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Enhancing sustainability of household water filters by mixing metallic iron with porous materials

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ABSTRACT

This study conceptually discusses the feasibility of enhancing the sustainability of conventional iron/sand filter (Fe^0/sand filter) for safe drinking water by partially or totally substituting sand (quartz) by porous materials. Relevant materials included activated carbon, dolomites, limestone, pumice, sandstone, and zeolites. The rational was to use the internal volume of porous additives as storage room for in situ generated iron oxyhydroxides (iron corrosion products) and thus delay time to filter clogging. Based on previous works a filter with a volumetric Fe^0:quartz ratio of 51:49 was used as reference system. The reference system is clogged upon Fe^0 depletion. Results showed that totally substituting quartz by pumice particles having a porosity of 80% yields to a residual porosity of 41%. This encouraging result suggested that the possibility of using Fe^0/MnO_2/pumice systems for a synergic promotion of Fe^0 reactivity (by MnO_2) and filter permeability (by pumice) should be investigated in more details.

Capsule: Partially or totally replacing quartz by porous materials is a potential efficient tool to lengthen iron/sand filter service life.

1. Introduction

Safe drinking water is becoming worldwide an increasingly scarce resource mostly due to industrialization [1–3]. The situation is exacerbated in rural areas of the developing world where no centralized drinking water system is available. Therefore, efforts have been made to develop simple, efficient and affordable methods for safe drinking water production at household or small community level [4–9]. An ideal water treatment system for developing countries should remove all possible biological and chemical contaminants in a single-stage filtration process (prerequisite 1). Only reverse osmosis membranes have been reported to achieve prerequisite 1. However, this high cost technology is not always affordable for the populations in need [1,10–12]. Therefore, efforts to develop simple, efficient and affordable filters (achieving prerequisite 1) for households and/or small communities are an area of ongoing active research [2,3,12–15].

In recent years, a great deal of work has been devoted at identifying suitable, low cost, and readily available materials to be used in efficient household filters. Potential media include activated alumina, agricultural by-products (e.g. rice hulls), apatite, clay minerals, granular activated carbon (GAC), industrial by-products, iron oxide (coated sands), manganese oxide (coated sands), metallic iron (Fe^0), peat and peat moss, phosphate rocks, seaweeds and their derivatives, wood chips, and zeolites [2,3,16,17]. Some enumerated materials are regionally readily available (e.g. apatite, clay minerals, zeolites) at no-expense or at a fairly low cost. However, only metallic iron (Fe^0) is universally available. Next to its universally availability, the superiority of Fe^0 is justified by the fact that during the dynamic process of its aqueous oxidative dissolution (iron corrosion), several classes of biological and chemical contaminant can be removed from water [14,18–23]. In particular Fe^0 beds could quantitatively remove aqueous inorganic (e.g. Mo^{VI}) and organic (e.g. non-polar carboxylated organics) substances that are not readily removed by iron oxyhydroxides [24,25]. Therefore, upon proper design, Fe^0 filters necessarily achieve prerequisite 1.

Ideally, a household filter should reduce contaminant concentrations to acceptable levels whilst retaining adequate permeability and reactivity over extended time periods (e.g. 12 months). Due to the volumetric expansive nature of iron corrosion [26–29], designing iron filters with long-term adequate permeability is a challenge for the scientific community [30]. In fact, very efficient Fe^0 filters (e.g. the 3-Kolshi filter) for safe drinking water have been tested in Bangladesh and Nepal for arsenic removal [31–34] but were abandoned because of service lives of only 6–24 weeks [35–37]. Hussam [37] reported that 3-Kolshi filters were “highly functional, but not sustainable” as the filters experienced perme-

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Table 1

Overview on the objectives of using iron/sand mixtures and relationship between percent iron mass (wt%) and percent iron volume (vol%). The conventional expression of the iron amount (wt%) does not directly accounts for the expansive nature of iron corrosion. For example the often used 1:1 (50 wt% Fe^0) corresponds to 25.4 vol% Fe^0. Filter or column clogging due to iron corrosion alone will not occur (threshold value 51 vol% Fe^0).

Iron (wt%)	Iron (kg)	Sand (kg)	Iron (vol%)	Scale	Objective	Ref.
22	6,100	21,500	8.8	Pilot study	Sustained permeability	[31]
20	0.60	2.40	7.8	Lab columns	Sustained reactivity	[33]
50	1.50	1.50	25.4			
100	3.00	0.00	100.0			
25	0.02	0.06	10.2	Lab columns	Fe^0 cost reduction	[37]
50	0.04	0.04	25.4			
75	0.06	0.02	50.5			
85	0.07	0.01	65.8			
100	0.08	0.00	100.0			

ability loss after 3–6 months. The alternative to 3-Kolshi filters was an improved filter called SONO filters [13,33,37]. The heart of SONO filters is a manufactured porous composite iron matrix (CIM). CIM is manufactured from Fe^0 and resulted filters could work for up to 11 years [37].

