Impact of Fe⁰ amendment on methylene blue discoloration by sand columns

Miyajima K.a, Noubactep C.a,b,*

aAngewandte Geologie, Universität Göttingen, Goldschmidtstraße 3, D-37077, Göttingen, Germany.
bKultur und Nachhaltige Entwicklung CDD e.V., Postfach 1502, D-37005 Göttingen, Germany

* corresponding author: e-mail: cnoubac@gwdg.de; Tel. +49 551 39 3191, Fax: +49 551 399379.

Abstract

The influence of metallic iron (Fe⁰) amendment on the efficiency of sand to discolor a 2.0 mg L⁻¹ methylene blue (MB) solution was investigated in column studies. MB was used as an indicator to identify the optimum Fe⁰/sand ratio for efficient filtration systems. Columns contained 0, 100 or 200 g of a Fe⁰ material. The volumetric proportion of Fe⁰ in the reactive layer of the columns with 100 g of material varied from 10 to 100 %. Results showed that, Fe⁰ amendment significantly impaired MB discoloration by sand for experiments lasting for up to 132 days. Early MB breakthrough in Fe⁰/sand columns delineated the paramount importance of particle cementation, which has caused preferential flow with a negative impact on discoloration efficiency. The most efficient Fe⁰/sand mixtures were the ones with 30 to 50 % Fe⁰ (v/v). These volumetric ratios correspond 33 to 41 % weight ratios showing that the commonly used 1:1 weight ratio (50 %) may not be optimal. Further research with compounds exhibiting different affinities to both Fe⁰ and sand is needed before this observation can be generalized.

Keywords: Fe⁰/sand filters, Particle cementation, Permeability loss, Water treatment, Zero-valent iron.

1 Introduction

Metallic iron (Fe⁰) has been demonstrated in numerous studies to represent one of the best available materials for subsurface permeable reactive barriers [1-6]. Fe⁰ is also a very efficient material for above-ground wastewater treatment and safe drinking water provision [7-9].
applications of Fe⁰ for water treatment usually involve extensive pilot-scale studies although several models have been developed for predicting the performance of Fe⁰ material [10-13]. Moreover, despite 20 years of intensive research, the question as to whether iron should be used alone or mixed to a cost efficient material is yet to be properly addressed [14-24].

The suitability of Fe⁰ for water treatment arises from its aqueous instability (Eq. 1 - 4). Immersed Fe⁰ is oxidized by water according to Eq. 1:

\[
\text{Fe}^0 + 2 \text{H}^+ \Rightarrow \text{Fe}^{2+} + \text{H}_2\uparrow
\]

(1)

\[
\text{Fe}^0 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \Rightarrow \text{Fe}^{2+} + 2 \text{HO}^{-}
\]

(2)

\[
2 \text{Fe}^{2+} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \Rightarrow 2 \text{Fe}^{3+} + 2 \text{HO}^{-}
\]

(3)

\[
\text{Fe}^{n+} + n \text{HO}^{-} \Rightarrow \text{Fe(OH)}_n \Rightarrow \text{FeOOH}/\text{Fe}_x\text{O}_y
\]

(4)

In the presence of dissolved O₂ the more favourable redox reaction is given by Eq. 2, but reaction following Eq. 1 still significantly occurs due to the abundance of water [25]. Moreover, it has been traceably shown that even under external oxic conditions, Fe⁰ is oxidized by water (Eq. 1) and Fe²⁺ by O₂ (Eq. 3) [26]. In other words, accelerated Fe⁰ oxidation under oxic conditions results from Fe²⁺ consumption by O₂ (Le Chatelier’s principle) and not from any direct interactions between Fe⁰ and O₂ [26,27].

The sustainability of Fe⁰ filtration systems primarily depends on the intrinsic reactivity of Fe⁰ which oxidative dissolution induces both contaminant removal [28] and porosity loss due to the volumetric expansive nature of iron corrosion [29]. Aqueous iron oxidation yields hydroxides (e.g. Fe(OH)₂) and oxides (e.g. Fe₃O₄) (Eq. 4) which volume varies from 2.1 to 6.4 times the volume of Fe⁰ in the metal [30]. The transformation of Fe⁰ to (hydr)oxides (Eqs. 1 through 4) goes through colloidal intermediates with cementing capacities. Here, cementation means that the inter-granular space is filled by Fe²⁺/Fe³⁺ precipitates and the solid particles are “cemented” to each other. This cementation results in material consolidation and in permeability loss in column experiments [14,16,31]. The ease with which cementation is observed primarily depends also on the reaction environments (oxic vs. anoxic). However, the
first tool to restrict cementation is to decrease the proportion of cement producers, that is to mix Fe⁰ with a non expansive material (e.g. activated carbon, anthracite, clay, gravel, organic substances, pumice, sand) [32].

The literature contains many contradictory findings regarding the question as to whether admixing inert materials to micro-scale Fe⁰ is beneficial for its performance or not [17,20,24,33]. Inert materials have been routinely mixed with Fe⁰ to (i) avoid/delay/minimize Fe⁰ cementation [14-16], (ii) increase the hydraulic conductivity [1,15,19] and (iii) decrease the cost of the barrier [18]. Recent theoretical works have demonstrated that admixing non expansive materials (e.g. gravel, MnO₂, pumice, sand, TiO₂) to Fe⁰ is a pre-requisite for sustainable Fe⁰ filtration systems [34].

The present work is the first attempt to experimentally test the validity of the concept that admixing non expansive materials to Fe⁰ is a pre-requisite for sustainable (e.g. long-term efficient) Fe⁰ filtration systems. For this purpose, the discoloration of aqueous methylene blue (MB) is investigated in ten columns containing 0 g (1 column), 100 g (8 columns) or 200 g (1 column) of a commercial Fe⁰. The tested Fe⁰/sand volumetric ratios were 0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 70/30, 80/20 and 100/0. Individual systems are characterized by the time-dependent evolution of (i) the extent of iron release, (ii) the MB breakthrough and (iii) the hydraulic conductivity.

2 Background of the experimental methodology

The choice of methylene blue (MB) as model pollutant to ascertain the optimal Fe⁰/sand ratio for sustainable efficient Fe⁰-based filters arises from three major factors: (i) the ease of MB determination by cost-efficiency colorimetric methods, (ii) the low affinity of MB to iron oxides (corrosion products) [35], and the high affinity of MB to sand [36,37]. The low affinity of MB for iron corrosion products suggests that the retention time of MB in a Fe⁰-based system will be minimal (rapid breakthrough). The breakthrough time is further lowered by working under atmospheric conditions (oxic conditions) where voluminous corrosion
products are generated [30,38]. Despite low affinity to iron oxides, MB is removed in Fe⁰-based filters mainly by adsorptive size-exclusion. However, adsorption and co-precipitation still occur [39], but their extent depends on the flow velocity or the residence time of the solution within the filter.

