The key role of contact time in elucidating the mechanisms of enhanced decontamination by Fe\(^0\)/MnO\(_2\)/sand systems

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Metallic iron (Fe\(^0\)) has shown outstanding performances for water decontamination and its efficiency has been improved by the presence of sand (Fe\(^0\)/sand) and manganese oxide (Fe\(^0\)/MnO\(_x\)). In this study, a ternary Fe\(^0\)/MnO\(_x\)/sand system is characterized for its discoloration efficiency of methylene blue (MB) in quiescent batch studies for 7, 18, 25 and 47 days. The objective was to understand the fundamental mechanisms of water treatment in Fe\(^0\)/H\(_2\)O systems using MB as an operational tracer of reactivity. The premise was that, in the short term, both MnO\(_x\) and sand delay MB discoloration by avoiding the availability of free iron corrosion products (FeCPs). Results clearly demonstrate no monotonous increase in MB discoloration with increasing contact time. As a rule, the extent of MB discoloration is influenced by the diffusive transport of MB from the solution to the aggregates at the bottom of the vessels (test-tubes). The presence of MnO\(_x\) and sand enabled the long-term generation of iron hydroxides for MB discoloration by adsorption and co-precipitation. Results clearly reveal the complexity of the Fe\(^0\)/MnO\(_x\)/sand system, while establishing that both MnO\(_x\) and sand improve the efficiency of Fe\(^0\)/H\(_2\)O systems in the long-term. This study establishes the mechanisms of the promotion of water decontamination by amending Fe\(^0\)-based systems with reactive MnO\(_x\).

Since the 1950s the world is conventionally divided into two groups with regards to the access to safe drinking water: (i) developed countries striving for selecting the best available technology for water treatment, and (ii) developing countries striving for making some appropriate technologies available for their mostly low-income and rural populations\(^1\)–\(^3\). In the meantime, cities have grown, but drinking water systems in peri-urban areas are comparable to that of rural environments without piped water\(^4\)–\(^6\). Appropriate technologies are essentially considered as interim solutions wherever a centralized water supply is not yet available\(^1\). Factors relevant for selecting an appropriate solution for safe drinking water supply include\(^7\),\(^8\): (i) Simplicity in operation (no special skilled personnel), (ii) robustness (no frequent break downs), (iii) affordability (low installation and operation costs), (iv) ability to function without electricity, and (v) use of local skills and readily available resources. Research during the past two decades has rediscovered filtration systems based on metallic iron (Fe\(^0\)) as an affordable, applicable, and efficient water treatment technology for decentralized water supply (e.g. households and small communities)\(^3\),\(^7\),\(^9\)–\(^11\). Such Fe\(^0\) filters are only sustainable upon admixing Fe\(^0\) with other aggregates like granular activated carbon, biochar, gravel, magnetite (Fe\(_3\)O\(_4\)), manganese oxides (MnO\(_x\)), pyrite (FeS\(_2\)), and sand\(^10\),\(^11\),\(^14\),\(^15\).

There are two fundamental challenges in designing Fe\(^0\) filtration systems: (i) “reactivity loss” and (ii) permeability loss\(^16\)–\(^20\). Permeability loss is not addressed herein. For the presentation, it suffices to recall that this issue has been partly resolved in earlier studies demonstrating that only hybrid Fe\(^0\) filters are sustainable\(^14\),\(^21\). The remaining task is a temporal issue regarding the reaction kinetics of Fe\(^0\) corrosion, which is material-specific and has received limited attention\(^22\)–\(^24\). Reactivity loss is the expression of the inherent time-dependent decrease of the
conditions25,28, this study premises that iron passivation is delayed by avoiding the precipitation of iron corrosion products in the vicinity of the metal. Thus, Fe²⁺ and Fe³⁺ ions are consumed instead of coating sand in Fe⁰/sand action of the reactive additive (here Fe₃O₄). Following the science of aqueous iron corrosion under environmental parallel experiments. The inclusion of an operational reference enables a better understanding of the specific systems, and Fe²⁺ ions are additionally consumed in the reductive dissolution of MnOₓ (Eq. 2) in the Fe⁰/MnOₓ/sand systems (Fig. 1). Note that all other aggregates including Fe₃O₄ and granular activated carbon are in-situ reduced by Fe⁰ (Eq. 2), but rather by Fe²⁺ (Eq. 3a) (Fig. 1). Equation 3b depicts that MnO₂ reductive dissolution additionally occurs under immersed conditions. The question is, how to ensure that Fe⁰ oxidation with changing corrosion rates still secures clean water in the long-term?

