phi_{\text{Fe}} = 0$; $\alpha_{\text{lime}} = 0.32$; and $\phi_{\text{lime}} = 0.25$. Calculations give $\Phi_0 = 1 - C + 0.32 \times 0.25 = 0.44$. Now, Eq. (11) ($\Phi_0 = 0.44$) should be written for the unknown system and solved for ϕ_{pumice} , given $\alpha_{\text{Fe}} = 0.32$ (or $\alpha_{\text{quartz}} + \alpha_{\text{pumice}} = 0.32$). That is, with $\phi_{\text{Fe}} = \phi_{\text{quartz}} = 0$:

$$\Phi_0 = 0.44 = 1 - C + \alpha_{\text{Fe}}\phi_{\text{Fe}} + \alpha_{\text{quartz}}\phi_{\text{quartz}} + \alpha_{\text{pumice}}\phi_{\text{pumice}} \quad (11a)$$

$$\alpha_{\text{pumice}} = \frac{0.08}{\phi_{\text{pumice}}} \quad (11b)$$

The pumices to be used are materials for which Eq. (11b) and the fundamental conditions $\alpha_{\text{quartz}} + \alpha_{\text{pumice}} = 0.32$ and $\phi_{\text{pumice}} < 0.9$ are respected. There are certainly a large number of possible solutions but the appropriate solution will be dictated by pumice's availability. Table 3 summarizes 5 appropriate solutions corresponding to ϕ_{pumice} values varying from 0.33 to 0.80.

Having the α_{pumice} (and α_{quartz}) the volumes and the masses can be derived and used as described above.

5. Concluding remarks

To date, the equivocal results published on contaminant removal in Fe⁰/H₂O systems demonstrate that the physico-chemical mechanisms of the remediation process still remain unclear [38]. Available data were produced and interpreted based on the concept that Fe⁰ is a reducing agent [1–4]. On the other side, available data are characterized by the diversity of experimental conditions under which they are obtained (Table 1). This situation is not favourable for reliable data comparison. In particular, further laboratory column studies aiming at optimising field Fe⁰ bed design efforts should be acquired under reproducible experimental conditions.

The present theoretical study has initiated a new path to an harmonized experimental protocol for column experiments. It is proposed that 100 g or 250 g of Fe⁰ is used in a volumetric proportion not larger than 50%. The equations for material mixtures are established. It is hoped that researchers will use the developed tools to avoid inconsistent results which are most likely the product of inaccurate experimental designs. For example, while bed clogging has been reported as the major drawback of the Fe⁰ technology, most researchers have used experimental designs favouring column clogging (Fe⁰ > 60 vol.%) [32].

Once the mass of Fe⁰ and its volumetric proportion are fixed several other factors can be purposefully discussed. For example,

the impact of: (i) the Fe⁰ average particle size, (ii) the solution pH, (iii) the water composition, and (iv) water flow velocity. In all the case the description of the experimental protocol should include and extensive description of used materials (density, porosity, measured bed porosity). Finally, because clogging is the major problem of Fe⁰ beds, expertise from other branches of environmental science dealing with porous media clogging could be helpful for proper Fe⁰ bed design. In particular, much impetus could come from the impact of bio-clogging on the evolution of the porosity of constructed wetland [39–42].