The suitability of Fe⁰-amended sand filters to investigate the impact of the corrosion process on the efficiency (MB discoloration, permeability loss) of a sand filter (reference system) arises from the historical observation by Mitchell et al. [35], that sand is a better adsorbing agent for MB than iron oxide coated sand. In other words, the discoloration performance of a Fe⁰-amended sand filter is worsen by the progressive coating of sand by in-situ generated iron oxides (assumption 1). On the other hand, the accumulation of corrosion products in a system will reduce the porosity and lower its hydraulic conductivity (assumption 2).

The used methodology for the investigation of the impact of the Fe⁰/sand ratio on the efficiency investigated system comprises testing the validity of assumption 1 and assumption 2 by following the extent of (i) MB discoloration and (ii) permeability loss in Fe⁰-amended sand columns.

3 Materials and methods

3.1 Solutions

3.1.1 Methylene blue (MB)

MB is widely used as model contaminant to characterize the suitability of various materials for water treatment [35-37, 40-42]. The used methylene blue (MB) was of analytical grade. The working solution has a concentration of 2.0 mg L⁻¹ and was weekly prepared by diluting a 1000 mg L⁻¹ stock solution using the tap water of the city of Göttingen. Its average composition (in mg L⁻¹) was: Cl⁻: 12.9; NO₃⁻: 7.5; SO₄²⁻: 35.5; Na⁺: 9.7; K⁺: 0.9; Mg²⁺: 8.2; Ca²⁺: 37.3. The pH value of the initial solution was 8.2. The used concentration 2.0 mg L⁻¹ or 6.3 μM was selected to approach the concentration range of natural waters (MB as model micro-pollutant).
3.1.2 Iron

A standard iron solution (1000 mg L\(^{-1}\)) from Baker JT\(^\circledR\) was used to calibrate the spectrophotometer used for analysis. All other chemicals used were of analytical grade. In preparation for spectrophotometric analysis, ascorbic acid 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 L(+)-ascorbic acid and L-ascorbic acid sodium salt.

3.2 Solid materials

3.2.1 Metallic iron (Fe\(^0\))

The used Fe\(^0\) material was purchased from iPutech (Rheinfelden, Germany). The material is available as fillings with a particle size between 0.3 and 2.0 mm. Its elemental composition as specified by the supplier was: C: 3.52%; Si: 2.12%; Mn: 0.93%; Cr: 0.66%. The material was used without any further pre-treatment. Fe\(^0\) was proven a powerful discoloration agent for MB with the particularity, that discoloration agents are progressively generated in-situ [39]. Therefore, the discoloration capacity of used Fe\(^0\) can not be exhausted within the experimental duration (here 132 days).

3.2.2 Sand

The used sand was a commercial material for aviculture (“Papagaiensand” from RUT – Lehrte/Germany). Papagaiensand was used as received without any further pre-treatment or characterization. The particle size was between 0.5 and 2.0 mm. Sand was used as an MB adsorbent [35] because of its worldwide availability and its use as admixing agent in Fe\(^0\)/H\(_2\)O systems [1,24,34]. The adsorption capacity of sand for MB can be exhausted within the experimental duration.

3.3 MB discoloration

As-received Fe\(^0\) from iPutec GmbH (Rheinfelden, Germany) was used. The materials were packed into columns in a dual manner. Sand (H\(_{\text{sand},1}\) and H\(_{\text{sand},2}\) – Tab. 1) and pure Fe\(^0\) layers
(columns 9 and 10 – Tab. 1) were wet packed. For all other reactive zones (< 100 % Fe⁰), dry homogenized Fe⁰/sand mixtures were introduced into the column in small lofts, which were wetted and compacted with manual tapping. To warrant optimal compaction, columns were gently tapped with a 100 mL PET flacon containing water. Tested volumetric ratios of Fe⁰ in the reactive zone (Tab. 1) were built while using the volume occupied by 100 g of Fe⁰ (32 mL – apparent volume) as unity. The resulting sand masses are documented in Tab. 1. For example, the system with 20 % (v/v) Fe⁰, was made up of one volume of Fe⁰ and four volumes of sand. The corresponding mass of sand was 77 g yielding a weight ratio of 43.5 %.

The 2.0 mg L⁻¹ MB solution was pumped upwards from PE bottles using a peristaltic pump (Ismatec, ICP 24). Tygon tubes were used to connect inlet reservoir, pump, column and outlet. Ten glass columns (40 cm long, 2.6 cm inner diameter) having a section of 5.31 cm² were used. The columns were mostly packed with sand (Tab. 1, Fig. 1). The extent of MB discoloration by packed materials and the extent of the permeability loss by individual column set-ups (Tab. 1) were the sole targets. The experiments were performed at room temperature (22 ± 3 °C). A stable flow rate of 0.1 mL min⁻¹ was maintained throughout the experiment.

The whole effluent was collected. The volume recorded as function of the elapsed time served for the assessment of flow velocity or hydraulic conductivity. Each collected fraction was analysed for MB and dissolved Fe.

3.4 Analytical methods

MB and aqueous iron concentrations were determined by a Cary 50 UV-Vis spectrophotometer (Varian) at a wavelength of 664.5 nm and 510 nm respectively. Cuvettes with 1 cm light path were used. The iron determination followed the 1,10 orthophenanthroline method [43]. The spectrophotometer was calibrated for MB concentrations ≤ 2.5 mg L⁻¹ and iron concentrations ≤ 10.0 mg L⁻¹. The pH value was measured by combined glass electrodes (WTW Co., Germany).

3.5 Presentation of experimental results
The MB breakthrough curves are expressed in terms of normalized concentration defined as the ratio of effluent dye concentration to inlet dye concentration \((C/C_0)\) as a function of time or volume of effluent for a given bed height. For each column set-up, the extent of MB discoloration (efficiency, \(E\) in %) at each time was calculated according to the following equation (Eq. 5):

\[
E = \left[ \frac{\sum V_i C_0 - \sum V_i C_i}{\sum V_i C_0} \right] * 100\%
\]  

where \(C_0\) is the initial aqueous MB concentration \((2.0 \text{ mg L}^{-1})\), while \(C_i\) gives the MB concentration in each collected sample \(V_i\).

In order to characterize the effect of the tested column set-ups on MB discoloration at the end of the experiment, the discoloration efficiency \((E)\) and the specific discoloration \((E_s)\) were calculated using Eq. 6 and Eq. 7.

\[
E = \frac{m_{\text{discol}}}{m_{\text{in}}} * 100
\]

\[
E_s = \frac{m_{\text{discol}}}{m_{\text{Fe}}} * 100
\]

where \(m_{\text{in}}\) is the mass of MB flowed into the column, \(m_{\text{discol}}\) is the MB mass discoloured within the reactive zone, and \(m_{\text{Fe}}\) the mass of \(\text{Fe}^0\) present in the column. It is operationally assumed that \(H_{\text{sand,2}}\) (Tab. 1) does not significantly impact MB discoloration if significant flow disturbance happens in the reactive zone (assumption 3). The extent of MB discoloration \((m_{\text{MB}}\) in mg) within the reactive zone of individual columns was calculated from \(H_{\text{sand,1}}\) using the rule of proportion. In this effort, column 1 was used as reference \((44 \text{ cm of sand for 48.78 mg MB})\) (Eq. 8). 48.78 mg is the value of \(m_{\text{discol}}\) \((m_{\text{discol}} = \sum V_i C_0)\) at MB breakthrough in the pure sand column.

\[
m_{\text{MB}} \text{ (mg)} = (H_{\text{sand,1}}/44) * 48.78
\]

4 Results and Discussion

4.1 Visual analysis of the columns at day 132

Figure 1 reveals 4 main colorations: blue, brown, dark-green and ‘white’. White is the operational colour of sand as seen in the upper part of columns 9 and 10, blue is the colour of
adsorbed methylene blue (column 1), brown is the product of Fe$^{0}$ oxidation by dissolved O$_2$, and dark-green is the colour of Fe$^{II}$ species (including green rust). The formation of rust (brown coloration) is the most tangible evidence of corrosion by O$_2$. That is either the local iron oxidation by O$_2$ or the migration of Fe$^{III}$ species (e.g. Fe(OH)$_3$, Fe$_2$O$_3$•H$_2$O). In other words, a brown coloration ‘far’ from the entrance zone of the reactive layer is an evidence of O$_2$ breakthrough.