During the past decade, substantial experiences have been accumulated on increasing the efficiency of Fe⁰/H₂O systems by admixing Fe⁰ with other materials (Table 1)15,36. However, these efforts were mostly misled by the misconception that Fe⁰ is a reducing agent36. Fortunately, available data can be re-interpreted based on the chemistry of the system. It suffices to consider that reduction is not a relevant contaminant removal mechanism, and that contaminant reduction is never mediated by electrons from the metal body34. For example, MnO₂ is not reduced by Fe⁰ (Eq. 2), but rather by Fe²⁺ (Eq. 3a) (Fig. 1). Equation 3b depicts that MnO₂ reductive dissolution by Fe²⁺ induces acidification of the system (releases protons). O₂ and other dissolved species are equally reduced by Fe²⁺ and other reductive species present in the Fe⁰/H₂O system (e.g., H₂, Fe₃O₄, green rust)37–40. Thus, it is established that contaminants are reduced by an indirect mechanism (Fig. 1), and that this process continues even after virtual surface passivation (which is thus not a "loss of their reactivity"). Successful efforts to overcome Fe⁰ passivation include the addition of gravel, magnetite, MnO₂, pyrite, and sand.

The presence of inert sand improves the efficiency of even batch Fe⁰/H₂O systems for water treatment49. However, the studies testing other reactive materials have not considered inert systems (e.g., sand) as operational references. Only Ndé-Tchoué et al.38 did such a comparison. However, the objective was to test pozzolan as an alternative filling material to sand for Fe⁰ filters. In other words, while testing magnetite (Fe₃O₄) as admixing agent for the reductive transformation of contaminants45, a reference Fe⁰/sand should have been considered in parallel experiments. The inclusion of an operational reference enables a better understanding of the specific action of the reactive additive (here Fe₃O₄). Following the science of aqueous iron corrosion under environmental conditions25–28, this study premises that iron passivation is delayed by avoiding the precipitation of iron corrosion products in the vicinity of the metal. Thus, Fe²⁺ and Fe³⁺ ions are consumed instead of coating sand in Fe⁰/sand systems, and Fe³⁺ ions are additionally consumed in the reductive dissolution of MnO₂ (Eq. 2) in the Fe⁰/MnO₂/sand systems (Fig. 1). Note that all other aggregates including FeO₂ and granular activated carbon are in-situ coated by FeCPs like sand and the postulated effects are not realizable in the long-term (Table 1).

Fe⁰ is used to efficiently remove various contaminants such as turbidity, pathogens, and dissolved species from aqueous solutions41–46. Chemical pollutants in the aqueous phase can be ions, molecules, and colloids. For reducible dissolved species, there is a trend to consider Fe⁰-based materials (E° = −0.44 V) as (strong) reducing agent41,56,60, and contaminant reductive transformation as an electrochemical process38. It is evident that colloids.

| Aggregate | Assigned function | Comments |
|-----------|-------------------|----------|
| Fe⁰ | Generates contaminant scavengers (FeCPs) | Confirmed |
| Fe⁰ | Donates electrons to contaminants | Disproved |
| GAC | Sustains iron corrosion (Fe⁰/GAC cells) | Questioned |
| GAC | Accumulates contaminants for reduction by Fe⁰ | Questioned |
| GAC | Sustains long-term iron corrosion | Confirmed |
| Sand | Scavengers of FeCPs (in-situ coating) | Confirmed |
| Sand | Impairs the efficiency of the Fe⁰ system | Disproved |
| Sand | Sustains long-term iron corrosion | Confirmed |
| MnO₂ | Corrodes Fe⁰ (as cathodic reaction) | Disproved |
| MnO₂ | Scavengers of Fe⁰ | Confirmed |
| MnO₂ | Sustains long-term iron corrosion | Confirmed |

