Research article

# Designing metallic iron based water filters: Light from methylene blue discoloration

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## ARTICLE INFO

## ABSTRACT

Available water filtration systems containing metallic iron ($Fe^0$ filters) are pragmatically designed. There is a lack of sound design criteria to exploit the full potential of $Fe^0$ filters. A science-based design relies on valuable information on processes within a $Fe^0$ filter, including chemical reactions, hydrodynamics and their relation to the performance of the filter. The aim of this study was to establish a simple method to evaluate the initial performance of $Fe^0$ filters. The differential adsorptive affinity of methylene blue (MB) onto sand and iron oxide is exploited to characterize the evolution of a $Fe^0$/sand system using the pure sand system as operational reference. Five systems were investigated for more than 70 days: pure sand, pure $Fe^0$, $Fe^0$/sand, $Fe^0$/pumice and $Fe^0$/sand/pumice. Individual systems were characterized by the extent of changes in pH value, iron breakthrough, MB breakthrough and hydraulic conductivity. Results showed that for MB discoloration (i) pure sand was the most efficient system, (ii) hybrid systems were more sustainable than the pure $Fe^0$ system, and (iii) the pores of used pumice are poorly interconnected. Characterizing the initial reactivity of $Fe^0$ filters using MB discoloration has introduced a powerful tool for the exploration of various aspects of filter design.

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## 1. Introduction

The water remediation industry has developed a wide range of technologies for the removal of biological, chemical and physical contamination (Ali, 2014; Ghauch, 2015). Relevant treatment approaches include adsorption, chemical and enzymatic degradation, electro-coagulation, membrane filtration, photo-catalysis and oxidation. Adsorption on packed beds has been established as the most popular treatment process for water treatment at small scale (Dabrowski, 2001; Brunazzi et al., 2002; Ali, 2014). Activated carbon is the most common adsorbent for this process because of its effectiveness and versatility. However, the use of activated carbon in water treatment is still limited by its high cost and difficulty in regeneration (Ali, 2014). Accordingly a frugal adsorption science (Reardon, 2013) for safe drinking water is yet to be developed.

During the past two decades, the use of metallic iron ($Fe^0$) based materials ($Fe^0$ materials) as affordable alternative to commercially available adsorbents has become popular because of their low cost, ready availability and lack of toxicity (Ghauch, 2015; Guan et al., 2015). Although initially used as reducing agents, the unique remediation property of $Fe^0$ materials arises from their ability to progressively produce highly reactive, iron hydroxides and oxides (Noubactep, 2010a, 2010b, 2013, 2015; Ghauch, 2015; Noubactep, 2015) that are excellent adsorbents for many chemicals (e.g. dyes, metals, nitrates, pesticides, pharmaceuticals, radionuclides) (Guan et al., 2015), pathogens (e.g. bacteria, viruses) (Bojic et al., 2001; You et al., 2005). These iron hydroxides with high specific surface area give $Fe^0$ materials a broad range of applications as demonstrated in numerous laboratory treatability studies, pilot plant studies and full scale applications over the past two decades (O'Hannesin and Gillham, 1998; Wilkin et al., 2014; Ghauch 2015; Guan et al., 2015).

Despite two decades of intensive research, there is still conflicting reports as to whether admixing $Fe^0$ and inert materials (e.g. pumice termed as PM herein or sand) should be beneficial for the

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efficiency of resulting systems (Bi et al., 2009; Ulsamer, 2011 and Refs. cited therein). The rationale for the enhanced efficiency of hybrid $Fe^0$ systems over pure $Fe^0$ systems is the volumetric expansive nature of metal corrosion (Pilling and Bedworth, 1923). Accordingly, in a pure $Fe^0$ system, all particles induce volumetric expansion and clogging occurs very soon (Hussam, 2009; Noubactep and Caré, 2010; Noubactep et al., 2010). In contrast, in a 1:1 (vol/vol) $Fe^0$:sand system, only one half of available particles undergo volumetric expansion and clogging is delayed (Caré et al., 2013; Rahman et al., 2013; Domga et al., 2015). Recently, methylene blue (MB) was demonstrated an operational non reactive tracer for characterizing processes occurring in a $Fe^0$/sand systems in the initial stage of their operation (Miyajima, 2012; Miyajima and Noubactep, 2013; Btatkeu-K. et al., 2014; Tepong-Tsindé et al., 2015a).

The suitability of MB as operational non reactive tracer for the characterization of chemical processes occurring in $Fe^0$/sand systems arises from the following facts: (i) sand is an excellent adsorbent for cationic MB (Mitchell et al., 1955; Miyajima, 2012), (ii) cations ($Fe^{2+}$ and $Fe^{3+}$) from $Fe^0$ oxidative dissolution compete with MB for the sand surface (Btatkeu-K. et al., 2014) and (iii) once the surface of sand is (in-situ) coated by iron oxides, it is a poorer adsorbent for MB than virgin sand (Mitchell et al., 1955). In other words, comparing the discoloration of MB in a pure sand column and a $Fe^0$/sand column is a tool to assess the reactivity of the used $Fe^0$ material. Similarly, because of the high $SiO_2$-content of many PM samples (Derakhshan et al., 2013), it can be postulated that comparing the efficiency of the three systems pure $Fe^0$, $Fe^0$/sand and $Fe^0$/PM for MB discoloration will enable to assess the suitability of replacing compact sand by porous PM. It is postulated that PM will sustain hydraulic conductivity (permeability) of the filter (Rahman et al., 2013).