It is important to notice that MB breakthrough is observed in all systems although an homogeneous blue coloration is only see in system 1 (0 % Fe$^{0}$) and in the lower part of all other columns (H$_{sand,1}$ – Tab. 1). This observation indicates that flow disturbance was caused within the Fe$^{0}$-containing layer. In other words, uniform flow may be limited to pure sand layers (column 1, H$_{sand1}$).

In general, from the inlet to the outlet, Fe$^{0}$-containing columns exhibited the following coloration sequence: (i) blue (H$_{sand,1}$), (ii) brown (entrance of the reactive layer), (iii) grey or dark (reactive layer), (iv) dark-green (entrance of H$_{sand,2}$) and (v) white (H$_{sand,2}$). Columns 7 and 8 exhibited a different behaviour as the entrance zone of the H$_{sand,2}$ layer was brown coloured (not green-dark). This coloration indicates that dissolved O$_2$ could be quantitatively transported across the reactive layer in these 2 systems. Additionally, a blue coloration is seen in the upper part of column 7.

The presence of a brown coloration in the connecting tube at the column outlet for all Fe$^{0}$-containing systems shows that there is an axial breakthrough of O$_2$ as a rule. In other words, the O$_2$ breakthrough is the first hint for preferential flow due to particle cementation. The second hint for preferential flow is the blue coloration in upper sand layer of column 7. The absence of the brown coloration in the upper sand layer of systems with less than 70 % Fe$^{0}$ is concordant with the use of Fe$^{0}$/sand mixtures as ‘O$_2$ scavengers’ [2,3,14].

4.2 Evidence for an optimal system with less than 70 % Fe$^{0}$
Table 2 summarizes the results from the 10 columns. It shows that about 38.0 L of the MB solution flow through each column during the 132 days. This corresponds to about 69 mg of MB (effective initial concentration 1.83 mg L\(^{-1}\)) from which 42.0 to 63.3 % was discoloured within the reactive layer in Fe\(^0\)-containing systems (columns 2 to 10). On the other hand, dissolved iron release from the same columns (4.0 to 47.1 mg) represented only less than 0.05 % of the initial Fe\(^0\) amount (100 or 200 g).

An important result from Tab. 2 is that the reference system (0 % Fe\(^0\) – column 1) was the most efficient system with 72.3 % MB discoloration efficiency at the day 132 (E value - Fig. 2). Therefore, assumption 1 is validated. However, at this date the discoloration capacity of this system is almost exhausted because this is a pure adsorption system [44,45]. In column 1 (97 % breakthrough), 48.79 mg MB is adsorbed onto 360 g of sand, yielding an adsorption capacity of 0.138 mg g\(^{-1}\). For Fe\(^0\)-containing system, not such adsorption capacity can be defined because MB is not adsorbed onto a defined surface, rather MB is adsorbed or enmeshed in the matrix of iron corrosion products [46]. Additionally, the extent of Fe\(^0\) depletion is difficult to access.

Figure 2 summarizes the results of the evolution of the specific MB discoloration (E\(_s\) in \(\mu g g^{-1}\)) as a function of the volumetric proportion of Fe\(^0\) in the reactive zone. It is seen that E\(_s\) evolves through a maximum at 30 % Fe\(^0\). E\(_s\) then decreases to a minimum at 80 % Fe\(^0\). The overall trend that, for long enough experimental durations, contaminant removal should be minimal (i) in the sand column (pure adsorbent with limited capacity) and (ii) in pure Fe\(^0\) column (no room for expansive iron corrosion) is found here. The fact that the pure Fe\(^0\) system (100 % Fe\(^0\)) is more efficient than the 80 % Fe\(^0\) system is due to the simplistic nature of assumption 3 (no MB discoloration in H\(_{sand,2}\)) as attested by the blue coloration in the H\(_{sand,2}\) layer in column 7 (Fig. 1). MB discoloration is normalized to 360 g of sand in the reference system and to (only) 100 g Fe\(^0\) in all other systems. This is the reason for the apparent discrepancy between E and E\(_s\) values in Fig. 2.
The most important output from Fig. 2 is that for the same mass of Fe⁰, various Eₚ values (143 to 239 μg g⁻¹) are obtained after 132 days. These results clearly question the suitability/validity of Eₚ as indicator of Fe⁰ efficiency when experimental conditions are not identical/similar. Fe⁰ is definitively not an adsorbent but a generator of ‘MB scavengers’. Accordingly, the discoloration efficiency/capacity of Fe⁰ for MB can not be universally defined. Therefore, results from Fig. 2 radically refute the generalized use of ‘removal capacity’ as indicator of the efficiency of Fe⁰ materials.

4.3 Iron breakthrough

Figure 3 summarizes the results of the evolution of dissolved iron concentration in the effluent (also see Tab. 2). It is seen that Fe release and migration occurs in three stages: (i) dissolution from Fe⁰, (ii) short distance migration due to the low solubility at pH > 5, and (iii) adsorption and precipitation on sand particle (in situ coating). This in situ coating is responsible for the accelerated MB breakthrough because of porosity loss and lower adsorptive affinity [35]. Fig. 3 shows that the largest iron release (up to 8.0 mg L⁻¹) was observed in the system with the lowest Fe⁰ volumetric proportion of Fe⁰ (10 %). This column corresponds to the system with Hₚ<sup>sand,2</sup> = 0. The next system (30 % Fe⁰) exhibiting noticeable iron breakthrough (> 2 mg L⁻¹) hast the lowest Hₚ<sup>sand,2</sup>-value (11 cm). This observation confirms the fact, that the long-distance transport of dissolved iron is not favoured at pH > 5 [47]. In all other systems, even more iron could have been dissolved but it is retained within the reactive layer and the under laying sand (Hₚ<sup>sand,2</sup> > 11 cm) (dark-green coloration – section 3.1). The retention mechanisms are (i) adsorption onto available iron oxides or onto sand, or (ii) precipitation as iron (hydr)oxides. It is very important to notice that the extent of iron release depends primarily on the intrinsic reactivity of used Fe⁰. Although data on iron release from column experiments are available in the literature [15] it is quite impossible to make a quantitative comparison. In fact, a parameter (or an index) to characterize the intrinsic reactivity of Fe⁰ is still lacking [48].
The fact that in situ dissolved iron mostly remains in the system is a hint, that MB should be 
more or less quantitatively removed by adsorption, co-precipitation and adsorptive size 
exclusion (straining) [46]. As recalled in section 3.2, all Fe⁰/sand systems should be more 
efficient that pure sand system (assumption 4). Testing the validity of assumption 4 will 
sustain the further presentation.