The present theoretical work is part of ongoing efforts, aiming at reviving conventional Fe^0 filters. The objective is to design efficient stand-alone Fe^0 filters for households and small communities. A recent article [30] has shown that mixing non-porous sand (quartz) with Fe^0 is an efficient way to lengthen Fe^0 filter service live while saving up to the half amount of used Fe^0. It was shown that a filter with 51 vol% Fe^0 necessarily has a longer service live than the conventional iron filter (100% Fe^0), likely with the same efficiency. In the present work calculations will be made to access the possibility to further optimize filter efficiency by partly or entirely replacing quartz by porous materials. Relevant materials (Supporting Information) included activated carbon and natural minerals (e.g. MnO_2, TiO_2, zeolites) and rocks (e.g. dolomite, limestone, pumice, sandstone). For the sake of clarity, the $Fe^0/sand/H_2O$ system will first be presented.

2. The Fe^0/sand/H_2O system

2.1. Descriptive aspects

Aqueous contaminant removal in the presence of Fe^0 (e.g. in Fe^0/H_2O systems) is an heterogeneous reaction ideally involving five steps: (i) contaminant mass-transfer from the bulk solution to the Fe^0 surface, (ii) contaminant adsorption on the Fe^0 surface, (iii) chemical reaction at the Fe^0 surface, (iv) desorption of the reaction products from Fe^0 surface, and (v) mass-transfer of the reaction products into the bulk solution [38,39]. The kinetics of the process of contaminant removal in a Fe^0/H_2O system are necessarily dependent on the availability of the Fe^0 surface as well as the rate of mass-transfer of the contaminant to the reactive Fe^0 surface (Fe^0 accessibility). Accordingly, mixing an inert material (e.g. sand) and Fe^0 is coupled with a decrease of the contaminant removal rate as the pathway to the Fe^0 surface is lengthened (assertion 1: mixing sand and Fe^0 decreases Fe^0 accessibility).

The process of aqueous iron oxidative dissolution at $pH > 4.0$ is characterized by the expansive nature of iron corrosion products (iron oxides and oxyhydroxides or simply iron oxyhydroxides). Depending on the nature of iron oxyhydroxide, a volumetric expansion of up to 6.4 has been reported [28]. In other words, an iron oxyhydroxide molecule may occupy a volume up to 6.4 times the volume of atomic Fe in the lattice structure. Accordingly, a pure iron bed (100% Fe^0) will clog sooner than a bed containing the same iron mixed with inert material (e.g. sand). Therefore, mixing sand and Fe^0 should be regarded as a tool to sustain permeability of an iron bed (assertion 2: mixing sand and Fe^0 increases bed service life).

Assertion 1 and assertion 2 clearly show that the role of sand in a Fe^0 bed is antagonistic. Accordingly, a well-designed Fe^0/sand bed must conciliate limited Fe^0 accessibility and extended service life. It is obvious that a critical volumetric Fe^0:sand ratio exists above which bed clogging will occur upon Fe^0 depletion. That is the Fe^0 proportion for which in situ generated iron oxyhydroxides will fill the inter-granular pore volume of the initial bed. The results of such calculations for the Fe^0:quartz is recalled in the next paragraph.

2.2. Literature review

Iron has been mixed with inert materials (including gravel and sand) since the early stage of investigations regarding the applicability of iron walls for groundwater remediation [40,41]. However, there has been no systematic study designed to rationalize the effects of sand on the efficiency of Fe^0 beds. Most researchers employ varying Fe^0:sand ratios for filtration beds in the laboratory and in the field on a pragmatic basis [42–48]. Fe^0:sand ratios are often given in weight percent without information on the available pore volume nor precise data on further operational conditions including the high of the Fe^0/sand bed (Table 1). As a result, controversial reports for the same systems have been reported. For example, while investigating As removal by Fe^0 in packed beds, Lien and Wilkin [46] concluded that Fe^0 alone performed better than a 50:50 sand:Fe^0 mixture. In contrary, Westerhoff et al. [47] observed higher As removal in a Fe^0:sand bed than with Fe^0 alone.

2.3. The importance of volumetric ratios

The main concern of available data on $Fe^0/sand/H_2O$ systems is their comparability. When the Fe^0:sand ratios are given in percent it is not always specified whether it is volumetric or weight based. However, given the large difference between the density of sand (<2000 kg/m^3) and iron (7800 kg/m^3), it should always explicitly said whether given percent are volumetric (vol%) or weight (wt%). Even in some cases (e.g. ref. [42]), the Fe^0:sand ratio is given without the high of the reactive zone nor the mass of either sand or iron.

