The Suitability of Methylene Blue Discoloration (MB Method) to Investigate the Fe\textsuperscript{0}/MnO\textsubscript{2} System

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Abstract: The typical time-dependent decrease of the iron corrosion rate is often difficult to consider while designing Fe\textsuperscript{0}-based remediation systems. One of the most promising approaches is the amendment with manganese dioxide (Fe\textsuperscript{0}/MnO\textsubscript{2} system). The resulting system is a very complex one where characterization is challenging. The present communication uses methylene blue discoloration (MB method) to characterize the Fe\textsuperscript{0}/MnO\textsubscript{2} system. Shaken batch experiments (75 rpm) for 7 days were used. The initial MB concentration was 10 mg L\textsuperscript{-1} with the following mass loading: [MnO\textsubscript{2}] = 2.3 g L\textsuperscript{-1}, [sand] = 45 g L\textsuperscript{-1}, and 0 < [Fe\textsuperscript{0}] (g L\textsuperscript{-1}) ≤ 45. The following systems where investigated: Fe\textsuperscript{0}, MnO\textsubscript{2}, sand, Fe\textsuperscript{0}/MnO\textsubscript{2}, Fe\textsuperscript{0}/sand, and Fe\textsuperscript{0}/MnO\textsubscript{2}/sand. Results demonstrated that MB discoloration is influenced by the diffusive transport of MB from the solution to the aggregates at the bottom of the test-tubes. Results confirm the complexity of the Fe\textsuperscript{0}/MnO\textsubscript{2}/sand system, while establishing that both MnO\textsubscript{2} and sand improve the efficiency of Fe\textsuperscript{0}/H\textsubscript{2}O systems in the long-term. The mechanisms of water decontamination by amending Fe\textsuperscript{0}-based systems with MnO\textsubscript{2} is demonstrated by the MB method.

Keywords: manganese oxides; MB method; reactivity materials; water treatment; zero-valent iron

1. Introduction

The use of metallic iron (Fe\textsuperscript{0}) for environmental remediation and water treatment has boomed during the past three decades [1–3]. Under environmental conditions, Fe\textsuperscript{0} is spontaneously oxidized to Fe\textsuperscript{II} and Fe\textsuperscript{III} oxides/hydroxides (iron corrosion products—FeCPs) which remove contaminants from an aqueous solution by adsorption and co-precipitation [4–7]. An inherent problem of Fe\textsuperscript{0} is that its corrosion rate decreases with increasing service life [8]. This property has been termed as reactivity loss in the Fe\textsuperscript{0} literature. Since the end of the 1990s, efficient tools have been sought to address “reactivity loss” or improve the corrosion rate. Tested approaches include [1,3]: increasing the specific surface area including using nano-Fe\textsuperscript{0}, alloying Fe\textsuperscript{0} with more noble metals (e.g., Fe\textsuperscript{0}/Pd\textsuperscript{0}), adding oxidizing solutions (e.g., H\textsubscript{2}O\textsubscript{2}, O\textsubscript{3}), and admixing with other aggregates (e.g., gravel, MnO\textsubscript{2}, pyrite, sand). Except for MnO\textsubscript{2} addition, it is very difficult to maintain the enhanced Fe\textsuperscript{0} oxidation effect for a long time. There are three main reasons: (i) added oxidizers are unstable solutions (e.g., H\textsubscript{2}O\textsubscript{2}), (ii) oxidation enhancers are in limited quantity (e.g., bimetallic coating), and (iii) the enhancing capacity of the aggregate is limited (e.g., gravel, sand). In contrary, the
addition of MnO$_2$ potentially creates a reactive Fe and Mn oxides mixture, for which long term reactivity is acknowledged but yet to be investigated [9,10].