4.4 Behaviour of the columns

Fig. 4 (a and b) and Tab. 3 summarize the results of the 10 columns (see also Tab. 2). Figure 4 
depicts the time-dependant evolution of the MB mass in the effluent. It can be seen that 
breakthrough occurs after at least 18 mg of MB was retained in all systems. This corresponds 
to complete discoloration of 9.0 L of the initial solution.

Fig. 4b shows that the reference system (0 % Fe⁰) is the most efficient at discoloring MB for 
the tested experimental duration (132 days). This observation seemingly disproves assumption 
4. However, it should be recalled that the adsorption capacity of sand is limited. Therefore, it 
can be argued that ‘early breakthrough’ in Fe⁰-amended systems is due to the low reactivity of 
used Fe⁰ as it could not produce enough ‘scavengers’ for MB removal (assumption 5).

The system with 80 % Fe⁰ was the less efficient (Tab. 2). The remaining systems could be 
ordered as follows: 70 % < 100 % < 10 % < 20 % < 50 % < 40 % < 30 %. Since sand is a 
good adsorbent for MB, the classification has to take the thickness of sand preceding the 
reactive layer into account (H_sand,1 - see sections 3.2 and 3.5). However, the absence of a 
monotone trend in the evolution of the systems disproves assumption 5. Therefore, another 
process, yet to be identified is responsible for the ‘early breakthrough’ of MB in Fe⁰-amended 
systems.

Fig. 4b compares the efficiency of the reference system (0 % Fe⁰) with that of pure Fe⁰ 
systems (column 9 and 10 – Tab. 1). The sand-column remains the most efficient but the 
column with 200 g Fe⁰ was more efficient than the column with 100 g Fe⁰. This is a further 
evidence that Fe⁰ disturbs the efficiency of sand for MB discoloration but not in a monotone
linear way. While further disproving assumption 5 (but validating assumption 1), this observation suggests that a stochastic process is responsible for the ‘early breakthrough’ of MB in systems with 100 g Fe\(^0\) (assumption 6).

Fig. 4 also shows that after breakthrough the mass MB (mg) in the effluent linearly increases. The regression parameters (a and b values) of the lines \([\text{MB}_{\text{effluent}} = a \times \text{MB}_{\text{influent}} + b]\) were determined with Origin 6.0 and summarized in Tab. 3. The slope of this line can be regarded as the rate of MB increase in the effluent after breakthrough. For a pure absorbent the ‘a value’ ideally approaches zero corresponding to a S-shape breakthrough. In other words, the smaller the ‘a value’, the more the system is close to an adsorbing system. The classification of the systems after the order of increasing ‘a values’ is: 0 % < 30 % < 40 % < 50 % < 20 % < 10 % < 75 % = 100 % < 80 %. It is interesting that both columns with 100 % Fe\(^0\) (100 and 200 g) exhibited the same a value (0.65). This fact is an important hint that despite differences in the thickness the same ‘stochastic processes’ are responsible for MB discoloration. The difference between both 100 % Fe\(^0\)-columns is the ‘b value’: -14.6 for 100 g and -23.0 for 200 g. Here again, the absence of a simple proportion between the two ‘b values’ is a hint of the stochastic nature of processes occurring in Fe\(^0\)/H\(_2\)O systems and leading to ‘early breakthrough’ relative to the pure sand system (0 % Fe\(^0\)).

4.5 Effect of the thickness \(H_{\text{sand},1}\)

Fig. 1 showed that the reference system (first column from left) was entirely blue colored while in all other systems, the uniform blue color is limited to the sand before the Fe\(^0\) layer or reactive zone (\(H_{\text{sand},1}\) - Tab. 1). This observation suggests that, in Fe\(^0\)-containing systems, granular particles (Fe\(^0\) and sand) are partly cemented and preferential flow is generated in the Fe\(^0\) layer.

If it is mentally assumed that the Fe\(^0\) layer depicted no interactions with MB, the solution would have ‘traversed’ the Fe\(^0\) layer non-disturbed and the uniform blue coloration would have continued after the pure Fe\(^0\) (columns 9 and 10) or the Fe\(^0\)-amended layer (columns 2 to
8). However, as reported by Imamura et al. [49] MB adsorbs strongly onto Fe\(^0\) materials. Therefore, the absence of a uniform blue coloration can be attributed to the flow disturbance in the Fe\(^0\) layer (assumption 2 is validated). Additionally, Mitchell et al. [35] have traceably demonstrated that iron oxide-coated sand is a poorer adsorbent for MB than pure sand. It is the objective of this study to characterize the processes occurring within the reactive layer. The initial Fe\(^0\) dissolution creates a local super-saturation of aqueous Fe which is short-term diffusive transported and precipitated as cement, in particular the observed brown coloration at the entrance of the reactive layer. Particle cementation is certainly a stochastic process, suggesting that assumption 6 may be valid.

Fig. 5 summarized the results of a mathematical modelling of the time to breakthrough in the Fe\(^0\)-amended columns. The time necessary for 0.5 breakthrough in the pure sand column (day 97) is used as reference. The model used Eq. 8 while replacing the mass by the time where 
\[
\frac{C}{C_0} = 0.5 \text{ in column } 1 (96.83 \text{ days - Eq. 9). In the case “sand1 & 2”, “H}_{\text{sand,1}} \text{ is replaced by “H}_{\text{sand,1}} + H_{\text{sand,2}}” (Tab. 1).}
\]
\[
\text{t}_{\text{BT}} \text{ (days) = (H}_{\text{sand,1}}/44) \times 96.83 \quad \text{(9)}
\]
As a rule, the longer the time to breakthrough, the more efficient a system. Fig. 5 shows that the most efficient systems were the systems with 30, 40 and 50 vol % Fe\(^0\). It is seen that the observed efficiency is always higher than the efficiency of \(H_{\text{sand,1}}\), while for Fe\(^0\) > 40 % the efficiency of the system was lesser than that of sand alone (‘sand 1 & 2’). This observation corroborates the complexity of processes in the Fe\(^0\)-amended and pure Fe\(^0\) layers. It should be kept in mind that the data presented in Fig. 5 (‘observed’ in particular) are static snap-shots of dynamic processes (time for 0.5 MB breakthrough in the sand column). However, they clearly show that systems with Fe\(^0\) volumetric ratios ≥ 70 % are less efficient than systems containing 30 to 50 vol % Fe\(^0\).