2.3.1. Rationale for use the volumetric ratio

The sole calculation that could be founded to rationalize used Fe^0:sand ratios is given by Leupin et al. [45] and mentioned by Gottinger [15,49]. The authors used 2.5 g of Fe^0 which occupied a volume of 0.32 cm^3 and lead to 4.78 g of $Fe(OH)_3$ with a volume of 1.35 cm^3 (i.e. 4.78 cm^3 as reported in the original work). Then the internal porosity of sand (40%) is considered to estimate the volume of sand necessary to contain the 1.35 cm^3 of iron oxides. Leupin et al. [45] came to the conclusion that at least 9.9 cm^3 (i.e. 35 cm^3) of sand should be used per gram of iron to avoid the clogging of more than a third of the void volume.

The calculus of Leupin et al. [45], considered as a rough estimate by the authors, has to be improved because they have not taken into account the inter-granular voids in the Fe^0/sand bed. In fact, the filter has to be considered as a granular medium with two types of porosity: (i) the internal porosity of particle (as mentioned in ref. [45]) and (ii) the inter-granular voids as a function of the compactness of the granular medium. A recent result [30] has allowed modelling the clogging of Fe^0/quartz bed. Quartz is an inert, non-porous material which can not contribute to porosity loss. This modelling gives the evolution of the inter-granular void as a function of the proportion of reactive Fe^0 in the Fe^0:quartz mixture. The results showed that it is possible to avoid the clogging of the filter by mixing Fe^0 particles with quartz particles. In particular, it was shown that 51 vol% Fe^0 (25 wt% when Fe^0 is mixed with quartz) is the critical proportion for which system clogging (porosity loss) will occur upon Fe^0 depletion. The present paper attempts to rationalize the admixture of Fe^0 particle with porous particles, including sandstone as used by Leupin et al. [45]. The filling of the total porosity (inter-particles voids and internal porosity) will be considered. The next section will discuss the efficiency of a Fe^0/sand filter.

3. Relevant parameters influencing the efficiency of the Fe^0/sand filter

3.1. Permeability of granular materials

Water permeability is essential for Fe^0/sand filter efficiency because it determines the rate of flow and, thus, the filtration ability. Many models have been proposed to relate the water permeability of granular medium to their microstructure characteristics [50–54]. These models show that permeability is controlled by the packing, shape, sorting (particle size distribution), and porous structure of used granular material, but it appears that porosity and tortuosity of granular materials are two of the primary factors that control water flow process [53–58]. In the most general way, permeability depends on the total porosity which is the ratio of the total volume of voids to the total volume of material. More importantly, however, permeability depends on the way in which the total porosity is distributed and thus on the effective porosity. The effective porosity characterizes the degree to which available pores are interconnected. As a rule, if all pores of a granular material are well interconnected, the total porosity is equal to the effective porosity. Tortuosity can be defined as the ratio of the real length that the water travels inside a filter to the thickness of the filter. For a mixture of non-porous particles, the tortuosity can be simply estimated as a function of the total porosity considering the solid grains as spherical inclusions in a fluid phase [59,60].

An idealized conventional Fe^0/sand filter is made up of spherical iron and quartz particles of approximately equal diameter. The non-porous spherical particles provide ample, unrestricted void spaces that are free from smaller grains and are very well linked. Consequently, a Fe^0/sand filter initially has a high permeability which is related to the total porosity as water flow will occur through the inter-particular voids. In case of using porous particles with poorly interconnected internal voids (as for pumices, ref. [57] and ref. therein), the water permeability is essentially related to the effective porosity due to the inter-particular voids. In this case the tortuosity of the mixing only depends on the effective porosity. Indeed, part of the water may remain apparently stagnant in the internal pores of particles and slowly diffuses out of the pores.

3.2. Efficiency of a Fe^0/sand filter

Due to the expansive nature of iron corrosion the voids are progressively filled by (i) in situ generated iron oxyhydroxides, (ii) immobilized contaminants and (iii) in situ generated biofilms [12,23,61,62]. The ability to accurately predict the process dependent evolution of the permeability of a Fe^0/sand filter depends on a detailed description of the processes yielding to porosity loss. In this study, the contribution of biofilms and contaminants to porosity loss is not considered. The volumetric expansive nature of iron corrosion is considered as the sole important path. A second simplification is necessary as iron oxyhydroxides are also porous in nature. It is considered that the pores of generated iron oxides are well interconnected. In this case, the filter permeability is solely modified by the process of oxide formation (pore filling). The permeability of a Fe^0/sand filter typically decreases from the beginning of the operation to the time of complete pore filling by iron oxyhydroxides (porosity equals zero).