Table 1. Summary of the operating mode of some representative aggregates relevant for hybrid Fe⁰ systems for water treatment. Their status according to the state-of-the-art knowledge on the Fe⁰/H₂O system is given as comments. Questioned aspects have been documented in short-term laboratory experiments, but are not likely to be valid when the aggregates are coated with iron corrosion products (FeCPs).
pathogens, and suspended solids (turbidity) are not removed by any chemical reaction. Rather, they are removed via coagulation and co-precipitation. The previous text has already demonstrated that no electrochemical contaminant reduction is possible in a Fe0/H2O system. Yet, published results using the Fe0/MnO2 mixtures are mainly premised on the wrong assumption that contaminant removal occurs via reduction by electrons from Fe0 (Fig. 1) (Table 1). Accordingly, there is still a need to further clarify the role of MnO2 in sustaining the efficiency of Fe0/H2O systems for water treatment. In particular, there is need to elucidate how insoluble Fe(OH)3 contribute to the co-precipitation of pollutants from the aqueous phase.

The objective of this study is to investigate the impact of MnOx addition on the efficiency of Fe0/H2O systems for MB discoloration as a function of the experimental duration (contact time). The specific objective is to confirm the suitability of MB discoloration as a powerful tool for the characterization of decontaminantion processes in Fe0/MnOx and sand to control the availability of ‘free’ FeCPs. The extent of MB discoloration is investigated in five different systems: (i) Fe0 alone, (ii) sand alone, (iii) Fe0/sand, (iv) Fe0/MnOx, and (v) Fe0/MnOx/sand for 7, 18, 25 and 47 days. A comparison of the results from the five systems provides critical information on the contaminant removal mechanisms and the role of MnOx.

Materials and methods

The theory of iron and manganese cycle in a Fe0/MnO2/sand system. Initially (t0 = 0), when Fe0, MnO2, and sand are put into the solution, there is no dissolved iron and no dissolved manganese in the system (Table 2). At t > t0, Fe0 is dissolved by protons (water) to generate H2 and Fe2+ (Eq. 1). Fe2+ induces the reductive dissolution of MnO2 (Eq. 3). At t > t0, the Fe2+/MnO2/sand system hosts dynamic processes which might continue after Fe0 depletion. In fact, the mixture of Fe and MnO2 minerals is a very complex reactive system that has been investigated for more than a century. The uniqueness of the Fe2+/MnO2/sand system is that Fe minerals are generated in-situ and are comparatively more reactive than aged minerals like goethite or hematite. Because the pH of the system is larger than 5.0, in the absence of ligands, Fe and Mn hydroxides have very low solubility and precipitate not far away from their points of nucleation. The dynamics within the Fe2+/MnO2/sand entail a series of interchanges of iron and manganese from older to younger forms as follows: (i) dissolution of Fe0 and MnO2, (ii) migration of Fe2+, Fe3+ and Mn2+ from the areas of their generation to areas where precipitation will occur, and (iii) precipitation in one or more forms of iron and manganese hydroxide.

In the Fe2+/MnO2/sand system, iron and manganese chemically precipitate at the surface of MnO2, sand or in the bulk solution. Due to the good adsorptive affinities of Fe2+ and Fe3+ for sand surface, it is assumed that...
the deposition of Fe hydroxides at its surface (coating) will compete with Fe²⁺ consumption by the reductive
dissolution of MnOₓ until sand coating is completed. Thereafter, the “free” precipitation of iron and manganese occurs and the final products are deposits of more or less pure iron and manganese ores. In other words, the investigated Fe⁰/MnOₓ/sand system is a ternary system only at the start of the experiment. It then turns to a mixture of Fe⁰, iron oxide-coated sand, iron oxide-coated MnOₓ, Fe/Mn shales, etc. Even after Fe⁰ depletion, the Fe/Mn mineral mixture will still be a reactive one, with a great potential for water treatment by both abiotic and biotic processes.

**Experimental details.** This experimental section is adapted from Cao et al. using the same experimental design and two more MnO₂ minerals.