The permeability of a system scales with its pore-size, which in turn is related to grain size, sorting, grain shape, grain packing, and the degree of cementation (Nur et al., 1998; Bland et al., 2009). The present study has used three different materials ($Fe^0$, PM and sand) to characterize solely the degree of cementation in $Fe^0$-based filters. In such systems, an important inherent cause of porosity loss is in-situ generated gelatinous iron (hydr)oxides ('iron cement'). The porosity loss induced by 'iron cement' progressively occludes the pores between host grains (e.g. $Fe^0$ and sand, $Fe^0$ and PM) (Miyajima 2012). To extend the knowledge of system permeability, the porosity of involved particles must be considered as well. For simplification $Fe^0$ and sand are assumed compact (non porous) while PM is porous (Derakhshan et al., 2013).

The present work examines the feasibility of using porous PM to lengthen the service life of a $Fe^0$/sand system. MB is used as an operational non reactive tracer. Parallel experiments with pure sand, pure $Fe^0$, $Fe^0$/sand, $Fe^0$/PM, and $Fe^0$/sand/PM were performed. The evolution of each system was characterized by measuring the time-dependent breakthrough of $H^+$ (pH), iron, MB, and changes of the hydraulic conductibility (permeability).

## 2. Material and methods

### 2.1. Solutions

#### 2.1.1. Methylene blue

The used methylene blue (MB) (Basic Blue 9 from Merck) was of analytical grade. The working solution was 2.0 mg $L^{-1}$. The solutions were prepared by diluting a 1000 mg $L^{-1}$ stock solution. The stock solution was obtained by dissolving accurately weighted MB in distilled water. MB was chosen in this study because of its known differential adsorption onto iron oxides and sand (Mitchell et al., 1955).

#### 2.1.2. Iron

A standard iron solution (1000 mg/L) from Baker JT® was used to calibrate the spectrophotometer used for analysis. All other chemicals used were of analytical grade. In preparation for spectrophotometric analysis, ascorbic acid (Janssen Chimica) was used to reduce $Fe^{III}$ in solution to $Fe^{II}$. 1,10 orthophenanthroline (ACROS Organics) was used as reagent for $Fe^{II}$ complexation. Other chemicals used in this study included ʟ(+)-ascorbic acid and ʟ-ascorbic acid sodium acetate (sodium ascorbate).

### 2.2. Solid materials

$Fe^0$, PM and sand are quantitatively available at many locations around the world and have been individually positively tested as MB discolouring agents (Mitchell et al., 1955; Noubactep, 2009; Derakhshan et al., 2013). Table 1 summarizes the point of zero charges ($pH_{pzc}$) of metal oxides relevant for the discussion of the results of this study (Kosmulski, 2009). $Al_2O_3$ is considered because of its high content in the tested PM (12.33%). Table 1 shows in particular that aluminium and iron hydroxides have the highest $pH_{pzc}$ (>8.0), making them positively charged over most pH ranges of this study (pH > 7.0) and thus exhibiting repulsion toward positively charged MB (Miyajima, 2012; Btatkeu-K. et al., 2014).

#### 2.2.1. Metallic iron

The used $Fe^0$ was a commercial material from iPutech GmbH (Rheinfelden, Germany). The material was available as fillings with a particle size between 0.30 and 2.0 mm. The material was fractionated by sieving. The fraction 0.4–0.8 mm was used without any further pre-treatment. This fraction was close to the particle size (0.50–1.00 mm) of sand used to build the reactive zone. The average elemental composition of the materials as specified by the supplier was: C: 3.52%; Si: 2.12%; Mn: 0.93%; Cr: 0.66%.

#### 2.2.2. Pumice

The used pumice (PM) originates from Lipari (Aeolian Islands, Sicily – Italy). Its mineralogical composition was determined as follows: $SiO_2$: 71.75%; $Al_2O_3$: 12.33%; $K_2O$: 4.47%; $Na_2O$: 3.59%; $Fe_2O_3$: 1.98%; moreover it contains about 4% of bound water entrapped in the PM structure during the sudden cooling of magma and traces of other compounds (e.g. CaO, $SO_3$, MgO, $TiO_2$, FeO, MnO, $P_2O_5$). The material is characterized by uniform grain size distribution. The coefficient of uniformity U is 1.4. The mean grain size ($d_{50}$) is about 0.3 mm. This PM type has been chosen since it was the available fraction closest to $Fe^0$ in dimension. The initial porosity $\Phi_0$ of the PM granular medium has been estimated to be $\Phi_0 = 73.3\%$ and the inner porosity $\varphi_{pp}$ of the PM (intra particular porosity $\varphi_{pp}$) to be 41% (Bilardi et al., 2013).

#### 2.2.3. Sand

The used sand was a natural material from Fontainebleau (France) purchased from Prolabo. The typical composition of this material is given as: $SiO_2$: >97.5%, $Fe_2O_3$: <0.17%, $Al_2O_3$: <1.2%,

**Table 1**
Point of zero charge ($pH_{pzc}$) of minerals used to discuss MB discoloration. Data from Kosmulski (2009).

| Mineral | | $pH_{pzc}$ |
|---|---|---|
| Name | Formula | |
| Aluminium oxide | $Al_2O_3$ | $8.5 \pm 1.5$ |
| Hydrous ferric oxide | $Fe_2O_3.H_2O_{(amorphous)}$ | $8.7 \pm 0.1$ |
| Goethite | $\alpha$-FeOOH | $6.6 \pm 2.6$ |
| Hematite | $\alpha$-$Fe_2O_3$ | $6.1 \pm 1.5$ |
| Sand (amorphous) | $SiO_2$ | $2.1 \pm 1.0$ |