References

- [1] S.F. O'Hannesin, R.W. Gillham, Long-term performance of an in situ "iron wall" for remediation of VOCs, *Ground Water* 36 (1998) 164–170.
- [2] A.D. Henderson, A.H. Demond, Long-term performance of zero-valent iron permeable reactive barriers: a critical review, *Environ. Eng. Sci.* 24 (2007) 401–423.
- [3] A.B. Cundy, L. Hopkinson, R.L.D. Whitby, Use of iron-based technologies in contaminated land and groundwater remediation: a review, *Sci. Total Environ.* 400 (2008) 42–51.
- [4] R. Thiruvengkatchari, S. Vigneswaran, R. Naidu, Permeable reactive barrier for groundwater remediation, *J. Ind. Eng. Chem.* 14 (2008) 145–156.
- [5] A. Ghauch, H.A. Assi, A. Tuqan, Investigating the mechanism of clofibrac acid removal in Fe⁰/H₂O systems, *J. Hazard. Mater.* 176 (2010) 48–55.
- [6] A. Ghauch, H.A. Assi, S. Bdeir, Aqueous removal of diclofenac by plated elemental iron: bimetallic systems, *J. Hazard. Mater.* 182 (2010) 64–74.
- [7] C. Noubactep, A. Schöner, P. Woaf, Metallic iron filters for universal access to safe drinking water, *Clean: Soil, Air, Water* 37 (2009) 930–937.
- [8] M.I. Litter, M.E. Morgada, J. Bundschuh, Possible treatments for arsenic removal in Latin American waters for human consumption, *Environ. Pollut.* 158 (2010) 1105–1118.
- [9] C. Noubactep, S. Caré, Enhancing sustainability of household water filters by mixing metallic iron with porous materials, *Chem. Eng. J.* 162 (2010) 635–642.
- [10] C. Noubactep, S. Caré, Dimensioning metallic iron beds for efficient contaminant removal, *Chem. Eng. J.* 163 (2010) 454–460.
- [11] A.M. Gottinger, D.J. Wild, D. McMartin, B. Moldovan, D. Wang, Development of an iron-amended biofilter for removal of arsenic from rural Canadian prairie potable water, in: X.A.M. Marinov, C.A. Brebbia (Eds.), *Water Pollution*, WIT Press, Ashurst, Southampton, 2010, pp. 333–344.
- [12] C. Noubactep, A. Schöner, Metallic iron: dawn of a new era of drinking water treatment research? *Fresen. Environ. Bull.* 19 (2010) 1661–1668.
- [13] C. Noubactep, Metallic iron for safe drinking water worldwide, *Chem. Eng. J.* 165 (2010) 740–749.
- [14] C. Noubactep, Processes of contaminant removal in "Fe⁰-H₂O" systems revisited. The importance of co-precipitation, *Open Environ. J.* 1 (2007) 9–13.
- [15] C. Noubactep, A critical review on the mechanism of contaminant removal in Fe⁰-H₂O systems, *Environ. Technol.* 29 (2008) 909–920.
- [16] C. Noubactep, An analysis of the evolution of reactive species in Fe⁰/H₂O systems, *J. Hazard. Mater.* 168 (2009) 1626–1631.
- [17] C. Noubactep, Elemental metals for environmental remediation: learning from cementation process, *J. Hazard. Mater.* 181 (2010) 1170–1174.
- [18] C. Noubactep, The fundamental mechanism of aqueous contaminant removal by metallic iron, *Water SA* 36 (2010) 663–670.
- [19] C. Noubactep, The suitability of metallic iron for environmental remediation, *Environ. Progr. Sust. Energy* 29 (2010) 286–291.
- [20] J.O. Peterson, G.F. Lee, Sorption capacity estimation for activated carbon packed columns, *Water Res.* 5 (1971) 717–721.
- [21] C. Su, R.W. Puls, In situ remediation of arsenic in simulated groundwater using zerovalent iron: laboratory column tests on combined effects of phosphate and silicate, *Environ. Sci. Technol.* 37 (2003) 2582–2587.
- [22] S. Kundu, A.K. Gupta, Analysis and modeling of fixed bed column operations on As(V) removal by adsorption onto iron oxide-coated cement (IOCC), *J. Colloid Interface Sci.* 290 (2005) 52–60.
- [23] K.L. McGeough, R.M. Kalin, P. Myles, Carbon disulfide removal by zero valent iron, *Environ. Sci. Technol.* 41 (2007) 4607–4612.
- [24] T.-H. Wang, M.-H. Li, S.-P. Teng, Bridging the gap between batch and column experiments: a case study of Cs adsorption on granite, *J. Hazard. Mater.* 161 (2009) 409–415.
- [25] C. Noubactep, A.-M.F. Kurth, M. Sauter, Evaluation of the effects of shaking intensity on the process of methylene blue discoloration by metallic iron, *J. Hazard. Mater.* 169 (2009) 1005–1011.
- [26] C. Noubactep, T. Licha, T.B. Scott, M. Fall, M. Sauter, Exploring the influence of operational parameters on the reactivity of elemental iron materials, *J. Hazard. Mater.* 172 (2009) 943–951.

