Characterizing the impact of pyrite addition on the efficiency of Fe⁰/H₂O systems

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The role of pyrite (FeS₂) in the process of water treatment using metallic iron (Fe⁰) was investigated. FeS₂ was used as a pH-shifting agent while methylene blue (MB) and methyl orange (MO) were used as an indicator of reactivity and model contaminant, respectively. The effect of the final pH value on the extent of MB discoloration was characterized using 5 g L⁻¹ of a Fe⁰ specimen. pH variation was achieved by adding 0 to 30 g L⁻¹ of FeS₂. Quiescent batch experiments with Fe⁰/FeS₂/sand systems (sand loading: 25 g L⁻¹) and 20 mL of MB were performed for 41 days. Final pH values varied from 3.3 to 7.0. Results demonstrated that MB discoloration is only quantitative when the final pH value was larger than 4.5 and that adsorption and co-precipitation are the fundamental mechanisms of decontamination in Fe⁰/H₂O systems. Such mechanisms are consistent with the effects of the pH value on the decontamination process.

The removal of anthropogenic and natural pollutants from aqueous systems is a major environmental concern. Several technologies have been developed for water treatment over the past 170 years¹⁻⁴. Technologies based on adsorption processes have been proven to be the most affordable and suitable for water treatment in low-income communities. During the past three decades, metallic iron (Fe⁰) has been intensively used for in-situ environmental remediation⁵⁻⁷ and ex-situ water treatment⁸⁻¹¹. However, controversy still exists on whether Fe⁰ acts as a reducing agent for several pollutants (e.g. selected chemicals)¹¹ or a generator of contaminant scavengers (iron corrosion products–FeCPs) for all classes of pollutants (e.g. chemicals and pathogens). It is certain that, while undergoing oxidative dissolution, Fe⁰ induces contaminant removal in aqueous systems, and this process can last for decades. This ability to remove contaminants for prolonged periods has prompted the use of granular Fe⁰ for decentralized water treatment.

Metallic iron (Fe⁰) and iron sulfide (FeS)-based materials (including pyrite–FeS₂) are two important components of Fe⁰-based water treatment technology²²,²³,²⁸⁻⁴¹. Both materials are reported to be stand-alone reducing agents that effectively degrade several aqueous contaminants. In this context, Henderson and Demond have explicitly compared the suitability of both materials, and observed the superiority of FeS (including FeS₂) over Fe⁰ with respect to the sustainability in terms of loss of permeability. During the past two decades, Fe⁰ and FeS have been often mixed in an effort to increase the efficiency of single-Fe⁰ systems. However, FeS₂ is mostly added to avoid the formation of a passive oxide scale (oxide film) which can hinder further reactions between the Fe⁰ and pollutants. This application contradicts the successful use of FeS to improve the removal of non-reducible contaminants (e.g. As) in Fe⁰/H₂O systems. Thus, there is a need to understand the real mechanism by which FeS₂ improves the efficiency of Fe⁰/H₂O systems, irrespective of any redox transformation. The oxidative dissolution of both Fe⁰ (Eq. 1) and FeS₂ (Eq. 2) typically releases Fe²⁺, which is also a stand-alone reducing agent for several contaminants. Fe²⁺ from Eq. (1) and/or Eq. (2) can be further oxidized to Fe³⁺ (Eq. 3).

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\text{Fe}^0 + 2H^+ \rightarrow \text{Fe}^{2+} + H_2 \]  
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\text{FeS}_2 + 7/2O_2 + H_2O \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2H^+ \]  

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It is evident that both reactions depicted by Eqs. (1 and 3) consume acidity ($H^+$), while reaction in Eq. 2 produces $H^+$. According to the Le Chatelier’s principle, the reactions consuming $H^+$ (Eq. 1 and 3) are accelerated by pyrite oxidation (Eq. 2). Here, the forward $Fe^0$ dissolution is given priority as it is the main reactant, while less attention is paid to the possible inhibitory effect of $FeS_2$ oxidation on $Fe^0$ dissolution (production of $Fe^{2+}$). In fact, using $FeS_2$ to enhance iron corrosion is consistent with scientific principles (“Background to the experimental methodology”). However, this understanding provides no insights on the mechanisms of decontamination (adsorption, co-precipitation) and/or induced redox transformation of contaminants (degradation, precipitation). The stoichiometry of the reaction in Eq. (1) shows that 1 mol of $FeO$ generates one mole of $Fe^{2+}$ and one mole of $H_2$, while 1 mol of $FeS_2$ generates only one mole of $Fe^{2+}$ (Eq. 2). Given that $Fe^{2+}$ and $H_2$ are stand-alone reducing agents, it is clear that there are more reducing agents (electron donors) in $FeO/H_2O$ than in $FeS_2/H_2O$ systems. The actual reductive characteristics of each system (i.e., $FeO/H_2O$, $FeS_2/H_2O$, and $FeO/FeS_2/H_2O$) primarily depend on the relative dissolution kinetics of $FeO$ and $FeS_2$. According to their relative electrode potentials (-0.44 V for $Fe^{2+}/Fe$ versus 0.25 V for $S^{2-}/S^{0}$), $FeS_2$ should be transforming $S^{2-}$ species back to $S^0$ ones. This would correspond to the blocking of oxidative dissolution of $FeO$. Although this reaction is thermodynamically feasible, it is masked by the more kinetically favourable $FeS_2$ oxidation by dissolved $O_2$. In the long-term (i.e., over the 41 d investigated herein), this process could contribute to the $FeS_2$ cycle within a $FeO/FeS_2/H_2O$ system.