**Solutions.** The used methylene blue (MB—Basic Blue 9 from Merck) was of analytical grade. The working solution was 10.0 mg L⁻¹ prepared by diluting a 1000 mg L⁻¹ stock solution. The stock solution was prepared by dissolving accurately weighted MB in tap water. The use of tap water rather than deionised water was motivated by the fact that tap water is closer to natural water in its chemical composition. The MB molecular formula is C₁₆H₁₈N₃SCl corresponding to a molecular weight of 319.85 g. MB was chosen in this study because of its well-known strong adsorption onto solids.

**Solid materials.** Metallic iron (Fe⁰). The used Fe⁰ material was purchased from iPutech (Rheinfelden, Germany). The material is available as filings 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% while the balance was Fe. The material was used without any further pre-treatment. Fe⁰ was proven as a powerful discoloration agent for MB given that discoloration agents in the form of FeCPs are progressively generated in-situ.

Manganese dioxide (MnO₂). The tested natural MnO₂-bearing minerals was Manganit from Ilfeld/Harz, Thüringen (Germany). The mineral was crushed and fractionated by sieving. The fraction 0.5–1.0 mm was used without any further pre-treatment. No chemical, mineralogical nor structural characterizations were performed. MnO₂ is a reactive mineral and is used to delay the availability of ‘free’ iron corrosion products (FeCPs) in the system. This results in a delay of quantitative MB discoloration.

Sand. The used sand was a commercial material for aviculture (“Papagaiensand” from RUT—Lehrte/Germany). The sand was used as received without any further pre-treatment. The particle size was between 2.0 and 4.0 mm. Sand was used as an adsorbent because of its worldwide availability and its use as admixing agent in Fe⁰ barriers. The adsorption capacity of sand for MB has been systematically documented as early as in 1955 by Mitchell et al.

**MB discoloration.** Quiescent batch experiments (non-shaken) were conducted in assay tubes for experimental durations of 7, 18, 25 and 47 d. The batches consisted of 0.0 or 1.0 g of sand, 0.0 or 0.1 g to Fe⁰, 0.0 or 0.05 g of MnO₂ and mixtures thereof in 22.0 mL of a 10.0 mg L⁻¹ MB solution. The investigated systems were: (i) Fe⁰ alone, (ii) sand alone, (iii) MnO₂ alone, (iv) Fe⁰/sand, (v) Fe²⁺/MnO₂ and (vi) Fe⁰/sand/MnO₂. The efficiency of individual systems at discolouring MB was characterized at laboratory temperature (about 22 °C). Initial pH was about 8.2. After equilibration, up to 3.0 mL of the supernatant solutions were carefully retrieved (no filtration) for MB measurements (no dilution). Each experiment was performed in triplicates, and averaged values are presented. Table 3 summarizes the aggregate content of the 6 Fe⁰/MnO₂/sand systems investigated herein. The operational reference (blank experiment) is also added. Note that the pure Fe⁰ system (Fe⁰ alone) is regarded as a ‘Fe²⁺/MnO₂/sand system’ without MnO₂ nor sand.

**Analytical methods.** Iron and MB aqueous concentrations were determined by a Cary 50 UV–Vis spectrophotometer (Varian). The working wavelengths for MB and iron were 664.5 and 510.0 nm, respectively. Cuvettes with 1.0 cm light path were used. The spectrophotometer was calibrated for Fe and MB concentrations ≤ 10.0 mg L⁻¹. The pH value was measured by combined glass electrodes (WTW Co., Germany).

| System | Fe⁰ (g L⁻¹) | Sand (g L⁻¹) | MnO₂ (g L⁻¹) | Materials | Comments |
|--------|-------------|--------------|--------------|-----------|----------|
| Reference | 0.0 | 0.0 | 0.0 | None | Blank experiment |
| System 1 | 4.5 | 0.0 | 0.0 | Fe⁰ alone | Blank for Fe⁰ |
| System 2 | 0.0 | 45.0 | 0.0 | sand alone | Blank for sand |
| System 3 | 0.0 | 0.0 | 2.3 | MnO₂ alone | Blank for MnO₂ |
| System 4 | 4.5 | 45.0 | 0.0 | Fe⁰/sand | Reference system |
| System 5 | 4.5 | 0.0 | 4.5 | Fe²⁺/MnO₂ | Reference system |
| System 6 | 4.5 to 45.0 | 45.0 | 4.5 | Fe⁰/sand/MnO₂ | Fe⁰ loading as variable |