The suitability of Fe^0 as reactive medium for drinking water filters relies on two essential characteristics: (i) the interactions of corroding iron with contaminants (adsorption, co-precipitation/enmeshment, oxidation, reduction), and (ii) the improved size exclusion by virtue of the expansive nature of iron corrosion. The efficiency of an iron filter depends on several factors including particle size of Fe^0, initial contaminant concentration, and influent pH. These factors are determinant to the time at which the initial porosity is reduced to zero. The present discussion will not address how these factors affect Fe^0 reactivity. The evolution of filter permeability due to filling of porosity by iron oxyhydroxides which is the most important parameter determining filter service life will be solely addressed.

3.3. Aim of the paper

Permeability variation in an iron filter is important for predicting filter service life. Understanding the dependence of filter permeability on the extent of iron consumption would be decisive in designing filters. An ideal iron filter is a random pack of identical spheres in a column. The porosity of such an ideal system has a fundamental value of 36% assuming a compactness of 64% with soft vibration [30,54–56]. The actual porosity value for a Fe^0/sand filter will depend on the size distribution of filling particles but this porosity is a good approximation for such mixing. As iron consumption progresses, residual Fe^0 particles become compacted and cemented, and the initial porosity (ideally 36%) progressively decreases down to zero. At porosity zero, the filter is clogged (Fig. 1). Cemented Fe^0 particles form a continuous frame which had been called “cake”. The described dynamic evolution of the porosity is somewhat equivalent to the formation of quartz (porosity zero) from sandstone (porosity 40%) by diagenesis [63] (Fig. 2).

As described above, clogging is inherent to Fe^0 filters working at near neutral pH values (more exactly at $pH > 4.0$). Therefore, lengthen filter service live initially depends on the ability to create additional space for in situ generated iron oxyhydroxides while maintaining filter efficiency. An obvious possibility is to use porous material which internal porous structure may store in situ generated iron oxyhydroxides (Fig. 1) leading to increase the residual effective porosity and thus the residual permeability of the mixing.

4. Efficiency of the Fe^0/sand/porous materials filter

4.1. Background

This work tests the hypothesis, that porous minerals and rocks have the potential to enhance the sustainability of metallic iron

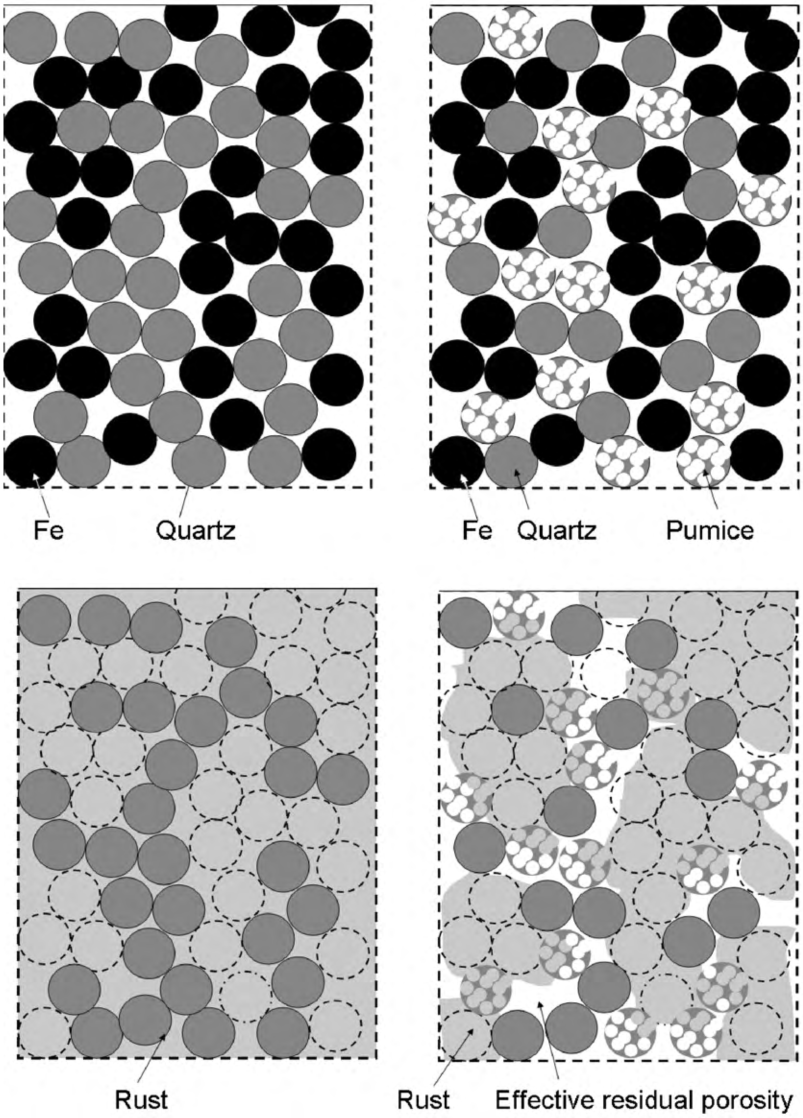

Fig. 1. Schematic diagrams showing the extend of porosity loss as influenced by the substitution of a part of sand by a porous material: initial stage (top) and final stage (down). The final stage corresponds to Fe^0 depletion (100% consumption). At Fe^0 depletion, the residual porosity is zero for the conventional Fe^0/sand filter. The effective residual porosity is increased for Fe^0/sand/pumice filter (see text).