Fe$^0$/MnO$_2$ systems have been extensively investigated during the past two decades and include: (i) Fe$^0$/MnO$_2$ composites [11,12] and (ii) Fe$^0$/MnO$_2$ mixtures [7,13]. There is an agreement on the MnO$_2$ enhancing decontamination effects in Fe$^0$/H$_2$O system, but reported disagreement on the actual operating mode of this system. Theoretically, MnO$_2$ can influence contaminant removal via adsorption, catalysis, and redox activities [14]. MnO$_2$ participates in oxidation of selected contaminants (e.g., aromatic amines, antibiotics). It can also function in a galvanic cell with iron to promote electron transfer on the surface of iron to alleviate Fe$^0$ passivation. The following three examples illustrate discrepancy in reports (i) Liang et al. [12] reported that there was no galvanic cells between Fe$^0$ and MnO$_2$ in Fe$^0$/MnO$_2$ composites for As removal. Rather, there is formation of a Fe/Mn binary oxides layer on the Fe$^0$ surface resulting in intensive corrosion. In other words, Liang et al. [12] argued that binary Fe/Mn oxides avoid or suppress the formation of crystalline iron (hydr)oxides. (ii) Gheju and Balcu [7] argued that the favorable synergistic effect of Fe$^0$/MnO$_2$ mixtures results from the capacity of MnO$_2$ to accelerate Fe$^0$ oxidative dissolution. Thereby, supplementary amounts of secondary adsorbents and reductants are generated for Cr$^{VI}$ removal and reduction. (iii) Dong et al. [14] enhanced electron transfer “on the surface of Fe$^0$ with the presence of MnO$_2$” in the process of tetracycline removal, yielding a more sustainable Fe$^0$/H$_2$O system to lengthen the lives of the Fe$^0$ filtration system. There is an urgent need to clarify the real operating mode of the Fe$^0$/MnO$_2$ system.

This study seeks to clarify the operating mode of Fe$^0$/MnO$_2$ systems using the methylene blue discoloration method (MB method). The MB method entails characterizing MB discoloration in Fe$^0$/sand systems [15,16]. The Fe$^0$/MnO$_2$/sand system is characterized for MB discoloration for 7 days. A commercial Fe$^0$ specimen and a natural MnO$_2$ mineral are used. Three single (Fe$^0$, MnO$_2$, sand), two binary (Fe$^0$/MnO$_2$ and Fe$^0$/sand) and one ternary (Fe$^0$/MnO$_2$/sand) systems are investigated and the results are comparatively discussed.

2. The Fe$^0$/MnO$_2$ System

Aqueous contaminant removal in the presence of Fe$^0$ primary depends on the chemical thermodynamics of two redox systems: Fe$^{III}$/Fe$^0$ (E$^0$ = −0.44 V) and H$^+$ /H$_2$O (E$^0$ = 0.00 V). Both aqueous solution behavior and redox thermodynamics should be considered. In addition, the eventual redox properties of contaminants (e.g., As, Cr, MB) and additives (e.g., Fe$_2$O$_4$, FeS$_2$, MnO$_2$) are to be equally considered. Table 1 summarizes the half-redox reactions relevant for the discussion in this paper and their electrode potential. As a rule, Fe$^0$ can be oxidized by the reducing agent of all couples with E$^0$ > −0.44 V.

| Reaction | E$^0$ (V) | Number |
|----------|-----------|---------|
| Fe$^{II} + 2e^−$ ⇔ Fe$^0$ | −0.44 | (1) |
| 2 H$^+$ + 2e$^−$ ⇔ H$_2$ | 0.00 | (2) |
| MB$^+$ + 2e$^−$ + H$^+$ ⇔ LMB | 0.01 | (3) |
| Fe$^{III} + e^−$ ⇔ Fe$^{II}$ | 0.77 | (4) |
| O$_2$ + 2H$_2$O + 4e$^−$ ⇔ 4OH$^-$ | 0.81 | (5) |
| MnO$_2$ + 4H$^+$ + 2e$^−$ ⇔ Mn$^{II}$ + 2H$_2$O | 1.23 | (6) |