Table 3. Overview on the six (6) investigated systems. The material loadings correspond to Fig. 2.
Expression of MB discoloration results (E value). In order to characterize the magnitude of the tested systems for MB discoloration, the discoloration efficiency (E) was calculated (Eq. 4). After the determination of the residual MB concentration (C), the corresponding percent MB discoloration (E value) was calculated as:

\[ E = \left(1 - \frac{C}{C_0}\right) \times 100\% , \]

where, \( C_0 \) is the initial aqueous MB concentration (ideally 10.0 mg L\(^{-1}\)), while C gives the MB concentration after the experiment. The operational initial concentration \( (C_0) \) for each case was acquired from a triplicate control experiment without additive material (so-called blank). This procedure was to account for experimental errors during dilution of the stock solution, MB adsorption onto the walls of the reaction vessels, and all other possible side reactions during the experiments.

Results and discussion

Evidence for the complexity of the Fe\(^0\)/MnO\(_2\)/sand systems. Figure 2 compares the extent of MB discoloration in the six investigated systems for 7 and 47 days. Figure 2a clearly shows that, after 7 d, only MnO\(_2\) had not significantly discolored MB (4%) while Fe\(^0\) alone depicts the best discoloration efficiency (62%). The E values for the other systems varied between 31 and 40%. The increasing order of efficiency was: MnO\(_2\) < sand < Fe\(^0\)/MnO\(_2\) < Fe\(^0\)/sand < Fe\(^0\)/MnO\(_2\)/sand < Fe\(^0\). These results can be regarded as counter-intuitive since binary (Fe\(^0\)/MnO\(_2\), Fe\(^0\)/sand) and ternary (Fe\(^0\)/MnO\(_2\)/sand) performed less than Fe\(^0\) alone. In conventional shaken or stirred batch experiments, involved processes are accelerated to the extent that achieved results are the intuitive ones observed after 47 days (Fig. 2b).

Figure 2b compares the extent of MB discoloration in the six systems after 47 days. Compared to the results after 7 days, the extent of MB discoloration has increased to more than 50% in all systems, except MnO\(_2\) alone. Based on the absolute E values, the increasing order of efficiency was: MnO\(_2\) (4%) < sand (51%) < Fe\(^0\)/sand.
(66%) < Fe₀/MnO₂ = Fe₀/MnO₂/sand = Fe₀ (72%). It is interesting to note that Fe₀/sand performed less than Fe₀ alone and the two MnO₂-bearing systems. This observation alone confirms that MnO₂-amendment enhances the efficiency of Fe₀/H₂O systems by “reinforcing” corrosion (Eq. 3), but only in the long-term. Thus, the complexity of the ternary system as well as the need to understand its operation model is apparent. This is achieved herein by investigating the systems for 7, 18, 25 and 47 days. This corresponds to following the fate of aqueous MB (discoloration) as the contact time increases from 7 to 47 days⁵⁹,⁷⁰,⁷¹. In particular the variation of the pH value in the systems will be discussed in detail.

Effect of the contact time on the Fe₀/MnO₂/sand system. Figure 3a compares the extent of MB discoloration in Fe₀/MnO₂/sand systems for the four tested contact times (7, 18, 25 and 47 d) and Fig. 3b depicts the corresponding changes in pH values. It is seen that the lowest extent of MB discoloration corresponds to 18 d contact time. This means that after 7 days the system performed better than after 18 d. The observation can be regarded as counter-intuitive, while the monotonous increase of the pH value (Fig. 3b) is intuitive. The investigated systems were 0 ≤ [Fe₀] (g L⁻¹) ≤ 45, with [MnO₂] = 2.3 g L⁻¹ and [sand] = 45 g L⁻¹. This means that [Fe₀] = 0.0 g L⁻¹ corresponds to a MnO₂/sand system or simplified to the sand system as MnO₂ has no adsorptive affinities for MB (Fig. 2). In other words, the counter-intuitive observation corresponds to the effect of MnO₂ on the Fe₀/H₂O system.