4.6 Hydraulic conductivity
The results presented in Fig. 6 clearly demonstrate that the hydraulic conductivity almost remained constant during the whole experiment. This unusual observation could be misinterpreted as the absence of porosity loss due to expansive iron corrosion. However, the used material is known for its reactivity and the observed brown coloration (section 3.1) attests that oxidative dissolution and subsequent precipitation of iron hydroxides has occurred. One should keep in mind, that permeability loss is observed whenever the sum of forces generated in the system (filter resistance) are superior to the pressure supplied by the peristaltic pump (initial driving force) (Eq. 10).

\[ \text{Flow rate} = \frac{\text{Driving force}}{\text{Filter resistance}} \]  

(10)

In the present work, it could be concluded that the used pump flow rate (0.1 mL min\(^{-1}\)) was sufficient to transport enough in situ generated iron oxides out of the reactive zone and so to avoid significant clogging (for 132 days). Fig. 1b shows that, in all Fe\(^0\)-based systems, colloidal Fe species have escaped from the columns and precipitated in the connection tubes. Figure 7 schematically shows the time-dependent evolution of the porosity in a Fe\(^0\)/sand cylindrical column while Fe\(^0\) experiences uniform corrosion. It is seem that porosity loss should increase with the experimental duration (assumption 2). This trend was not observed in the current study (Fig 6). This observation is rationalized by the fact that the filter resistance generated by 100 or 200 g of Fe\(^0\) for up to 132 days was not sufficient to significantly induce a decrease of the flow rate (hydraulic conductivity). However, material compaction was observed and its thickness was smaller in systems with higher Fe\(^0\) proportions (Tab. 2). Accordingly, although no significant permeability loss is noticed, particle cementation has impacted the uniform flow in various extent in individual columns. Assumption 2 is thus validated.

The driving force (hydraulic pressure) from Eq. 10 is ideally uniformly distributed in the whole column. That is on all Fe\(^0\) and sand particle within the 44 cm effective length. However, due to the cementation process described above, there are local ‘irregularities’, as
cemented particles are non accessible and cemented regions non/less permeable. For example, Eq. 10 suggests that if a 50 % porosity loss occurs (t/2 in Fig. 7), the hydraulic pressure should be doubled to maintain the observed constant flow. Actually, a local increase of the hydraulic pressure has occurred and has caused preferential flow at a certain distance from the ‘clogged zone’. This accelerated flow is illustrated the best by the brown colour in the $H_{\text{sand,2}}$ layer as observed in columns 7 and 8 (Fig. 1, section 3.1).

The fact that column 7 and 8 depicted the lowest Es efficiency (Fig. 2) is a further confirmation of assumption 4 (“all Fe$^0$/sand systems should be more efficient that pure sand system”) as the observed anomaly results from the particular difficulty to uniformly mix Fe$^0$ and sand when Fe$^0$ is in volumetric abundance. It should be recalled that sound theoretical works [50] have proven the needlessness of testing these volumetric proportions. Therefore, it is not worth to continue the discussion on these systems. Accordingly, further research should focus on Fe$^0$ ratios < 60 % while eventually test the pure Fe$^0$ as negative reference.

4.7 MB breakthrough

Figure 8 summarizes the results of MB breakthrough. A S-shaped breakthrough curve was obtained for all systems but only the reference system experienced a complete breakthrough ($C/C_0 = 0.97$ at day 132). The breakthrough time (time for $[\text{MB}] \neq 0$) varied largely and was primarily dependent on the thickness of $H_{\text{sand,1}}$. As shown in Fig. 8a, individual columns depicted slightly different behaviour but the discoloration efficiency was levelled at about $C/C_0 = 0.70$. This levelling at $C/C_0 = 0.70$ suggests that the ‘residual’ (steady state) corrosion rate was sufficient to induce the discoloration of about 30 % of a 2.0 mg L$^{-1}$ MB. In other words, an effluent solution containing about 0.60 mg L$^{-1}$ MB (30 % of 2 mg L$^{-1}$) could be efficiently treated (no MB breakthrough) for the 132 days of the experiment. As a rule, natural waters contain much lower levels of contaminants termed ‘micro-pollutants’ [51]. Remember that the experiments were designed to characterize the efficiency of Fe$^0$ at various Fe$^0$/sand ratios using limited
amounts of Fe\textsuperscript{0}. Accordingly, both MB breakthrough and the characterization of the system thereafter were intended.

Fig. 8b summarized the MB breakthrough behaviour in the 3 pure material systems (100 % sand or Fe\textsuperscript{0}). Its shows that the sand systems is the most efficient for 132 days but that the breakthrough is quantitative (100 %) suggested that the adsorption capacity is exhausted. From this moment on, no significant MB discoloration is expected. On the contrary, in the pure Fe\textsuperscript{0} systems the initial S-shape breakthrough starting after 25 and 50 days respectively is levelled at about 70 % (C/C\textsubscript{0} = 0.70). Fig. 8b reveals that after a short levelling at 70 % breakthrough, ‘additional removal’ occurred in the system with 200 g Fe\textsuperscript{0} followed by a phase of limited removal efficiency. This ‘fluctuation’ is also be evident from Fig. 8a, in particular for the 30 % Fe\textsuperscript{0} system. These ‘fluctuations’ document the uncertainty in the long-term reactivity of Fe\textsuperscript{0} materials. This observation supports the quest to accumulate data on long-term reactivity of various Fe\textsuperscript{0} materials at laboratory scale [48].

The breakthrough results suggest the efficient use of Fe\textsuperscript{0}/sand systems in beds for water treatment in deep filtration modus. However, design efforts are urgently needed. It is observed from Fig. 8a that the time to achieve breakthrough is the highest for systems containing 30 to 50 % Fe\textsuperscript{0} (v/v).

4.8 Discussion

4.8.1 Validating the used experimental methodology

The presentation herein is centred on testing the validity of two fundamental (1,2) and four operational (3-6) assumptions. Assumptions 1 through 6 are summarized and commented in this section.
Assumption 1: the (initial) MB discoloration performance of a Fe$^0$-amended sand filter is worsen by the progressive coating of sand by in-situ generated iron oxides. Assumption 1 is verified by experimental data for up to 132 days, clearly showing that the sand system (reference system) is the most efficient for MB discoloration.

Assumption 2: the accumulation of corrosion products in a system reduces its porosity and lowers the hydraulic conductivity (permeability loss). Assumption 2 is indirectly verified as the used pump flow rate (0.1 mL min$^{-1}$) was sufficient to avoid accumulation of corrosion products in columns containing only 100 g of Fe$^0$ during 132 days. It is recommended that lower pump flow rates are tested in future works. Alternatively, higher Fe$^0$ amounts (> 100 g) may be tested using the pump flow rate of 0.1 mL min$^{-1}$.

Assumption 3: the sand layer after the Fe$^0$ layer ($H_{sand,2}$ - Tab. 1) does not significantly impact MB discoloration if significant flow disturbance happens in the reactive zone. This assumption was not verified showing the complexity of processes coupled to Fe$^0$ amendment of sand filters.