The presentation above demonstrates the extreme complexity of the $FeO/FeS_2/H_2O$ system and accounts for the controversies in the literature on the role of $FeS_2$ in enhancing the efficiency of $FeO/H_2O$ systems. Thus, a detailed investigation of the efficiency of the $FeO/H_2O$ system as influenced by the presence of $FeS_2$ is warranted. A critical evaluation of the $FeO$ literature suggests that one major limitation has been to test the efficiency of the $FeO/H_2O$ system on individual contaminants or groups of contaminants (e.g. As, dyes, halogenated carbons). The net result is that increased adsorption, co-precipitation, degradation or precipitation have been reported as the supposed removal mechanisms. An innovative approach was introduced by Miyajima and colleagues using methylene blue (MB) as an indicator of reactivity for the $FeO/H_2O$ system (MB method). The MB method exploits the differential adsorptive behaviour of MB onto sand and iron oxides or iron-coated sand specimens, the most reactive system has been the one exhibiting the least MB discoloration, or the one producing the largest amount of iron oxides. Note that the exact nature of the oxide is not very important, but its coating activity is the key aspect for the MB method. For example, Banerji and Chaudhari did not add any sand in their $FeO$ bed to avoid oxide loss by sand coating. The objective of the current study was to characterize the impact of $FeS_2$ addition on the reactivity of the $FeO/H_2O$ system using the MB method. Thus, six different $FeS_2$ mass loadings were used to achieve different final pH values (Eq. 2) (4.5 ≤ pH<sub>final</sub> ≤ 5.2).

**Material and methods**

The present research is based on the chemistry of the $FeO/FeS_2/sand/H_2O$ system. Therefore, the operating mode of the system will be first discussed. In this study, various amounts of a reactive $FeS_2$ mineral were added to a $FeO/sand$ mixture to investigate their effects on pH shifts and dye removal.

**Background to the experimental methodology.** At neutral pH values, immersed reactive $FeO$ corrodes and generates solid iron corrosion products (FeCPs), which progressively coat the surface of sand. The process of iron corrosion causes a pH shift to higher values (Eq. 1). The extent of sand coating depends among other factors on: (i) the $Fe^{2+}$ intrinsic reactivity, (ii) the volume of the solution, (iii) the initial pH value of the solution, (iv) the $FeO/sand$ ratio, and (v) the duration of the experiment. Under given experimental conditions, the removal efficiency of the system for individual contaminants depends on the final pH value, the extent of sand coating, and the availability of “free” FeCPs. The final pH value determines the speciation of the contaminant and the surface charges of sand and FeCPs.

When a $FeS_2$ mineral is added to a $FeO/sand$ system (at a given $FeS_2/sand$ ratio) a pH shift to lower values occurs. The extent of pH shift depends on the $FeS_2$ intrinsic reactivity and the amounts added. Lower pH values avoid or delay sand coating and modify the speciation of dissolved contaminants. It then follows that, when $FeS_2$ is added to a $FeO/sand$ mixture, there are two counteracting processes controlling the pH value of the system. Previous results observed with the $FeS_2$ mineral used in the current study suggest that pyrite dissolution occurs with much rapid kinetics than $FeO$ corrosion. Consequently, the system will not achieve a steady state before the initial pH of the $FeO$-free system is achieved. The larger the pH shift the larger the amount of FeCPs generated, which will in turn precipitate at pH > 4.5 and induce contaminant removal by adsorption and co-precipitation.

The methodology used for characterizing the impact of $FeS_2$ on the efficiency of $FeO/H_2O$ systems comprises monitoring the discoloration of a methylene blue solution (MB method) by $FeO/sand$ systems amended with various $FeS_2$ amounts. Clearly, the availability of FeCPs and their reactivity is modified by lowering the initial pH value to various extents while observing MB discoloration in systems having a final pH value between 4.0 and 5.0. The discoloration of methyl orange (MO) in parallel experiments is used to support the findings based on the MB method. This approach is radically different from the conventional approach testing dyes as model contaminants. For example, Chen et al. recently investigated the removal of three different azo dyes (Orange II, Reactive Red X-3B and Amino Black 10B) in the $FeO/FeS_2/H_2O$ system. All the three dyes are negatively charged, and were explicitly reported to be removed via reductive transformations. Following the conventional approach, Chen et al. monitored the concentrations of dyes, iron and protons (pH value), and performed solid phase characterizations using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). On the contrary, the MB method does not imply such solid phase
characterizations because all FeCPs are positively charged and the extent to which they cover sand is reflected in the extent of MB discoloration.