A key feature from Fig. 3a is that there is an intuitive monotonous increase of the E value with increasing Fe₀ loading for all four tested contact times. This suggests that if the experiments were performed by different investigators, the given interpretations would have been conclusive and even convincing. The tested experimental conditions were selected based on past works⁶⁰,⁷⁹ to achieve such results. In addition, most of the observations...
made by researchers in Fe\textsuperscript{0}/H\textsubscript{2}O systems are just static snap-shots (mostly inaccurately measured) of processes occurring over an enormous range of time scales\textsuperscript{80}. Following this premise, it was necessary to further vary the experimental conditions to maximize the chance to make more relevant observation\textsuperscript{7}. One really intriguing observation is that the MB previously removed (t < 7 days) was released back to the solution at day 18 such that MB discoloration was lower even in the sand system (Fig. 3a).

This MB desorption is rationalized by the pH decrease accompanying MnO\textsubscript{2} reductive precipitation as given in Eq. (3b). By decreasing the pH value, further adsorption onto sand is inhibited and the previously adsorbed MB is desorbed and released into solution (Fig. 3a). On the other hand, the process of Fe\textsuperscript{0} dissolution by MnO\textsubscript{2} implies intensified interactions at the bottom of the assay tubes which slowed down the diffusion of MB from the bulk solution. Iron corrosion determined the extent of MB discoloration and the intuitive increase of MB discoloration with increasing Fe\textsuperscript{0} loading is observed in all systems only after a pseudo-steady state is established in the systems or the capacity of MnO\textsubscript{2} is exhausted. Alyoussef\textsuperscript{59,70,71} tested a parallel system with 4.5 g L\textsuperscript{-1} of MnO\textsubscript{2} and observed a larger decrease of MB discoloration for 18 days. Similar observations were made by Noubactep et al.\textsuperscript{82} in their experiments for uranium removal.

Figure 3b shows that for [Fe\textsuperscript{0}] > 7.5 g L\textsuperscript{-1}, the pH value monotonously increases with increasing Fe\textsuperscript{0} loading. For [Fe\textsuperscript{0}] < 7.5 g L\textsuperscript{-1}, there were some fluctuations justified by the co-occurrence of Fe\textsuperscript{0} corrosion (consuming protons—Eq. 1) and MnO\textsubscript{2} reductive dissolution (producing protons—Eq. 3b) to fix the pH of the systems. Again, once the oxidation capacity of MnO\textsubscript{2} is exhausted, iron corrosion controls the pH of the system.

The comparative evaluation of the time-dependent changes of E and pH values has clarified the operating mode of MnO\textsubscript{2} in enhancing the efficiency of the Fe\textsuperscript{0}/H\textsubscript{2}O system without any solid phase characterization. This discussion has equally not considered the redox reactivity of MnO\textsubscript{2} for Fe\textsuperscript{0} (and MB). Only the availability of “free” Fe\textsubscript{CPs} was considered in the investigated single, binary and ternary aggregate systems. Achieved results corroborate the usefulness of varying several operational parameters to better understand complex dynamic systems\textsuperscript{81,83,84}.