The five theoretically possible redox reactions (E$^0$ > −0.44 V) are Fe$^0$ oxidation by: (i) water (H$^+$), (ii) methylene blue (MB$^+$), (iii) ferric iron (Fe$^{III}$), (iv) dissolved oxygen (O$_2$), and (v) manganese dioxide (MnO$_2$). However, it has been clearly established that, at pH > 4.5 only water oxidized Fe$^0$ [18,19]. In other words, Fe$^0$ cannot be the anodic reaction
simultaneous to the reduction of MB\textsuperscript{+}, O\textsubscript{2} and MnO\textsubscript{2}. Clearly, wherever these species have been reduced in a Fe\textsuperscript{0}/H\textsubscript{2}O system, electron donors were primary (Fe\textsuperscript{II}, H\textsubscript{2}) or secondary (Fe\textsubscript{3}O\textsubscript{4}, green rust) iron corrosion products. This knowledge is century old [2,18]. The major reason why electrons from Fe\textsuperscript{0} are not available to dissolved species is that the Fe\textsuperscript{0} surface is always covered by an oxide scale which acts as a diffusion barrier for dissolved species, and an electronic barrier for electrons. Concerning ferric ions (Table 1 (4)), it is considered that Fe\textsuperscript{3+} ions are generated in the vicinity of Fe\textsuperscript{0} and may exchange electrons with the metal body. Clearly, the only two possible electrochemical reactions in a Fe\textsuperscript{0}/H\textsubscript{2}O system are (Equations (1) and (2)):

\[
\text{Fe}^0 + 2 \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \tag{1}
\]

\[
\text{Fe}^0 + 2 \text{Fe}^{3+} \rightarrow 3 \text{Fe}^{2+} \tag{2}
\]

There are many possible reaction combinations emanating from Table 1. The discussion is limited on the fate of MB\textsuperscript{+}, MnO\textsubscript{2} and O\textsubscript{2}, which are reactants in this study. The survey of the E\textsuperscript{0} values reveals two key issues: (i) Fe\textsuperscript{3+} and MnO\textsubscript{2} oxidize LMB to MB\textsuperscript{+}, and (ii) O\textsubscript{2} and MnO\textsubscript{2} oxidize Fe\textsuperscript{2+}. In other words, MB discoloration by a redox process is not possible in the Fe\textsuperscript{0}/H\textsubscript{2}O system, while the production of Fe\textsuperscript{III} species might be quantitative. Fe\textsuperscript{III} oxides are contaminant scavengers and in this study discoloring agents for MB [16]. Clearly, Fe\textsuperscript{2+} from iron corrosion (Table 1 (1)) is initially used to reduce MnO\textsubscript{2} (Equation (3)). Once the oxidative capacity of MnO\textsubscript{2} is exhausted, “excess” Fe\textsuperscript{III} oxides are generated for MB quantitative discoloration by adsorption and co-precipitation.

\[
2 \text{Fe}^{2+} + \text{MnO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Mn}^{2+} + 2 \text{FeOOH} + 2 \text{H}^+ \tag{3}
\]

To summarize, the chemistry of the Fe\textsuperscript{0}/MnO\textsubscript{2} system shows two important features: (i) Fe\textsuperscript{0} cannot exchange electrons with any dissolved species, and (ii) MnO\textsubscript{2} cannot form a galvanic cell with Fe\textsuperscript{0}. The remaining theoretical possibilities are: (i) MnO\textsubscript{2} influences contaminant removal via adsorption, catalysis, co-precipitation and redox activities (Assertion 1), (ii) MnO\textsubscript{2} participates in the oxidation of selected contaminants (Assertion 2), and (iii) MnO\textsubscript{2} disturbs the formation of oxide scales in the vicinity of Fe\textsuperscript{0} (Assertion 3). Assertion 3 is obvious and universally valid as even external Fe\textsuperscript{2+} disturbs the formation of oxide scale [6,17]. The remaining task is to check the validity of Assertion 1 and Assertion 2 on a case specific basis. Herein, the discussion is eased by the evidence that MB has not adsorptive nor reductive affinities with the species in presence. In other words, MB discoloration results from co-precipitation with excess FeCPs. Adding sand to the system is inherent to the MB method [16], wherein the discoloration of MB by sand is inhibited as it is progressively coated by in-situ generated FeCPs. The validity of Assertion 1 and Assertion 2 will be tested for the Fe\textsuperscript{0}/MnO\textsubscript{2}/MB system.