Assumption 4: All Fe$^0$/sand systems are more efficient than the pure sand system. This assumption was disproved by experimental data for up to 132 days. However, the fact that the MB removal capacity of the reference system (sand only) was almost exhausted at day 132 suggests that this assumption could be valid for longer experimental durations if the systems are not clogged. Exactly this was the goal of the present study: identifying the optimal Fe$^0$/sand ratio concealing increased permeability (more sand) and decreased efficiency (more sand or less Fe$^0$). It is essential to point out, that MB presents all the characteristics of a tracer [52,53]. In particular, its very low affinity to the Fe$^0$/H$_2$O system makes it an ideal compound to characterize the impact of iron corrosion on the hydraulic properties of a Fe$^0$ amended filter.

Assumption 5: the ‘early’ MB breakthrough in Fe$^0$-amended systems is due to the low reactivity of used Fe$^0$ as it could not produce enough ‘scavengers’ for MB removal. This
assumption was disproved an corroborates the ‘tracer nature’ of MB for characterizing the process of iron corrosion in packed-bed filtration systems. In essence, produced iron oxides either accelerated MB breakthrough.

Assumption 6: a stochastic (non linear) process is responsible for the ‘early’ MB breakthrough in Fe⁰-amended systems. Assumption 6 was validated by experimental data. This validation seriously questions the current approach of correlating Fe⁰ reactivity with monitored parameters at the system outlet including the extent of H₂ evolution and the extent of contaminant removal [22-24].

The validation of the two fundamental assumptions (1 and 2) is regarded as the validation of the theory of Fe⁰-based filtration systems presented in ref. [34]. This makes the assertion that pure Fe⁰ systems (100 % Fe⁰) are not sustainable universal. This was even already experimentally observed as Fe⁰ systems used for As removal in South East Asia (Bangladesh, Nepal) were very efficient but not sustainable [7]. With respect of the longed optimal Fe⁰/sand ratio, the present work could identify the domain in which it should be sought: 30 to 50 % Fe⁰ (v/v).

4.8.2 Significance of achieved results

The present study was designed to characterize the behaviour of Fe⁰ columns at discolouring MB when the 100 g Fe⁰ represents a volumetric proportion varying from 10 to 100 %. Using identical columns, the same initial flow rate (multi-channel peristaltic pump) and the same sand as an additive material, initial differences include the thickness of the reactive layer (Hrz) and the thickness of sand after the reactive layer (Hsand,2). To better discuss the impact of the thickness of sand after the reactive layer on the extend of Fe release from the column, the thickness of sand before the reactive layer (Hsand,1) was also varied (Tab. 1).

Figure 9 summarizes the results of the cumulative MB discoloration (Eq. 5) as function of Hsand,1, Hrz and Hsand,2. It is evident that from each system, the E value decreases with increasing experimental duration. For example, the 0 % Fe⁰ system (Hsand,1 = 44 cm; Hrz =
sand,2 = 0 cm) exhibits E values of 100.0, 89.5 and 72.3 % for 55, 77 and 132 days respectively.

Fig. 9 shows a rough trend that (i) E values increase with increasing H_{sand,1} value; (ii) there is an optimum H_{rz} value of around 10 - 15 cm, (ii) no trend is observed for the H_{sand,2} values. The optimum in the H_{rz} (11 to 15 cm) curve coincides with the results discussed in 3.5 showing that 30 to 50 % Fe^{0} is the optimal range for efficient systems. This coincidence suggests that, despite variation in the H_{sand,1} values, the proportion of Fe^{0} in the reactive layer is of paramount significance for system sustainability.

Used originally as a model pollutant, methylene blue has exhibited the characteristic of an ‘operational tracer’ or a true indicator. This study has demonstrated that there is much more uncertainty about data collection and their interpretation for the design of Fe^{0}/H_{2}O systems than is currently acknowledged. A significant uncertainty arises from the difficulty to assess the time-dependant extent of Fe^{0} consumption. An accurate evaluation of the extent of Fe^{0} consumption would facilitate the prediction of long-term efficiency of Fe^{0}/H_{2}O systems. Accordingly, characterization efforts need to be coordinated. Based on the results of the present work, it is suggested that 100 g Fe^{0} making about 40 % (v/v) of reactive layers is routinely used in laboratory columns (corresponding H_{rz} about 13 cm for 2.6 cm ID). Ideally each experiment testing porous additives should be accompanied by a reference system where tested Fe^{0} is admixed to quartz.

4.8.2 Promoting Fe^{0} filtration systems

The results of this work lead to an avenue for reducing uncertainties in designing Fe^{0}-based filtration systems. Volumetric Fe^{0} ratios ensuring long-term efficiency are lower than 50 %. This conclusion determines a 20 years lasting discussion on the suitability and the efficiency of admixing Fe^{0} with other materials (e.g. anthracite, gravel, pumice, sand).

These results further demonstrated that contaminants should be characterized and tested according to their physical and chemical properties and particularly, their affinity to the
Fe\(^0\)/H\(_2\)O system or to iron corrosion products. The current approach of testing contaminants by their origin (e.g. agricultural wastes (fertilizers and pesticides), heavy metals, human wastes, industrial wastes, organic dyes, pharmaceuticals or radionuclides) is confusing [51]. For example, dyes are not an homogeneous class of substances as some of them contain the hydroxyl group (e.g. erichrome black T, bromoresol green, bromophenol blue, fluorescein) and some other (methyl orange, methyl red, and methylene blue) not [54]. With regard to interactions in Fe\(^0\)/H\(_2\)O systems, dyes with hydroxyl groups exhibit a greater affinity to iron corrosion products. Accordingly, duplicating the experiments reported herein with fluorescein or bromophenol blue as model pollutant will result in longer experimental duration.

The results reported herein will enable/facilitate a science-based design of Fe\(^0\)-based filtration systems. Based on the observation herein and the theory of the system established before [34], many reported discrepancies can be elucidated. In particular, it is unambiguously established that pure Fe\(^0\) systems are not sustainable. Accordingly, the recent article by Ruhl et al. [24] questioning the theory of the Fe\(^0\)-based filters, validated herein, should be regarded as a classical case, illustrating the inefficiency of the data-based approach of developing a theory. This long history of mainstream science teaches that this approach can not be successful [55].

Ruhl et al. [24] have recently depreciated the theory of Fe\(^0\)-based filters to an assumption and presented data seemingly challenging this theory. They tested anthracite (porous), gravel (compact), pumice (porous) and sand (compact) in dual granular mixtures with a commercial Fe\(^0\) (100 g) in long term column experiments (> 200 days) for the treatment of a trichloroethylene (TCE) contaminated groundwater. Their results confirmed differences in porosity for the tested materials but no difference in 'reactivity' as derived from H\(_2\) evolution. Due to increased cis-dichloroethylene (a TCE metabolite) concentrations in the effluent from all columns (TCE was completely removed), they concluded that "the mixed reactive filters are therefore not applicable for treatment of the here tested groundwater with its indigenous microorganisms". However, this conclusion disproved the results of O'Hannesin and Gillham
who have demonstrated the suitability of Fe$^0$ for contaminant removal at a site contaminated with TCE and PCE (tetrachloroethylene) using a Fe$^0$:sand weight mixture of 22:78.