- [27] M. Gheju, I. Balcu, Hexavalent chromium reduction with scrap iron in continuous-flow system. Part 2. Effect of scrap iron shape and size, *J. Hazard. Mater.* 182 (2010) 484–493.
- [28] C. Noubactep, Characterizing the reactivity of metallic iron in $\text{Fe}^0/\text{EDTA}/\text{H}_2\text{O}$ systems with column experiments, *Chem. Eng. J.* 162 (2010) 656–661.
- [29] A. Luna-Velasco, R. Sierra-Alvarez, B. Castro, J.A. Field, Removal of nitrate and hexavalent uranium from groundwater by sequential treatment in bioreactors packed with elemental sulfur and zero-valent iron, *Biotechnol. Bioeng.* 107 (2010) 933–942.
- [30] P. Westerhoff, J. James, Nitrate removal in zero-valent iron packed columns, *Water Res.* 37 (2003) 1818–1830.
- [31] N. Moraci, P.S. Calabrò, Heavy metals removal and hydraulic performance in zero-valent iron/pumice permeable reactive barriers, *J. Environ. Manage.* 91 (2010) 2336–2341.
- [32] C. Noubactep, S. Caré, F. Togue-Kamga, A. Schöner, P. Woaf, Extending service life of household water filters by mixing metallic iron with sand, *Clean: Soil, Air, Water* 38 (2010) 951–959.
- [33] Y.B.G. Varma, T. Gopichand, D. Venkateswarlu, Particle size distribution in compacts of solids, *J. Chem. Eng. Data* 13 (1968) 498–503.
- [34] A. Felinger, G. Guiochon, Optimization of the experimental conditions and the column design parameters in displacement chromatography, *J. Chromatogr. A* 609 (1992) 35–47.
- [35] S.I.F. Badawy, M.A. Hussain, Effect of starting material particle size on its agglomeration behavior in high shear wet granulation, *AAPS Pharm. Sci. Technol.* 5 (2004) (Article 38) <http://www.aapspharmscitech.org>.
- [36] R.S. Maier, D.M. Kroll, R.S. Bernard, S.E. Howington, J.F. Peters, H.T. Davis, Enhanced dispersion in cylindrical packed beds, *Philos. Trans. R. Soc. Lond. A* 360 (2002) 497–506.
- [37] R.S. Maier, D.M. Kroll, H.T. Davis, Diameter-dependent dispersion in packed cylinders, *AIChE J.* 53 (2007) 527–530.
- [38] S. Comba, A. Di Molfetta, R. Sethi, A comparison between field applications of nano-, micro-, and millimetric zero-valent iron for the remediation of contaminated aquifers, *Water, Air, Soil Pollut.* 215 (2011) 595–607.
- [39] M. Thullner, Comparison of bioclogging effects in saturated porous media within one- and two-dimensional flow systems, *Ecol. Eng.* 36 (2010) 176–196.
- [40] A. Wanko, G. Tapia, R. Mosé, C. Gregoire, A new empirical law to accurately predict solute retention capacity within horizontal flow constructed wetlands, *Ecol. Eng.* 37 (2011) 636–643.
- [41] D. Yuan, L. Zhang, B. Xi, L. He, C. Yan, H. Liu, Design and performance of a filtration-adsorption pool train and drawing water system for small urban recreational water pollution control, *Ecol. Eng.* 37 (2011) 648–653.
- [42] A. Brovelli, O. Carranza-Diaz, L. Rossi, D.A. Barry, Design methodology accounting for the effects of porous medium heterogeneity on hydraulic residence time and biodegradation in horizontal subsurface flow constructed wetlands, *Ecol. Eng.* (2010) 031, doi:10.1016/j.ecoleng.2010.04.