3. Materials and Methods

This experimental section is adapted from Xiao et al. [20] using the same experimental design but quiescent experiments (0 rpm) and pyrite (FeS\textsubscript{2}) as an additive.

3.1. Solutions

The used methylene blue (MB-Basic Blue 9 from Merck) was of analytical grade. The working solution was 10.0 mg L\textsuperscript{-1} prepared by diluting a 1000 mg L\textsuperscript{-1} stock solution. The stock solution was prepared by dissolving accurately weighted MB in tap water. The use of tap water rather than deionized water was motivated by the fact that tap water is closer to natural water in its chemical composition. The MB molecular formula is C\textsubscript{16}H\textsubscript{18}N\textsubscript{3}SCl corresponding to a molecular weight of 319.85 g. MB was chosen in this study because of its well-known strong adsorption onto solids [20].
3.2. Solid Materials

3.2.1. 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 [20].

3.2.2. 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 [21,22] 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 [16].

3.2.3. 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 [23,24]. The adsorption capacity of sand for MB has been systematically documented as early as in 1955 by Mitchell et al. [25].

3.3. MB Discoloration

Shaken batch experiments at 75 rpm were conducted in assay tubes for an experimental duration of 7 d. The batches consisted of 0.0 or 1.0 g of sand, 0.0 to 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 six investigated systems were: (i) Fe⁰ alone, (ii) sand alone, (iii) MnO₂ alone, (iv) Fe⁰/sand, (v) Fe⁰/MnO₂ and (vi) Fe⁰/sand/MnO₂. The efficiency of individual systems at discoloring 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 triplicate, and averaged values are presented. Table 2 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 ‘Fe⁰/MnO₂/sand system’, without MnO₂ nor sand.

Table 2. Overview of the six (6) investigated systems. The material loadings correspond to Figure 1.

| 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 | Fe⁰/MnO₂ | Reference system |
| System 6 | 4.5 to 45 | 45.0 | 4.5 | Fe⁰/sand/MnO₂ | Fe⁰ loading as variable |
Figure 1. Comparison of the efficiency of tested materials for methylene blue (MB) discoloration for 7 days. Experimental conditions: [Fe⁰] = 0 to 45 g L⁻¹; [sand] = 45 g L⁻¹; and [MnO₂] = 2.3 g L⁻¹, shaken intensity: 75 rpm.

3.4. 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 a 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., Oberbayern, Germany).

3.5. 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 (Equation (4)). After the determination of the residual MB concentration (C), the corresponding percent MB discoloration (E value) was calculated as:

\[ E = [1 - (C/C_0)] \times 100\% \]  \hspace{1cm} (4)

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.

4. Results and Discussion

4.1. Evidence for the Complexity of the Fe⁰/MnO₂ System

Figure 1 summarizes the extent of MB discoloration in the six investigated systems. It is seen that the pure MnO₂ system does not exhibit any significant MB discoloration
while the remaining systems exhibited E values varying from 30 to 40%. All these systems have in common the presence of sand (45.0 g L$^{-1}$) and those containing Fe$^0$, additionally contains 4.5 g L$^{-1}$ of this reactive material. The evidence that adding 4.5 g L$^{-1}$ of Fe$^0$ and 2.3 g L$^{-1}$ of MnO$_2$ to 45.0 g L$^{-1}$ sand does not significantly improve the extent of MB discoloration can be regarded as intriguing. Previous reports using quiescent batch experiments even reported on an initial decrease of E values in Fe$^0$/H$_2$O systems due to the presence of both MnO$_2$ and sand [16]. Clearly, while increasing the available surface area (different materials), MB discoloration is not initially improved. This can be justified by one or both of the following hypotheses: (i) chemical reactions occurring in the system hinder MB discoloration by adsorption onto sand (Hypothesis 1), and (ii) there are chemical interactions between available aggregates (e.g., Fe$^0$ and MnO$_2$) avoiding or delaying MB discoloration (Hypothesis 2). Hypothesis 1 corresponds to the historical observation by Mitchell et al. [25] that clean sand is a better adsorbent for MB that iron oxide-coated sand. This idea is also the cornerstone of the MB method and the reason why sand was added in the present study. Hypothesis 2 considers the reactive nature of MnO$_2$ [21,22] and encompasses the fact that by using Fe$^{2+}$ for its reductive dissolution (Equation (3)), MnO$_2$ is delaying the availability of 'free' FeCPs for MB discoloration by co-precipitation [26].