The work presented in ref. [24] shows clearly how misconceptions could be propagated based on wrong interpretation of good experimental observations. To accurately interpret their results, the authors would have additionally tested reference systems (e.g. pure anthracite, Fe$^0$, gravel, pumice and sand). The results presented herein clearly demonstrated that for short experiments, an inert material could be more efficient than a reactive one. This result confirms that there are no generally efficient or non efficient materials but selected materials should be used to meet the site-specific requirements. In other words, there are appropriate and non appropriate materials. The present work hopes to have opened new avenues to optimised the appropriateness of Fe$^0$ materials in packed filtration beds, whether they are used for groundwater remediation, wastewater treatment or save drinking water provision.

5 Concluding remarks

This study clearly demonstrates that a pure Fe$^0$ (100 % Fe$^0$) filtration system for water treatment is not sustainable. Moreover, even the commonly used 50 % weight ratio is demonstrated not to be the most efficient one. Accordingly, Fe$^0$ filtration systems must contain less than 50 % (w/w) Fe$^0$ to be sustainable. The presented work has also validated the suitability of using limited amount of Fe$^0$ (here 100 g) to investigate relevant processes within reasonable experimental duration (here 4 months) [50]. The rationale for the selection of the admixing materials (e.g. activated carbon, biomaterials, charcoal, gravel, MnO$_2$, pumice, wood gravel, sand) is yet to be realized. Future works under similar conditions, should use lower pumping rates to increase the probability to experimentally observe permeability loss. In fact, the tested pumping rate (0.1 mL min$^{-1}$) has solely identified a region (30 to 50 vol % Fe$^0$) of the optimal Fe$^0$/sand ratio. An interesting case will consist to test gravity flow which is
relevant for household water filters and for small water treatment plants in remote, low-income communities.

This study has further delineated the unsuitability of the expression of “removal capacity” for Fe\(^0\) materials. This expression could only be acceptable if materials are used under similar conditions, have similar intrinsic reactivity and used in the same mass loading.

The last important feature from this study concerns the long-term reactivity of Fe\(^0\)/sand systems. This study has shown that upon an initial increased reactivity Fe\(^0\) oxidation experienced a steady state which was able to produce enough scavengers for the quantitative removal of about 0.6 mg/L methylene blue (30 % of 2.0 mg L\(^{-1}\)). Designing a Fe\(^0\)/H\(_2\)O system could be regarded as finding out such a steady state or creating the conditions for such a state with respect to the actual contaminant flux and the nature of the contaminant of interest. For future works more care should be taken while collecting and interpreting experimental data.

Acknowledgments

The draft manuscript was improved by the insightful comments from Thomas Ptak (Geosciences Center - University of Göttingen). Gerhard Max Hundertmark and Mohammad Azizur Rahman from the Geosciences Center (University of Göttingen) are acknowledged for technical support. The manuscript was improved by the insightful comments of anonymous reviewers from Chemical Engineering Journal.

References


Table 1: Parameters of the packed columns. $H_{\text{sand,1}}$ is the thickness of sand preceding the reactive layer; $H_{\text{rz}}$ is the thickness of the reactive layer and $H_{\text{sand,2}}$ is the thickness of sand after the reactive layer. The internal diameter of the column is 2.6 cm, its length 40 cm as given by the manufacturer but the measured length was 44 cm. The effective volume of the column was 230 mL. The volume occupied by 100 g of Fe$^0$ was used as unit for the mixture of Fe$^0$ and sand.

<table>
<thead>
<tr>
<th>Column</th>
<th>Fe$^0$ (g)</th>
<th>Sand (% w/w)</th>
<th>Fe$^0$ (% v/v)</th>
<th>Sand (cm)</th>
<th>$H_{\text{sand,1}}$ (cm)</th>
<th>$H_{\text{rz}}$ (cm)</th>
<th>$H_{\text{sand,2}}$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>100</td>
<td>0.0</td>
<td>44.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>87</td>
<td>10.0</td>
<td>46.5</td>
<td>10.0</td>
<td>34.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>77</td>
<td>20.0</td>
<td>43.5</td>
<td>11.0</td>
<td>20.0</td>
<td>13.0</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>66</td>
<td>30.0</td>
<td>40.5</td>
<td>18.0</td>
<td>15.0</td>
<td>11.0</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>58</td>
<td>40.0</td>
<td>36.6</td>
<td>19.0</td>
<td>13.0</td>
<td>12.0</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>48</td>
<td>50.0</td>
<td>32.5</td>
<td>18.0</td>
<td>11.0</td>
<td>15.0</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>29</td>
<td>70.0</td>
<td>22.4</td>
<td>15.0</td>
<td>7.5</td>
<td>21.5</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>19</td>
<td>80.0</td>
<td>16.2</td>
<td>13.0</td>
<td>6.5</td>
<td>24.5</td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>13.0</td>
<td>6.0</td>
<td>25.0</td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>15.0</td>
<td>12.5</td>
<td>16.5</td>
</tr>
</tbody>
</table>
Table 2: Summary of the results of the column experiments after 132 days. $V_T$ is the total volume of MB solution which has flowed through each column, $Fe_{effluent}$ and $MB_{effluent}$ are the cumulative mass of Fe and MB in the effluent. $MB_{influent}$ is the total mass of MB which has flowed through the columns. $Fe_{effluent} \%$ is the ratio of dissolved Fe which has escaped from the column relative to the used mass of Fe$^0$. $E$ (%) and $E_s$ (mg/g) are the MB discoloration efficiencies (see text). $H_{cake}$ is the thickness of the cake at the entrance of the Fe$^0$-containing layer as measured at the end of the experiments.

<table>
<thead>
<tr>
<th>Column</th>
<th>$V_T$ (L)</th>
<th>$Fe_{effluent}$ (mg)</th>
<th>$MB_{effluent}$ (mg)</th>
<th>$MB_{influent}$ (mg)</th>
<th>$E$ (%)</th>
<th>$Fe_{effluent}$ (%)</th>
<th>$E_s$ (mg/g)</th>
<th>$H_{cake}$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.6</td>
<td>0.00</td>
<td>19.1</td>
<td>68.89</td>
<td>72.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>37.8</td>
<td>47.08</td>
<td>36.4</td>
<td>69.34</td>
<td>47.5</td>
<td>0.047</td>
<td>0.218</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>37.6</td>
<td>4.01</td>
<td>35.5</td>
<td>68.88</td>
<td>48.4</td>
<td>0.004</td>
<td>0.211</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>37.8</td>
<td>17.82</td>
<td>25.5</td>
<td>69.39</td>
<td>63.3</td>
<td>0.018</td>
<td>0.239</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>36.5</td>
<td>6.05</td>
<td>26.6</td>
<td>66.96</td>
<td>60.3</td>
<td>0.006</td>
<td>0.192</td>
<td>2.3</td>
</tr>
<tr>
<td>6</td>
<td>37.5</td>
<td>8.40</td>
<td>28.6</td>
<td>68.73</td>
<td>58.4</td>
<td>0.008</td>
<td>0.201</td>
<td>1.5</td>
</tr>
<tr>
<td>7</td>
<td>37.6</td>
<td>6.96</td>
<td>36.4</td>
<td>68.97</td>
<td>47.2</td>
<td>0.007</td>
<td>0.159</td>
<td>1.3</td>
</tr>
<tr>
<td>8</td>
<td>37.5</td>
<td>9.71</td>
<td>40.0</td>
<td>68.74</td>
<td>41.9</td>
<td>0.010</td>
<td>0.143</td>
<td>1.1</td>
</tr>
<tr>
<td>9</td>
<td>38.1</td>
<td>7.82</td>
<td>35.8</td>
<td>69.77</td>
<td>48.7</td>
<td>0.008</td>
<td>0.195</td>
<td>1.0</td>
</tr>
<tr>
<td>10</td>
<td>37.8</td>
<td>4.91</td>
<td>22.0</td>
<td>69.37</td>
<td>68.3</td>
<td>0.002</td>
<td>0.154</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 3: Correlation parameters of the straight lines $[\text{MB}]_{\text{effluent}} = a*[\text{MB}]_{\text{influent}} + b$ for the 10 columns. “a” is the rate at which MB concentration increases in the effluent after breakthrough. “b” is the point at which each straight line MB meets the $[\text{MB}]_{\text{effluent}}$ axis. R is the correlation factor and N is the number of experimental points used for the plot. Fig. 4 suggests that the smaller the a values, the more efficient the systems.