**Significance of the findings. Operating mode of remediation Fe\textsuperscript{0}/H\textsubscript{2}O systems.** This study has confirmed that Fe\textsuperscript{0} in engineered filtration systems is oxidized by protons to ferrous ion (Fe\textsuperscript{2+}) (Eq. 1). Fe\textsuperscript{3+} ions are partly transferred to the surface of available aggregates (e.g. MnO\textsubscript{2} and sand) and is oxidized further to ferric ion (Fe\textsuperscript{3+}) and deposited on the aggregates as hydroxides (in-situ coating) (Fig. 1). Iron oxide-coated sand is a good adsorbent for several contaminants including chromium\textsuperscript{39,85}, pathogens\textsuperscript{46,47} and phosphates\textsuperscript{88,89}. Fe\textsuperscript{0} oxidation also contributes to produce anoxic conditions which are favorable for the abiotic reductive transformation of several dissolved species including chlorinated compounds\textsuperscript{98,99}. Unlike sand and other inert aggregates, MnO\textsubscript{2} is reactive and uses Fe\textsuperscript{3+} for its reductive dissolution (Eq. 3). Because the reaction occurs at the surface of MnO\textsubscript{2} (Fig. 1), Fe\textsuperscript{3+} passivation is delayed until the oxidative capacity of MnO\textsubscript{2} is exhausted. Results presented herein have demonstrated these mechanisms excellently, while benefiting from the tracer nature of methylene blue (MB method)\textsuperscript{80,79}. In fact, mechanistic discussions are often complicated by the need to consider the redox reactivity of both Fe\textsuperscript{0} and MnO\textsubscript{2} with the contaminant of concern\textsuperscript{11}. In other words, one major output of this research is that the popular hypothesis to rationalize reductive transformations in Fe\textsuperscript{0}/H\textsubscript{2}O systems is faulty\textsuperscript{80}. The hypothesis that Fe\textsuperscript{0} is an electron donor for dissolved has been seriously challenged during the past 15 years, however, the questioned view is still prevailing\textsuperscript{11,36,59}.

The stoichiometry of electrochemical reactions (similar to Eq. 2) has been routinely used to design Fe\textsuperscript{0} remediation systems\textsuperscript{82,83}. The evidence that twice more Fe\textsuperscript{0} is needed to exchange the same number of electrons when hybrid systems are considered (two or more Fe\textsuperscript{0} layers) cannot be ignored. The statement is valid regardless of the approach used to estimate the efficiency of the system. However, the main problem has been the failure to properly consider the expansive nature of iron corrosion, which makes only hybrid systems viable in the long term\textsuperscript{89}.

**The importance of hybrid Fe\textsuperscript{0}/H\textsubscript{2}O systems.** The long history of Fe\textsuperscript{0} filtration systems teaches that only hybrid systems are sustainable. The Bischof filters, applied both for household and large-scale uses, contained a reactive zone made up of 25% sponge iron (vol/vol) mixed with gravel\textsuperscript{41,94}. The Multi-Soil-Layering of Wakatsuki et al.\textsuperscript{89} contained only 15% Fe\textsuperscript{0} (w/w) (iron fillings) mixed with 15% Fe\textsuperscript{0} (w/w) pelletized jute and balanced with zeolite (60%). The phosphate filters of Erickson et al.\textsuperscript{95} contained only up to 5% steel wool balanced with sand. All these systems operated for more than 1 year without clogging. In the framework of subsurface permeable reactive barrier systems operated for more than 1 year without clogging. In the framework of subsurface permeable reactive barrier systems92,93. The evidence that twice more Fe\textsuperscript{0} is needed to exchange the same number of electrons when hybrid systems are viable in the long term14.

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based systems have not built on existing knowledge as Se is still reported to be reduced by electrons from the metal body\(^{40,41-103}\). Following the state-of-the-art knowledge on the sustainability of Fe\(^0\) filtration, hybrid Fe\(^0\) systems should have been tested as stand-alone technology for Se removal. In essence, such work was independently conducted by Huang and his colleagues\(^{5,43,104,105}\) who developed and demonstrated the efficiency of a hybrid Fe\(^0\)/Fe\(^{3+}\) for the removal of several micro-pollutants, including Mo\(^{VI}\), NO\(_3\)\(^-\), and Se\(^{VI}\), and recently for the mitigation of pathogens (bacteria) from dairy manure. The fact that a hybrid system, initially developed for chemically reducible micro-pollutants is performing well for pathogens corroborate the idea that it suffices to sustain iron corrosion to achieve water treatment\(^{37,52-54,106}\). As discussed in the “Introduction”, Huang et al.\(^{43}\) have not convincingly demonstrated the specificity of their hybrid system (Fe\(^0\)/Fe\(^{3+}\)). This is particularly the case in a context where Fe\(^0\)/sand systems are already essentially more sustainable than pure Fe\(^0\) (100%)\(^{14,49}\). The present work also confirms previous results that any additive to Fe\(^0\) basically delay the availability of corrosion products under typical field conditions. The observed enhanced performance results from sustained iron corrosion in the whole system. The question then arises, what makes MnO\(_2\), a specific admixing aggregate for Fe\(^0\) filters?