**Solutions.** Dyes. Methylene blue (MB) was used as a tracer of reactivity, while methyl orange (MO) was a model organic contaminant. Both dyes are widely used to characterize the suitability of various systems for water treatment. The used dyes were of analytical grade. MB was supplied by Sinopharm Chemical Reagent Co. Ltd, Shanghai (China) and MO by Tianjin Chemical Reagent Research Institution Co. Ltd, Tianjin (China). The dyes were selected due to: (i) similarity in their molecular size, and (ii) differences in their affinity to positively charged iron oxides (Table 1). The initial dye concentration used was 10 mg L⁻¹, equivalent to 31.5 μM for MB and 30.7 μM for MO. The working solutions were prepared by diluting concentrated stock solutions (3150 μM for MB and 3070 μM for MO) using deionized water. The pH values of the initial solutions were 6.5 (MB) and 7.0 (MO).

Iron. A standard iron solution (1000 mg L⁻¹) from General Research Institute for Nonferrous Metals was used to calibrate the UV/VIS spectrophotometer used for analysis. In preparation for spectrophotometric analysis, ascorbic acid was used to reduce FeIII in solution to FeII. 1,10 orthophenanthroline was used as reagent for FeII complexation. Other chemicals used in this study included L(+)-ascorbic acid and L-ascorbic acid sodium salt. Ascorbic acid also degrades dyes (in particular MO) and eliminates interference during iron determination.

**Solid materials.** Metallic iron (Fe⁰). The Fe⁰ material was purchased from Shanghai Institute of Fine Technology (China). The material is available as scrap iron with a particle size between 0.05 and 5 mm. Its elemental composition as specified by the supplier was: Fe: > 99.99%; C: < 0.1%; N: < 0.1%; O: < 0.1%. Its kₚHEN value is 13 mg h⁻¹. The kₚHEN value is the kinetic constant of Fe⁰ dissolution in a 2 mM 1,10 orthophenanthroline solution, and characterizes the material’s intrinsic reactivity. The material was used without any further pretreatment. Fe⁰ was proven as a powerful discoloration agent for MB specifically because the discoloration agents are progressively generated in-situ. Therefore, the discoloration capacity of the used Fe⁰ cannot be exhausted within the experimental duration used in the current study (41 d).

Sand. The sand conformed to the China ISO standard, and was used as received without any further pretreatment or characterization. The particle size was between 1.25 and 2.00 mm. Sand was used because it is cheap and readily available and is widely used as admixing agent to prevent rapid permeability loss in Fe⁰/H₂O systems.

Pyrite (FeS₂). The FeS₂ mineral was from Tongling City, Anhui province, China. The particle size was between 38 and 48 μm. Its weight composition was 46.0% Fe and 52.2% S, which is equivalent to a purity of 98.2%. FeS₂ was used because of its demonstrated suitability as a pH shifting agent in Fe⁰/H₂O systems.

**Dye discoloration experiments.** Quiescent batch experiments were conducted in glass test tubes for an experimental duration of 41 d. Dye discoloration was initiated by adding 20.0 mL of the dye solution to a test tube containing 0.1 g of Fe⁰, 0.0 to 0.6 g of FeS₂, 0.0 or 0.5 g of sand, and Fe⁰/FeS₂/sand mixtures containing varying FeS₂ loadings. Table 2 summarizes the aggregate content of the 8 Fe⁰/FeS₂/sand systems and one operational reference (blank experiment), giving a total of 9 experimental treatments. Note that the pure Fe⁰ system (0.1 g of

| Dye | Formula | MW (g mol⁻¹) | Molecular size (nm³) | Nature | kₚHEN (nm) |
|-----|---------|-------------|----------------------|--------|------------|
| Methylene blue (MB) | C₁₆H₁₈ClN₃S.3H₂O | 319.00 | 1.3 nm × 1.5 nm × 0.8 nm | Cationic | 664.5 |
| Methyl orange (MO) | C₁₄H₁₂N₃O₃NaS | 327.34 | 1.19 nm × 0.67 nm × 0.38 nm | Anionic | 464.0 |

Table 1. Some physico-chemical characteristics of two tested dyes. MW stands for molecular weight.