**Hypothesis 1:** Chemical reactions occurring in the system hinder MB discoloration by adsorption onto sand.

**Hypothesis 2:** There are chemical interactions between available aggregates (e.g., Fe$^0$ and MnO$_2$) avoiding or delaying MB discoloration.

A closer look at Figure 1 reveals the following increasing order of E values: MnO$_2$ (3%) < sand (30%) < MnO$_2$/sand (31%) < Fe$^0$/MnO$_2$ (34%) < Fe$^0$/MnO$_2$/sand (36%) < Fe$^0$/sand (40%). Considering the standard deviations (Figure 1) it is clear that there was no significant difference between the performance of the three Fe$^0$-bearing systems: Fe$^0$/MnO$_2$ (34 ± 4%) < Fe$^0$/MnO$_2$/sand (36 ± 7%) < Fe$^0$/sand (40 ± 9%). Considering the absolute values, the ternary system (Fe$^0$/MnO$_2$/sand) performed less than the binary system with sand (Fe$^0$/sand). For binary systems, Fe$^0$/MnO$_2$ exhibited the lowest extent of MB discoloration. These observations collectively validate Hypothesis 2: MnO$_2$ reductive dissolution initially decreases the number of active sites for MB discoloration. This is because Fe$^{2+}$ oxidation (Equation (3)) occurs at the MnO$_2$ surface and resulting Fe$^{III}$ oxides coat the MnO$_2$ surface and is thus not available for the co-precipitation of the cationic dye (MB).

The remainder of the presentation discusses changes in the ternary Fe$^0$/MnO$_2$/sand system as the Fe$^0$ loading varies from 0 to 45 g L$^{-1}$ while the sand loading is 45 g L$^{-1}$ and the MnO$_2$ loading 2.3 g L$^{-1}$.

### 4.2. MB Discoloration

Figure 2 summarizes changes of the E values in the systems Fe$^0$/MnO$_2$, Fe$^0$/sand, and Fe$^0$/MnO$_2$/sand as the Fe$^0$ loading varied from 0 to 45 g L$^{-1}$. It is seen that at [Fe$^0$] = 0 g L$^{-1}$, the two sand-bearing systems exhibited an E value close to 30%. This corresponds to the results reported in Figure 1 and is in tune with the observation of Mitchell et al. [25], that sand is an excellent adsorbent for MB [15,16]. It is also seen that the E value monotonously increases with increasing Fe$^0$ loadings reaching a maximum value of about 52% for the Fe$^0$/sand system and 64% for the ternary system respectively. The observation that the ternary system performed better than the binary may be misunderstood as contrary to the reports in Section 1 (Figure 1). However, data in Figure 1 corresponds to [Fe$^0$] = 4.5 g L$^{-1}$. Figure 2 clearly shows that for this Fe$^0$ loading, Fe$^0$/sand performs better than Fe$^0$/MnO$_2$/sand. The better performance of the ternary system relative to Fe$^0$/sand for [Fe$^0$] > 10 g L$^{-1}$, is attributed to the action of MnO$_2$ in reinforcing Fe$^{0}$ corrosion and producing “excess” FeCPs for MB co-precipitation. This operating mode is illustrated the
best in the binary Fe\(^0\)/MnO\(_2\) system which performed lower that the sand-bearing systems for [Fe\(^0\)] < 10 g L\(^{-1}\), and far higher for [Fe\(^0\)] > 10 g L\(^{-1}\), reaching 70% at [Fe\(^0\)] = 45 g L\(^{-1}\).