**The suitability of hybrid Fe\(^0\)/MnO\(_2\) systems.** The presentation until now has demonstrated that applying Fe\(^0\) for water treatment is promising as mixing Fe\(^0\) with other aggregates delays passivation or sustain treatment efficiency. Moreover, substantial experiences have been accumulated on the functionality of hybrid systems for water treatment (“The importance of hybrid Fe\(^0\)/H\(_2\)O systems”). The knowledge that Fe\(^0\) acts as generator of contaminant scavengers (and never as reducing agent) implies that adsorption and co-precipitation are the fundamental mechanisms of contaminant removal in Fe\(^0\)/H\(_2\)O systems. Hybrid systems tested as means to prevent iron passivation include amendment with granular activated carbon (GAC), magnetite (Fe\(^{3+}\)), manganese oxides (MnO\(_x\)), pyrite (FeS\(_2\)), and sand\(^{15}\). Among these aggregates, MnO\(_2\) and FeS\(_2\) are the most chemically reactive\(^{60-72}\). Both aggregates induce a pH shift to more acidic values. However, because iron corrosion increases the pH, it is possible to find the optimal Fe\(^0\)/FeS\(_2\) and/or Fe\(^0\)/MnO\(_2\) ratio for case-specific water treatment. Therefore, long-term systematic testing with well-characterized materials is necessary.

Note that Fe\(^0\) is a generator of iron oxides, and adding Mn oxides (MnO\(_x\)) to the system creates a very complex system, which is not new to geochemists, but which is yet to be investigated in the context of water treatment\(^{68,72}\). In fact, taken individually, the redox reactivity of these minerals plays important roles in the fate and transformation of many contaminants in natural environments\(^{69,81-84,70-72}\). Available works mostly investigate simple model systems with few contaminants\(^{68,72}\). To bridge the gap between simple model systems and complex environmental systems, a profound understanding of the redox reactivity of Mn- and Fe-oxides in complex model systems toward water decontamination is urgently needed. The effects of natural ligands (Cl\(^-\), HCO\(_3\)\(^-\), PO\(_4\)\(^{3-}\), SO\(_4\)\(^{2-}\)) and natural organic matter (NOM) on the redox reactivity of Fe\(^0\)/MnO\(_2\) systems need to be investigated as well. Moreover, there is need to investigate the following: (i) fate of contaminants in Fe\(^0\) systems, and (ii) the safe disposal of spent Fe\(^0\) materials, including their use as filler material in novel construction materials, and the behavior of contaminants in such materials.

**Concluding remarks**

This study clearly delineates the important role of reactive MnO\(_2\) minerals on the process of water treatment using Fe\(^0\)-based systems. The presence of MnO\(_2\) induces Fe\(^{3+}\) oxidation at the mineral surface, resulting in a significant delay of Fe\(^0\) passivation compared to that attained in Fe\(^0\) and Fe\(^0\)/sand systems. Being a natural mineral or a soil resource, its incorporation in Fe\(^0\) filters reinforces the frugality of this already demonstrated affordable system. It is expected that adding MnO\(_2\) to Fe\(^0\)/H\(_2\)O will create geochemical dynamics in the system which would sustain iron corrosion and maintain the efficiency of system for water decontamination for the long term. This would make Fe\(^0\) filters a sustainable solution for decentralized safe drinking water provision and enable the realization of universal access to safe drinking water and even on a self-reliant manner. To bridge the existing knowledge gaps, the need for further research entailing long-term testing of Fe\(^0\) systems was highlighted.

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Author contributions
G.A., V.C., N.G.-B. and C.N. conceived the presented idea and developed the theory. G.A. carried out the experiments. C.N. supervised this work. W.G. supervised the redaction of the first draft by V.C. and N.G.-B. All authors discussed the results and contributed to the final manuscript.

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