| System | ZVI (g L⁻¹) | Sand (g L⁻¹) | Pyrite (g L⁻¹) | Materials | Comments |
|--------|-------------|-------------|---------------|-----------|----------|
| Reference | 0.0 | 0.0 | 0.0 | None | Blank experiment |
| System 1 | 5.0 | 0.0 | 0.0 | Fe²⁺ alone | Blank for Fe⁰ |
| System 2 | 0.0 | 25.0 | 0.0 | Sand alone | Blank for sand |
| System 3 | 0.0 | 0.0 | 20.0 | FeS₂ alone | Blank for FeS₂ |
| System 5a | 5.0 | 25.0 | 5.0 | Fe²⁺/sand/FeS₂ | First final pH value |
| System 5b | 5.0 | 25.0 | 10.0 | Fe²⁺/sand/FeS₂ | Second final pH value |
| System 5c | 5.0 | 25.0 | 20.0 | Fe²⁺/sand/FeS₂ | Third final pH value |
| System 5d | 5.0 | 25.0 | 25.0 | Fe²⁺/sand/FeS₂ | Fourth final pH value |
| System 5e | 5.0 | 25.0 | 30.0 | Fe²⁺/sand/FeS₂ | Fifth final pH value |

Table 2. Overview on the nine (9) investigated systems.
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clearly shows that lower pH values correspond to higher [Fe] values. Specifically, the [Fe] values dropped from 100 mg L$^{-1}$ for pH 4.7 to 0.7 mg L$^{-1}$ for pH 7.0. A sharp decrease of the iron concentration between pH 4.7 and 5.5 is observed and corresponds to the solubility behavior of Fe under oxic conditions$^{62,63}$. Again, there is no significant difference evident between both dyes.

The fact that iron dissolution from any reactive material increases with decreasing pH value is intuitive (Fig. 2a). However, the extent to which iron is dissolved under any given operational conditions should be

**Table 3.** Time-dependent inventory of reactive species in the four investigated systems. $t_0$ corresponds to the start of the experiment, while $t_{\infty}$ corresponds to Fe depletion. It is assumed that because of FeII cycling FeS$_2$ will be depleted the last. FeCPs = Fe corrosion products. FeCPs can be free or coated on sand.

| System | Fe$^0$         | FeS$_2$         | Sand       | Fe$^0$/FeS$_2$/Sand |
|--------|----------------|-----------------|------------|---------------------|
| $t_0$  | Fe$^0$         | FeS$_2$         | Sand       | Fe$^0$ + FeS$_2$ + Sand |
| $t_{\infty}$ | Fe$^0$ + FeCPs | FeS$_2$ + FeCPs | Sand       | Fe$^0$ + FeS$_2$ + Sand + FeCPs |
| $t_{\infty}$ | FeCPs         | FeS$_2$ + FeCPs | Sand       | FeS$_2$ + Sand + FeCPs |

Figure 1. Changes of the dye discoloration efficiency (E values) in single-aggregate and ternary system (a) and changes of final pH value as a function of the FeS$_2$ dose (b). Experimental conditions: V = 20 mL, $m_{iron} = 0.0$ or 0.1 g, $m_{sand} = 0.0$ or 0.5 g, $m_{pyrite} = 0$ to 0.6 g, and $t = 41$ d. The lines are not fitting functions, they simply connect points to facilitate visualization.

The extent to which iron dissolution under any given operational conditions should be
characterized (Fig. 2b), and their impact on the investigated process (dye discoloration in this case) discussed. Past efforts to characterize the Fe⁰/FeS₂ system have not properly considered these issues as the final pH value was not always recorded and/or not used in discussing the results. Moreover, in earlier efforts it was commonplace to vary both the initial pH value and the FeS₂ loading (Table 5), thereby making it difficult to determine the effect of each parameter. By using only various FeS₂ loadings to shift the pH value of a Fe⁰/sand/H₂O system, the present study is an extension of earlier efforts from the early 2000s. Moreover, the current study applied a recently developed tool using MB as an indicator of Fe⁰ reactivity.

Table 4. Variations of the pH value, the iron concentration ([Fe]) and the extent of dye discoloration (E) in the single-aggregate and the ternary systems after 41 days of equilibration.

| System  | pH (–)  | [Fe] (mg L⁻¹) | E (%) | pH (–)  | [Fe] (mg L⁻¹) | E (%) |
|---------|---------|---------------|-------|---------|---------------|-------|
| Reference | 6.9 ± 0.1  | 0.0 ± 0.0  | 0.0 ± 1.5  | 6.7 ± 0.1  | 0.0 ± 0.0  | 0.0 ± 1.5  |
| Fe⁰     | 7.0 ± 0.2  | 0.7 ± 0.1  | 96.8 ± 3.3  | 6.5 ± 0.3  | 0.6 ± 0.2  | 94.5 ± 2.5  |
| Sand    | 6.9 ± 0.1  | 0.0 ± 0.4  | 1.7 ± 3.0  | 6.7 ± 0.2  | 0.0 ± 0.9  | 51.2 ± 8.7  |
| FeS₂    | 3.3 ± 0.1  | 72.3 ± 4.8  | 45.6 ± 2.4  | 3.4 ± 0.1  | 68.0 ± 4.2  | 29.8 ± 1.3  |
| Fe⁰/sand/FeS₂ | 4.7 ± 0.1  | 62.9 ± 4.4  | 71.2 ± 0.8  | 4.8 ± 0.1  | 65.4 ± 3.4  | 72.9 ± 4.5  |