<table>
<thead>
<tr>
<th>$\text{Fe}^0$ (% vol)</th>
<th>N</th>
<th>R</th>
<th>a</th>
<th>$\delta a$</th>
<th>b</th>
<th>$\delta b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4</td>
<td>0.9881</td>
<td>0.31</td>
<td>0.03</td>
<td>-26.3</td>
<td>3.3</td>
</tr>
<tr>
<td>10</td>
<td>14</td>
<td>0.999</td>
<td>0.64</td>
<td>0.01</td>
<td>-14.4</td>
<td>0.4</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>0.998</td>
<td>0.63</td>
<td>0.02</td>
<td>-15.3</td>
<td>0.6</td>
</tr>
<tr>
<td>30</td>
<td>8</td>
<td>0.997</td>
<td>0.55</td>
<td>0.02</td>
<td>-17.1</td>
<td>0.8</td>
</tr>
<tr>
<td>40</td>
<td>8</td>
<td>0.996</td>
<td>0.56</td>
<td>0.02</td>
<td>-16.8</td>
<td>0.9</td>
</tr>
<tr>
<td>50</td>
<td>8</td>
<td>0.998</td>
<td>0.60</td>
<td>0.02</td>
<td>-17.8</td>
<td>0.7</td>
</tr>
<tr>
<td>70</td>
<td>12</td>
<td>0.999</td>
<td>0.65</td>
<td>0.01</td>
<td>-13.4</td>
<td>0.3</td>
</tr>
<tr>
<td>80</td>
<td>12</td>
<td>0.999</td>
<td>0.74</td>
<td>0.01</td>
<td>-14.4</td>
<td>0.3</td>
</tr>
<tr>
<td>100</td>
<td>11</td>
<td>0.998</td>
<td>0.65</td>
<td>0.01</td>
<td>-14.6</td>
<td>0.5</td>
</tr>
<tr>
<td>100</td>
<td>6</td>
<td>0.999</td>
<td>0.65</td>
<td>0.01</td>
<td>-23.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Figure 1
Figure 2

![Graph showing the relationship between $E_s$ and $E$ with $\text{Fe}^0$ content.](image)

$E_s / \mu g/g$ vs. $\text{Fe}^0 / [%]$
Figure 3

![Graph showing Fe concentration (mg/L) over elapsed time (days) for different Fe ration (vol %).]
Figure 4

(a) 

% Fe\(^{0}\) (v/v) 
- 10 
- 20 
- 30 
- 40 
- 50 
- 70 
- 80 
- 100

ΣMB / [mg]

elapsed time / [days]

(b) 

% Fe\(^{2+}\) (v/v) 
- 0 
- 100 (100 g) 
- 100 (200 g)

ΣMB / [mg]

elapsed time / [days]
Figure 5

![Graph showing $t_{gr}$ vs. $Fe^0$ ratio for sand 1, observed, and sand 1 & 2](image)
Figure 6

![Graph showing flow velocity vs. elapsed time with different Fe^0 concentrations.](image-url)
Figure 7

$t_0$  $t_{1/2}$  $t_{3/4}$  $t_{inf}$
Figure 9

(a) 55 days
△ 77 days
☆ 132 days

(b) 55 days
△ 77 days
☆ 132 days

(c) 55 days
△ 77 days
☆ 132 days
Figure captions

Figure 1: Photograph of the experimental design, showing the 10 columns at the end of the experiment (day 132). Uniform migration of the MB front is observed before the Fe\textsuperscript{0} layer (H\textsubscript{sand,1} - Tab. 1). MB breakthrough is observed in all systems. The absence of an MB adsorption front beyond the Fe\textsuperscript{0} layer evidences the disturbance of the flow regime within this layer.

Figure 2: Effect of Fe\textsuperscript{0} amendment on the discoloration (E and E\textsubscript{s}) of methylene blue after 132 days. The lines are not fitting functions, they simply connect points to facilitate visualization.

Figure 3: Time-dependant evolution of the iron concentration of column effluent. The lines are not fitting functions, they simply connect points to facilitate visualization.

Figure 4: Effect of Fe\textsuperscript{0} amendment on the performance of sand column for methylene blue discoloration: (a) 100 g of Fe\textsuperscript{0} occupying a volumetric proportion of 10 to 100 % of the reactive zone; and (b) 100 and 200 g of Fe\textsuperscript{0} in a pure Fe\textsuperscript{0} reactive zone. The lines are not fitting functions, they simply connect points to facilitate visualization.

Figure 5: Comparison of model predictions of MB breakthrough with experimental observations after 97 days. The model assumes uniform MB adsorption onto sand 1 and sand 2 (see Table 1). The lines are not fitting functions, they simply connect points to facilitate visualization.
Figure 6: Time-dependant evolution of the flow velocity curves in the 8 tested systems. The lines are not fitting functions, they simply connect points to facilitate visualization.

Figure 7: Cross-sectional diagram of the time-dependent evolution of the porosity in a Fe^0/sand cylindrical column in which Fe^0 experiences uniform corrosion. t_0, t_1/2, t_3/4 and t_∞ (t_Inf) are the times at which porosity loss is 0, 50, 75 and 100 % respectively. As a rule the ‘filter resistance’ increases with increasing porosity loss.

Figure 8: Breakthrough curves of MB discoloration in the 8 tested systems (a) and in the 3 pure material systems (b). The lines are not fitting functions, they simply connect points to facilitate visualization.

Figure 9: Correlation of the cumulative extent of MB discoloration at days 55, 77 and 132 as function of the high of (a) sand before the reactive zone (H_sand,1), (b) the reactive zone (H_rz) and (c) sand after the reactive zone (H_sand,2). The reference system (0 % Fe^0) corresponds to H_sand,1 = 44 cm or H_rz = H_sand,2 = 0 cm. For the 10 % Fe^0 system, H_sand,2 = 0.