(Fe^0) filter. Therefore, it is not important to work with a well-characterized porous material. The concept of "critical porosity" [63] will be used for the discussion. Critical porosity is defined as "the porosity above which the rock can exist only as a suspension". The critical porosity, separates two fundamentally different domains – one of consolidated, frame-supported rocks, and another of fluid-supported suspensions (see ref. [63] for more details). Table 2 summarizes the critical porosity value of various rock types. The major feature from Table 2 is that the potential exists to find rocks of porosity 0% (quartz) to 80% (pumice). The highest value from Table 2 will be used to qualitatively demonstrate the feasibility of extending filter service live by replacing sand by porous material in a conventional Fe^0/sand filter. Some suitable porous materials are presented in Supporting Information. It can be noticed that the permeability of porous materials is linked to their porous structure (pore connectedness). In general, due to diffusive processes in porous structures, slower kinetics of water flow will be observed comparative to a conventional Fe^0/sand filter. Regardless from the pore connectedness, it is expected that material porosity will effectively store in situ generated iron oxyhydroxides.

This section presents modelling works to evaluate the feasibility of lengthening the service live of conventional Fe^0/sand filter for safe drinking water by partially or totally substituting sand (quartz) by a porous material. The delay time to filter clogging is evaluated from the evolution of the total residual porosity. Results for pumices are presented and discussed. It can be noticed that the calculus can

Table 2
Density and critical porosity of selected potential additives for improved reactivity of conventional Fe^0 filters. All critical porosity's values for rocks are from Nur et al. [63]. The value for activated carbon is an indicative average value from the literature.

Material	Density (g/cm^3)	Average density (g/cm^3)	Critical porosity (%)
Quartz	2.65	–	0
Sandstone	2.2–2.8	2.50	40
Limestone	2.3–2.7	2.50	40
Dolomites	2.8–2.9	2.85	40
Pumice	0.36–0.91	0.64	80
Chalks	1.8–2.6	2.20	65
Rock salts	2.5–2.6	2.55	40
Oceanic basalts	2.8–3.0	2.90	20
Activated carbons	0.44–2.50	1.47	55

Table 3
Composition and thickness (H_{rz}) of the reactive zone for 3 kg of Fe^0. Fe^0 and sand particles are 1.2 mm in diameter. The value $C = 0.64$ is considered for compactness. The residual porosity $\Phi/\Phi_0 = 0$ is obtained for 100% consumed Fe.

$[Fe^0]_0$ (vol%)	$[Fe^0]_0$ (kg)	$[Sand]_0$ (kg)	H_{rz} (cm)	Φ/Φ_0 (−)	$[Fe^0]_\infty$ (%)	$[Fe^0]_\infty$ (kg)
51	3.00	0.98	1.67	0.0	0.00	0.00

Fig. 2. Schematic diagrams showing the evolution of the porous structure during the diagenesis of quartz. As diagenesis progresses, sand grains become compacted and cemented. The initial porosity (40%) decreases down to zero. Modified after ref. [63].

be made with other porous particles (by changing its critical porosity); the results will be slightly different but the general conclusions will remain identical.

4.2. Design and modelling

A reactive zone (rz) of Fe^0 with a thickness H_{rz} is introduced in the fine sand layer of a conventional biosand filter (Fig. 3) [7,64]. The reference reactive zone is made up of 51 vol% Fe^0 and 49 vol% quartz. This system was demonstrated to allow increased filter efficiency compared to a conventional reactive zone with 100% Fe^0 [30]. The characteristics of the reactive zone are given in Table 3. All particles are considered spherical in shape with an average diameter of 1.2 mm. The specific weight of Fe^0 and quartz are $\rho_{Fe} = 7{,}800\ kg/m^3$ and $\rho_{sand} = 2{,}650\ kg/m^3$ respectively. The biosand filter is supposed to work under anoxic conditions. Thus, Fe_3O_4 is the sole iron corrosion product with a coefficient of volumetric expansion η equal to $V_{Fe3O4}/V_{Fe} = 2.1$.