Figure 2. Changes of the iron concentration as function of the pyrite dose (a) and the final pH value (b). Experimental conditions: V = 20 mL, miron = 0.1 g, msand = 0.5 g, mpyrite = 0 to 0.6 g, and t = 41 d. The lines are not fitting functions, they simply connect points to facilitate visualization.
Dye discoloration in Fe$_0$/sand/H$_2$O systems. Figure 3a shows the extent of dye discoloration (E values) by the ternary system as the FeS$_2$ loadings increase from 0 to 30 g L$^{-1}$. Figure 3b depicts the variation of E values as a function of the final pH value. It is evident that there is a general linear decrease in E value with increasing FeS$_2$ loading or decreasing pH values (Fig. 2a). However, three important issues have to be considered: (i) the highest E value for each system corresponds to [FeS$_2$] = 0 g L$^{-1}$ (Issue 1); (ii) for [FeS$_2$] = 5 g L$^{-1}$ and [FeS$_2$] > 20 g

Table 5. Overview of selected experimental conditions used for batch experiments in investigating the role of FeS$_2$ in enhancing the efficiency of Fe$_0$/H$_2$O systems. X stands for the used contaminant. Only this research and refs.37–39 have used quiescent systems and experimental durations longer than one day. (1) Carbon tetrachloride; (2) Nitrobenzene; TR This research.

| X   | t    | pH$_0$ | Fe$^0$ | FeS$_2$ | FeS$_2$/Fe$^0$ | V   | Stirring | References |
|-----|------|--------|--------|---------|---------------|-----|----------|------------|
|     | (h or d) | (-)    | (g L$^{-1}$) | (g L$^{-1}$) | (-) | (mL) | (rpm) |           |
| CT  | 1 h   | 6.5 to 12.4 | 5      | 5.0 to 30.0 | 1   | 25   | 170 | TR        |
| U   | 120 d | 7.2     | 5      | 15     | 3   | 22   | 0   | 37–39     |
| As  | 3 h   | 3.0 to 9.0 | n.s   | n.s    | 0.3 to 1.7 | 500 | 400     |            |
| NB  | 5 h   | 5.0 to 10.0 | 0.5   | 0.5 to 3.0 | 1.0 to 6.0 | 150 | 200     | 41         |
| MB & MO | 41 h | 7.0     | 5.0    | 5.0 to 30.0 | 1.0 to 6.0 | 20  | 0       | TR         |

Figure 3. Changes of the dye discoloration efficiency (E values) as function of the pyrite dose (a) and the final pH value (b). Experimental conditions: V = 20 mL, m$_{ müdahale} = 0.1$ g, m$_{sand} = 0.5$ g, m$_{pyrite}$ 0 to 0.6 g, and t = 41 d. The lines are not fitting functions, they simply connect points to facilitate visualization.

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L⁻¹, there is a significant difference in the E values for both dyes (Issue 2), and (iii) for [FeS₂] = 10, 15 and 20 g L⁻¹, there is no profound difference in the E values for both dyes (Issue 3). It is evident that such results would be considered controversial if coming from different independent studies. That is why considering the experimental conditions is crucial in discussing experimental result from independent studies. For the so-called bottle-neck technique used here as well as relevant operational variables include: Fe⁰ pre-treatment, Fe²⁺ particle size (mm, mm, nm), Fe²⁺ mass loading, volume of used vessels, volume of solution, buffer application, mixing type (e.g. stirring, shaking), mixing intensities (e.g. 200 rpm), and experimental duration. A more detailed discussion of the three issues is given below.

Issue 1 implies that FeS₂ addition inhibits the efficiency of Fe²⁺/H₂O systems for dye discoloration. Similar results were reported by Noubactep et al. while investigating U⁷⁺ removal in Fe⁰/H₂O systems. Note that the single-FeS₂S₂, disclosed both dyes (Fig. 1a). This observation raises questions about the assertion that FeS₂ increases contaminant removal in Fe²⁺/H₂O systems. This work posits that Fe(OH)₃ discolors the dye solutions mainly by co-precipitation. Thus, dye discoloration is only quantitative when Fe(OH)₃ precipitation is intensive (pH > 4.5).