The Fe\(^0\)/MnO\(_2\) system shows a diphasic pattern in the process of MB discoloration. The initial discoloration (up to [Fe\(^0\)] = 12 g L\(^{-1}\)) is very rapid, followed by slower discoloration for higher [Fe\(^0\)] values. It can be considered that for [Fe\(^0\)] < 12 g L\(^{-1}\), the Fe\(^0\)/MnO\(_2\) ratio is optimal to avoid intra-particle diffusion such that "excess" FeCPs is immediately available for MB co-precipitation. For [Fe\(^0\)] > 12 g L\(^{-1}\), MB must diffuse through a thicker layer of Fe\(^0\) particles at the bottom of the test-tubes. Remember that in the presence of sand, the diffusion paths are larger and explain why, for higher Fe\(^0\) loadings, the ternary system performed less than the Fe\(^0\)/MnO\(_2\) system, despite initial rapid adsorption onto sand. In other words, after the complete coverage of sand by FeCPs, MB discoloration solely results from co-precipitation with free FeCPs. These free FeCPs are less available in the ternary system compared to the binary Fe\(^0\)/MnO\(_2\) system.

![Figure 2](image_url)

**Figure 2.** Methylene blue discoloration in Fe\(^0\)/sand/MnO\(_2\) systems as impacted by the addition of various Fe\(^0\) loading for 7 days. Experimental conditions: [Fe\(^0\)] = 2.3 to 45 g L\(^{-1}\); [sand] = 45 g L\(^{-1}\); and [MnO\(_2\)] = 2.3 g L\(^{-1}\), shaken intensity: 75 rpm. The lines are not fitting functions, they simply connect points to facilitate visualization.

### 4.3. pH Value

Figure 3 summarizes changes of the pH values in the systems Fe\(^0\)/MnO\(_2\), Fe\(^0\)/sand, and Fe\(^0\)/MnO\(_2\)/sand as the Fe\(^0\) loading varied from 0 to 45 g L\(^{-1}\) (pH\(_0\) = 8.2). It is seen that for [Fe\(^0\)] < 10 g L\(^{-1}\), the three systems exhibited very different behaviors; the pH value (i) first decreased to a minimum of 7.8 for [Fe\(^0\)] = 2.3 g L\(^{-1}\) in the Fe\(^0\)/MnO\(_2\)/sand system, (ii) is constant to 8.1 in the Fe\(^0\)/sand system, and (iii) monotonously increased in the Fe\(^0\)/MnO\(_2\) system. The two processes determining the final pH value in each systems are: (i) iron corrosion consuming protons (Equation (1)), and MnO\(_2\) reductive dissolution releasing protons (Equation (3)). Accordingly, in the Fe\(^0\)/sand system, only iron corrosion fixes the pH and the constant value for [Fe\(^0\)] < 11 g L\(^{-1}\) corresponds to H\(^+\) adsorption onto
the surface of sand. The pH starts to increase only after the ion exchange capacity of sand for H\(^+\) is exhausted.

Concerning the Fe\(^0\)/MnO\(_2\) system, there was a slight pH decrease for [Fe\(^0\)] = 0.5 and 1.1 g L\(^{-1}\) but from [Fe\(^0\)] = 2.3 g L\(^{-1}\) onwards, there was an increase of the pH value. This means that under the experimental conditions (e.g., used mass loading and shaken at 75 rpm for 7 days), MnO\(_2\) reductive dissolution fixed the final pH value only for [Fe\(^0\)] < 2.3 g L\(^{-1}\). For higher Fe\(^0\) loadings, the pH is fixed by iron corrosion and the final pH values determined by the extent to which free protons are released to the solution above the mixture of aggregates (e.g., Fe\(^0\), MnO\(_2\) and sand). For this reason, the Fe\(^0\)/MnO\(_2\) (without sand) exhibited larger final pH values than the Fe\(^0\)/MnO\(_2\)/sand in which protons are fixed at the negatively charged sand surface.

![Figure 3](image-url) **Figure 3.** pH value in Fe\(^0\)/sand/MnO\(_2\) systems as impacted by the addition of various Fe\(^0\) loading for 7 days. Experimental conditions: [Fe\(^0\)] = 2.3 to 45 g L\(^{-1}\); [sand] = 45 g L\(^{-1}\); and [MnO\(_2\)] = 2.3 g L\(^{-1}\), shaken intensity: 75 rpm. The lines are not fitting functions, they simply connect points to facilitate visualization.