Quartz particles are replaced by porous particles in order to increase the initial total porosity Φ_0 of the reactive zone given by:

$$\Phi_0 = \Phi_{0(51\%\ \mathrm{Fe}-49\%\ \mathrm{Quartz})} + \varphi_{pp} f_{pp} \tag{1}$$

where the porosity $\Phi_{0(51\%\,\mathrm{FE}-49\%\,\mathrm{sand})} = 1 - C$. C is the compactness of the granular material ($C = 0.64$) [54–56] and "$1 - C$" corresponds to the inter-particular voids (porosity of the mixing without porous particles);

φ_{pp} (−) is the critical porosity of the porous particles (e.g. 0.8 for pumice, Table 2); f_{pp} (−) is the porous particle volume fraction determined by $fpp = Vpp/V$ with V_{pp} the volume of the porous particles and V the volume of the reactive zone.

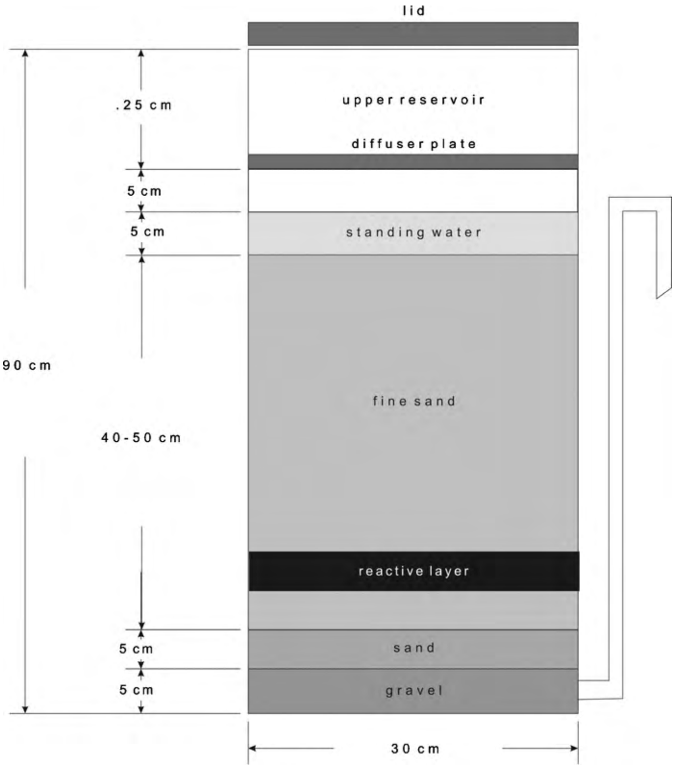

Fig. 3. Schematic diagram of an iron-reactive-zone containing biosand filter. The illustration highlights major principles and generic size dimensions. Modified after ref. [64]. The thickness of a reactive layer containing 3 kg Fe^0 representing 51% (vol.) of the filling is 1.67 cm (see Table 3).

The filling of the porosity by iron oxyhydroxides can be estimated from a simplified modelling (Fig. 1) based on the following assumptions:

(i) uniform corrosion: the diameter reduction of the particle is the same for all the Fe particles,
(ii) the compactness C and then the initial porosity $\Phi_{0(51\%\,\mathrm{FE}-49\%\,\mathrm{sand})}$ remain constant. The volume of the granular material is not modified by the corrosion process: no pressure induced by rust formation around Fe particles and

Table 4
Composition of the reactive zone for 51% Fe^0 (3 kg of Fe^0) and 49% of additive particles (quartz or porous materials). Fe^0 and additives particles are 1.2 mm in diameter. The residual porosity $\Phi/\Phi_0 = 0$ is given for 100% consumed Fe. The value $C = 0.64$ is considered for compactness. The thickness H_{rz} of the reactive zone is 1.67 cm. The specific weight and the critical porosity of pumice are respectively $\rho_{pumice} = 640\ kg/m^3$ and $\varphi_{pumice} = 0.8$ (−).

Pumice (%)	Fe^0 (kg)	Quartz (kg)	Pumice (kg)	Φ_0 (−)	Φ/Φ_0 (−)
0	3	0.98	0.00	0.36	0.00
10	3	0.88	0.02	0.39	0.07
20	3	0.78	0.05	0.41	0.12
30	3	0.69	0.07	0.44	0.18
40	3	0.59	0.09	0.46	0.22
50	3	0.49	0.12	0.49	0.26
60	3	0.39	0.14	0.51	0.30
70	3	0.29	0.17	0.54	0.33
80	3	0.20	0.19	0.56	0.36
90	3	0.10	0.21	0.59	0.39
100	3	0.00	0.24	0.61	0.41