Issue 2 can be regarded as a striking feature as there is either a larger extent of MO discoloration relative to that of MB ([FeS₂] = 5 g L⁻¹) or the opposite ([FeS₂] > 20 g L⁻¹). Note that the ion-selectivity principle of the Fe⁰/H₂O system implies that in the presence of FeCPs in aqueous systems, the anionic MO is better discoloured than the cationic MB. This is the case at [FeS₂] = 5 g L⁻¹ where enough FeCPs is generated to cover the surface of sand, thereby inducing a larger E value for MO than for MB. The observation that for Fe⁰/H₂O systems without FeS₂ (i.e., at [FeS₂] = 0 g L⁻¹), MO discoloration was only slightly higher than that of MB is also noteworthy. This indicates that for the experimental duration used in the current study (41 d), enough FeCPs were generated to co-precipitate both dyes. For further clarification of this issue, a binary Fe⁰/sand system should have been investigated, but this was beyond the scope of the current study. The higher MB discoloration relative to MO observed at [FeS₂] > 20 g L⁻¹ is explained by the formation of complexes between Fe and MO which delay co-precipitation.

Finally, Issue 3 can also be regarded as a striking observation because despite all differences (solubility, affinity), there is no difference in the E values for the two dyes. It can be assumed that, under the experimental conditions, MB and MO which have almost the same molecular size (Table 1) are both disclosed by co-precipitation. This assumption is corroborated by results in Fig. 3b showing clearly that there is no quantitative dye discoloration (E > 60%) at pH < 4.5. This corresponds to the observations of Noubactep et al. for the Fe⁰/U⁷⁺/H₂O system. The fact that MB, MO and UVI exhibited very similar behaviors in the Fe⁰/FeS₂/H₂O system is an indication that contaminant removal might be a pure positive side effect of aqueous iron corrosion. The most tangible proof for this assertion is the kinetics of Fe²⁺ oxidation by dissolved oxygen (O₂). According to Langmuir, the kinetics of this reaction increases by a factor 65 between pH 4.0 and 5.0. Thus, quantitative dye discoloration is observed only in systems where Fe²⁺ oxidation to Fe³⁺ was quantitative for the 41-d experimental period. The in-situ generated Fe⁰ precipitates are good contaminant scavengers.

**Mechanisms of contaminant removal in Fe⁰/H₂O systems.** This study has investigated the effect of FeS₂ addition on the efficiency of Fe⁰/sand systems for MB and MO discoloration. No enhanced dye discoloration could be attributed to FeS₂ addition at mass loading of 0 to 30 g L⁻¹ for 41 d. Two questions arise: First, why is there no increased dye discoloration in a context where the expected pH shift and increased iron dissolution are evident? (Question 1). It is noteworthy that each individual aggregate (Fe⁰, FeS₂, sand) tested herein can achieve MB discoloration as depicted in Fig. 1a. Second, why did the ternary system perform far lower than the single-Fe⁰ systems? (Question 2). By applying a known experimental approach consisting of varying individual operational parameters to better understand complex systems and, accounting for the relative slow kinetics of Fe⁰ and FeS₂ dissolution, this study has adopted a novel approach to answer Questions 1 and 2. Specifically, the current study assessed the role of FeS₂ enhancement of contaminant removal in Fe²⁺/H₂O system. MB is used herein as an operational reactive tracer (“Introduction”) and the achieved results corroborated earlier reports on U(VI) removal and account for discrepancies and inconsistencies reported in literature.

The evidence that FeS₂ oxidation produces acidity (Eq. 2) is corroborated in the current study (Fig. 2a). By consuming acidity, Fe⁰ (Eq. 1) and Fe⁴⁺ (Eq. 3) oxidation are accelerated by Eq. (2) (Le Chatelier’s principle). Fe⁴⁺ from Eq. 2 catalyses FeS₂ oxidation and produced less soluble Fe(OH)₃. Thus, mixing Fe⁰ and FeS₂ can be regarded as continuously generating less soluble Fe(OH)₃, until one of the reactants is depleted or until a pseudo-steady state is established. This work posits that Fe(OH)₃ discolors the dye solutions mainly by co-precipitation. Thus, dye discoloration is only quantitative when Fe(OH)₃ precipitation is intensive (pH > 4.5). However, the extent of dye discoloration depends on the amount of free in-situ generated Fe(OH)₃ which is determined by the kinetics of Fe⁴⁺ oxidation by dissolved O₂. As expected, for a longer experimental duration (> 41 d), the efficiency of the ternary mixture will surpass that of the single-Fe⁰ systems. This answers Question 1, and demonstrates that enhanced dye discoloration needs more time to occur under quiescent conditions. Accordingly, the documented delay of quantitative dye discoloration is not a negation of the view that FeS₂ addition enhances the efficiency of Fe²⁺/H₂O systems. This study aims to better understand why Fe²⁺/H₂O systems are more efficient upon the addition of pyrite (FeS₂) relative to those without pyrite.