### 4.4. The Operating Mode of Fe\(^0\)/MnO\(_2\) Systems

The efficiency of Fe\(^0\)/H\(_2\)O systems for water decontamination relies primarily on the electrochemical corrosion of Fe\(^0\) by water (Equation (1)). This oxidative dissolution is followed by a series of chemical reactions in the vicinity of the Fe\(^0\) surface yielding to the formation of an oxide scale which is known as passive film [1,3]. The enhanced efficiency of Fe\(^0\)/MnO\(_2\)/H\(_2\)O systems compared to their Fe\(^0\)/H\(_2\)O counterparts has been correctly justified by sustained generation of native FeCPs for contaminant adsorption and co-precipitation. However, the further interpretation of achieved results were species-dependent. For example, Bui et al. [26] considered that there are oxidative species like OH radicals in the system to oxidize As\(^{III}\) to As\(^{V}\) with better adsorptive affinities to FeCPs. This explanation becomes speculative when one considers that quantitative removal of Se which has also been documented [27], premised the reduction of Se\(^{VI}\) to Se\(^{IV}\). By using MB
as operational tracer for the availability of FeCPs in investigated systems, this study has elegantly explained the operating mode of the Fe$^0$/MnO$_2$/H$_2$O system.

By adding sand to the system as per the MB method [15,16], this study has thoroughly characterized MB discoloration in the Fe$^0$/MnO$_2$/sand/H$_2$O system. Changes of the E and pH values clearly show that sand is coated in situ by FeCPs and thus, can be regarded as storage room for fresh FeCPs, avoiding their accumulation in the Fe$^0$ vicinity and thus, delaying Fe$^0$ passivation. Fe$^0$ passivation is also delayed by two major factors attributed to the presence of MnO$_2$: (i) consumption of Fe$^{2+}$ for the MnO$_2$ reductive dissolution (Equation (3)) [28], and (ii) disturbance of the generation of “protective” oxides by virtue of the presence of Mn$^{2+}$ ions.

The discussion of the chemistry of the Fe$^0$/MnO$_2$/H$_2$O systems has excluded the formation of galvanic cells between Fe$^0$ and MnO$_2$ as a reason for enhanced efficient of Fe$^0$/H$_2$O systems through MnO$_2$ amendment. Given that the reductive transformation of any dissolved species by electrons from the metal body is impossible [18,19,29], this study established that adding MnO$_2$ to Fe$^0$/H$_2$O systems should be regarded as creating a reactive Fe/Mn mineral mixture. The geochemistry of such mixtures is well-known to geochemists [9,10,30,31]. However, their suitability for decontaminating engineered systems is yet to be systematically investigated [30,31].

Finally, the working hypotheses shall be tested: (i) MnO$_2$ influences contaminant removal via adsorption, catalysis, co-precipitation and redox activities (Assertion 1), and MnO$_2$ participates in the oxidation of selected contaminants (Assertion 2). Both assertions are valid as the MB method is just like a “separation of variables” enabling to trace the availability of native FeCPs which are Fe minerals. The mixture of Fe and Mn minerals is a reactive system that shall be tested for several contaminants and groups of contaminants to prepare for the advent of sustainably engineered Fe$^0$/MnO$_2$ systems.

5. Conclusions

The MB method proved to accurately describe the complexity of the Fe$^0$/MnO$_2$/sand system. In particular, despite the absence of chemical, mineralogical/structural and morphological characterization of used aggregates, this method sufficiently described the dynamics within the named system. The uniqueness of the MB method is its simplicity and its affordability as only a UV spectrophotometer is needed. The method can be adapted to all Fe$^0$-based systems. However, it should be carefully considered that site-specific experiments with relevant contaminants are still unavoidable. This is because the affinity of individual contaminants to FeCPs depends on its speciation as well. The major output of this research is that MnO$_2$ sustains Fe$^0$ corrosion and thus the decontamination efficiency of Fe$^0$/H$_2$O systems. Thus adding, calculated amounts of well-characterized MnO$_2$ minerals to Fe$^0$ filters is one highway to more sustainable filtration systems. In exploring this avenue, the reactivity of used aggregates should receive particular attention.

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