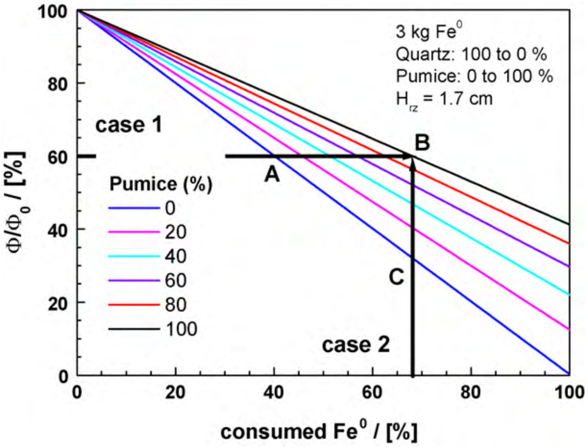

Fig. 4. Evolution of the residual porosity Φ/Φ_0 versus the % consumed Fe for 51% Fe^0 (3 kg of Fe^0) and 49% of quartz/pumice particles. Fe^0 and quartz/pumice are 1.2 mm in diameter. The %consumed Fe is given by $\%\ \text{consumed Fe} = 100(R_0^3 - R^3)/R_0^3$ with R_0 the initial radius of Fe^0 and R the residual radius. The value $C = 0.64$ is considered for compactness. The thickness H_{rz} of the reactive zone is 1.67 cm. The specific weight and the critical porosity of pumice are respectively $\rho_{pumice} = 640\ \text{kg/m}^3$ and $\varphi_{pumice} = 0.8$ (−).

no compaction of the Fe^0/sand mixture during the corrosion process.

(iii) iron oxyhydroxides are fluid enough to progressively fill the available pore space between particles ($\Phi_{0(51\%\,FE-49\%\,sand)}$) and the porosity of the porous particles. The porous particles are enough close to the iron particles to be filled by the iron oxyhydroxides.

Under these assumptions, the residual porosity of the mixing Fe^0-quartz-porous particles is given by:

$$\Phi/\Phi_0 = 1 - \frac{N(\eta - 1)4/3\pi(R_0^3 - R^3)}{V\Phi_0} \qquad (2)$$

where R_0 (m) is the initial radius of the iron particle, R (m) is the residual radius of the consumed iron particle and η the coefficient of volumetric expansion.

The proportion of consumed iron (% consumed Fe) is given by:

$$\%\ \text{consumed Fe} = 100\left(\frac{R_0^3 - R^3}{R_0^3}\right) \qquad (3)$$

4.3. Results and discussion for Fe^0/quartz/pumice mixture

The total residual porosity of the mixture Fe^0/quartz/porous particle is given in Table 4 and in Figs. 4 and 5. Calculations showed that it is possible to increase the total residual porosity by replacing quartz by porous pumice. For instance, totally substituting quartz by pumice particles having a porosity of 80% yields to a residual porosity of 41% when iron is depleted (Table 3, Fig. 4). For a given residual porosity (case 1, Fig. 4), more iron is consumed by replacing quartz by pumice. For instance for $\Phi/\Phi_0 = 60\%$, the % consumed Fe is about 40% for 100% quartz (point A) and 68% for 100% pumice (point B). Accordingly, the long-term reactivity of the filter is improved. Furthermore, for a given % consumed Fe, the residual porosity Φ/Φ_0 increases with increasing proportion of pumice. For 68% consumed Fe^0 (case 2), the residual porosity is about 32% for 100% quartz (point C) and 60% for 100% pumice (point B). The long-term permeability of the filter may be improved by up to 45%.

As shown previously, water permeability depends on the effective porosity and not on the total porosity. Some water can remain more or less stagnant in the internal porous structure of a material exhibiting low interconnectivity of pores (or voids). Water flow in the internal porous structure is always slow compared to water flow in the inter-particular voids. Nevertheless the residual effective porosity of the mixture is increased because corrosion iron products are at least partly stored in the porous structure of particles and not totally in the inter-particular voids (see Figs. 1 and 4). Assuming that the porosity of the porous particles (pumice) is totally filled by iron oxyhydroxides, the residual porosity of the inter-particular voids (effective porosity) is 30% leading to better permeability.

Experimental studies to validate the efficiency of porous materials to lengthen conventional Fe^0/sand filter service life will consist to evaluate the actual permeability related to the storage of iron oxyhydroxides in porous particles. For instance, 3D imaging by X-ray micro tomography will be an efficient tool to evaluate the residual porosity of the inter-particular voids.

4.4. Generalization: Fe^0/quartz/porous materials

The results discussed above for a pumice exhibiting a porosity of 80% can be extended to pumices of various porosities and any other porous particles including activated carbons, dolomites, manganese oxides, rock salts, sandstone, and zeolites. Fig. 5 depicts the general trend of the results are similar on the sole basis of the porosity (Supporting Information). As a rule, the total residual porosity of the filter increases with increasing particle porosity. For example a material with a grain porosity of 90% still exhibits 44% of the initial porosity upon Fe^0 depletion, while a material with a grain porosity of 20% shows a residual porosity of only 15%. In practical laboratory experiments, it may be difficult to homogeneously mix materials of very different densities. Remember that the discussion is based on the volumetric filling of the reactive zone by Fe^0 and additives (quartz and porous materials) having the same size. The used mass of individual porous materials should be calculated from tabulated density's values (Table 2).