In a ternary system sand, system, sand is non-reactive (inert) and is in-situ coated by iron oxides from the dissolution of the two other aggregates (“Background to the experimental methodology” and Table 2). This in-situ coating of sand delays the availability of free Fe(OH)₃ for dye co-precipitation. Initially, MB and Fe²⁺/Fe⁴⁺ compete for adsorptive removal at the negatively charged sand surface. Once the sand surface is completely coated, it will be no longer attractive for MB. This competition for active adsorption sites explains the observations in Fig. 3a. But neither Fe⁰ nor FeS₂ are the discoloring agents, but rather the products of their oxidative
dissolution which are variably available in the investigated systems (Table 3). To completely answer Question 2, the ternary mixture performed less than the single-aggregate systems because: (i) sand is in-situ coated, thereby retarding the availability of free Fe(OH)$_3$, and (ii) the synergy of Fe$^0$ and FeS$^2$ has not yet produced enough free Fe(OH)$_3$. The latter is the case whenever the pH value of the system has not exceeded 4.5 (Fig. 3b).

The presentation until this point has not addressed the redox properties of MB and MO. The thermodynamics predict MO reduction by Fe$^{0.55,61}$. The results reported herein demonstrate that even the ion-selective nature of the individual dyes was not the key factor accounting for dye discoloration when the pH was lower than 4.5. Thus, regardless of any redox properties, the current work has demonstrated that Fe$^0$-based systems are only efficient when the final pH value is larger than 4.5. Unlike the current study, several previous works have mostly failed to record the final pH values of their systems and use them in their discussion (Table 5).

**Significance of the results.** Fe$^0$-based systems have been important components of the water treatment industry for the past 170 years.$^{8,27,70}$. Research reported before 1990 is not really considered by current active scientists whose starting point is the advent of in-situ permeable reactive barriers (PRBs), and the premise that Fe$^0$ is an environmental reducing agent.$^{18,23,72,73}$. Conventional PRBs use micro-scale or granular Fe$^0$ specimens (g Fe$^0$). During the past two decades, some tools have been developed to improve the efficiency of g Fe$^0$. In this regard, the following three tools have been introduced: (i) using nano-scale Fe$^0$, (ii) alloying g Fe$^0$ with metals such as Pd or Ni (also at nano-scale), and (iii) admixing another aggregate with g Fe$^0.^{11,24,25}$ The Fe$^0$/FeS$^2$/sand system investigated herein is part of the third category. It has been reported that in sulfide-containing environments, using g Fe$^0$ results in the formation of iron sulfides which are conductive and sustain electron transfer from Fe$^0$ to the contaminant.$^{22,74–76}$ On the other hand, such iron sulfides are stand-alone reducing agents for the reductive transformations of many contaminants.$^{70,77,78}$ Because Fe$^0$ and FeS$^2$ have in common the release of Fe$^{II}$ species, it can be assumed that the material containing more Fe will be first passivated by Fe$^{III}$ species. However, when both materials are mixed, FeS$^2$ accelerates Fe$^0$ corrosion and none of both materials is really available for quantitative reductive transformation of other foreign species, including contaminants. Consequently, any observed enhancement of contaminant removal in a Fe$^0$/H$_2$O system by virtue of the presence of FeS$^2$ is an indirect process. This assertion was elegantly demonstrated in the present study by slowing down the process of iron precipitation via addition of various FeS$^2$ doses to the same Fe$^0$/sand system for 41 d. It then follows that, FeS$^2$ is mostly a pH shifting agent for the Fe$^0$/H$_2$O system.$^{57,59,70}$. Table 5 reveals that all other investigations on the Fe$^0$/FeS$^2$ system were performed under shaken/stirred conditions. However, under such conditions, the target FeS$^2$ intrinsic properties (including semi-conduction) are undermined. For example, how can FeS$^2$ act as a 'mediator' for electron transfer' from Fe$^0$ to contaminants (Fig. 4) when the whole system is mechanically stirred at 400 rpm? Such a high stirring speed was explicitly selected to ensure that both Fe$^0$ and FeS$^2$ could be uniformly dispersed in the reaction solution$^{22}$. This example clearly shows that using FeS$^2$ to enhance the efficiency of Fe$^0$/H$_2$O systems is a simple tool to design more sustainable Fe$^0$-based systems. However, current rationalization efforts are not really based on scientific principles$^{22,23}$. Thus, only when the scientific principles are well-understood can better systems be designed$^{22,23}$. A typical design problem is how to cope with the increased Fe$^0$ dissolution specifically in column operations intrinsically prone to clogging$^{78,80}$. Thus, in solving the enigma of the Fe$^0$/FeS$^2$/H$_2$O system, this work leads to several avenues for sustaining the efficiency of conventional Fe$^0$/H$_2$O remediation systems. This result is especially important as Fe$^0$-based (filtration) systems are an excellent candidate to help the international community to solve the long-lasting issue of universal safe drinking water.$^{23,14,15,27,29,30,81,82}$.