Beside the porosity, further physical and chemical properties of individual porous materials should be considered on a case-specific basis. For example, while rocks and activated carbons are inert in water, MnO_{1+x} will be reductively dissolved in Fe^0/sand/H_2O systems. The reductive dissolution of MnO_{1+x} by Fe^{II} (and Fe^0) is necessarily coupled with a volumetric variation (MnO_{1+x} is reduced to MnOOH or dissolved Mn^{II}). However, the discussion of the resulting volumetric variation and its impact on the filter perme-

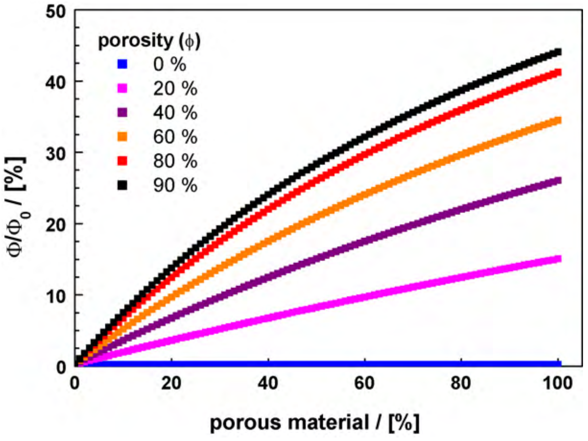

Fig. 5. Evolution of the residual porosity Φ/Φ_0 versus the % replaced quartz particles for 51% Fe^0 (3 kg of Fe^0) and 49% of quartz/porous particles. Fe^0 and additives are 1.2 mm in diameter. The residual porosity $\Phi/\Phi_0 = 0$ is given for 100% consumed Fe for various porous particles with porosity φ_{pp}. The value $C = 0.64$ is considered for compactness. The thickness H_{rz} of the reactive zone is 1.67 cm.

ability is over the scope of this communication. On the other hand, while using activated carbons as porous additive to sustain filter permeability, the pore size distribution of individual materials should be carefully considered. Remember that porous materials are mainly used as magazine for iron oxyhydroxides. Therefore, mesoporous materials are like more suitable than microporous materials because available pores must be accessible to iron oxyhydroxides.

5. Concluding remarks

The theoretical principles essential to experimentally test the use of porous materials to sustain Fe^0/sand filters are exposed in this study. This approach was rendered possible by revisiting the nature of Fe^0-based filters. It was recalled that a filtration system basically works on the size-exclusion principle [14]. Accordingly, at any time, the pore space must be large enough to enable the expansion/compression cycle inherent to iron corrosion. Iron corrosion products (iron oxyhydroxides) reduce filter porosity and thus permeability while increasing size-exclusion efficiency. The first task to enable long-term iron corrosion was to replace a part of Fe^0 by an inert material (e.g. quartz) [30]. Table 1 clearly shows that the conventional approach of expressing the proportion of Fe^0 by a weight percent is not consistent with the fact that pore volume availability is discussed (expansive nature of iron corrosion). For example, 75 wt% Fe^0 corresponds to 50.5 vol% which is almost the threshold value for which system clogging will occur upon Fe^0 depletion (in a Fe^0:quartz system). In other words, for systems with less than 50.5 vol% Fe^0, system clogging due to iron corrosion alone is not likely to occur. Moreover, for much lower Fe^0 contents, contaminant breakthrough is likely. Accordingly, some available data are to be re-evaluated. For example, Bi et al. [48] reported on decline in the reactivity of Fe^0 for trichloroethylene reduction when the iron content fell below 50 wt% (25.4 vol%; only one halve of the threshold value). The discussion above has shown that this iron content is necessarily insufficient for quantitative contaminant removal.

The present study positively tests the possibility to extend Fe^0 reactivity by replacing quartz by porous materials. Substituting quartz by porous material increased the residual porosity from 0% to 40% upon Fe^0 depletion. It is expected, that different porous materials (minerals and rocks) will be tested worldwide for use in Fe^0 filters. The option to synthesize porous materials combining permeability and reactivity sustention should be carefully checked for commercial Fe^0 filters. However, the initial goal of this communication is to encourage researchers to improve Fe^0/sand filter efficiency by adding readily available porous material.

Based on the universal availability of both Fe^0 and suitable porous additives, it can be anticipated that the Millennium Development Goal of halving "by 2015 the proportion of people without sustainable access to safe drinking water" can still be achieved [65].

Supporting information

Selected suitable porous materials to sustain Fe^0/sand filters (8 pages)

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.06.012.

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