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**Figure 4.** Schematic diagram of interactions between metallic iron (Fe$^0$), pyrite (FeS$^2$) and contaminants (RCI) in the remediation process: (a) Fe$^0$/H$_2$O and (b) Fe$^0$/FeS$^2$/H$_2$O. In the Fe$^0$/H$_2$O system, anode and cathode are different sites on the same grain. In the Fe$^0$/FeS$^2$/H$_2$O system, granular Fe$^0$ is additionally the anode and FeS$^2$ the cathode. The representation is based on the knowledge that Fe$^0$ is not a reducing agent. Therefore, electrochemical contaminant reduction of RCI is possible in (a) and not in (b).
| Contaminant | Fe$_0$ | Fe$_{S_2}$ | Mixing rate | Duration | pH$_{0}$ | Fe$_0$ characterization tools | References |
|------------|-------|-----------|-------------|----------|----------|-------------------------------|------------|
| X          | [X] (mg L$^{-1}$) | type          | loading (g L$^{-1}$) | loading (g L$^{-1}$) | mixing rate (rpm) | duration (min or d) | pH$_{0}$ | tools |
| NB$^{(3)}$ | 25.0  | Powder    | 0.5          | 0.5 to 3.0 | Shaken, 200 | 300 min | 6.0 | XRD$^{(4)}$, XPS$^{(5)}$, SEM–EDS$^{(6)}$, XAS$^{(7)}$ and Mossbauer spectroscopy; |
| TCE$^{(3)}$| 1.0   | Powder    | 0.0 to 10.0  | 0.0 to 10.0 | Stirred, 100 | n.s. (n) | n.s. (n) | None |
| Cr(VI)     | 20.0  | Powder    | 5.0          | 10.0      | Shaken, 200 | 120 min | 4.0 | RET$_N$, adsorption, XPS$^{(3)}$, and SEM–EDS$^{(4)}$ |
| As(III)    | 2.0   | Powder    | ≤ 1.0        | ≤ 1.0     | Stirred, 400 | 180 min | 6.8 | SEM$^{(4)}$, XPS$^{(5)}$, and XRD$^{(6)}$ |
| Dyes       | 6.2 to 17.5 | Powder | 0.25 or 0.5  | 0.25 to 2.0 | Shaken, 200 | ≤ 240 min | 7.0 | SEM–EDS$^{(3)}$ and XPS$^{(3)}$ |
| Dyes       | 10.0  | Scrap iron | 5.0          | 2.5 to 30  | Quiescent | 41 d | 6.5–7.0 | None |
| None       | –     | Powder    | 10.0         | 100.0     | Shaken, 120 | 21 d | –5.6 | SEM–EDX$^{(3)}$ and ATR/FTIR$^{(9)}$ |

Table 6. Experimental conditions of selected studies using the Fe$_0$/Fe$_{S_2}$/H$_2$O system. X stands for the tested contaminant and [X] its initial concentration. It is seen that only this study used quiescent systems and the longest experimental duration. This study has also performed no solid phase Fe$_0$ analysis. (1) Nitrobenzene; (2) Carbon tetrachloride; (3) n.s. = not specified; (4) XRD = X-ray diffraction; (5) XPS = X-ray photoelectron spectroscopy; (6) SEM–EDS = scanning electron microscopy—energy dispersive X-ray spectroscopy; (7) XAS = X-ray absorption spectroscopy; (8) SEM = scanning electron microscopy; (9) ATR/FTIR = attenuated total reflection /Fourier transform infrared spectroscopy; TR = This research.

A further argument against the electrochemical nature of Fe$_{S_2}$ in mediating electron transfer from Fe$_0$ to contaminants (Fig. 4) is given by recent investigations in efforts to suppress Fe$_{S_2}$ oxidation under environmental conditions$^{43–46}$. For example, Seng et al.$^{44}$ reported that Fe$_0$ is able to stop Fe$_{S_2}$ oxidation, and thus remediate acid mine drainage. In essence, Seng et al.$^{44}$ investigated a contaminant-free Fe$_0$/Fe$_{S_2}$/H$_2$O system (Table 6) and concluded that from the intrinsic properties the addition of Fe$_0$ selectively suppress pyrite oxidation. Table 6 shows that the experimental conditions of Seng et al.$^{44}$ are very close to those of remediation Fe$_0$/Fe$_{S_2}$/H$_2$O systems. The only two distinct differences are: (i) the higher Fe$_{S_2}$ mass loading (Fe$_{S_2}$: Fe$_0$ = 10), and (ii) the longer experimental duration (41 days versus < 10 h). By using an even longer experimental duration (41 days) and quiescent conditions (0 rpm), the present work has demonstrated the essential virtue of working under near-field conditions. In other words, it is fair to state that the Fe$_0$/Fe$_{S_2}$ literature is full of possibly reproducible results, but with low practical value. As already shown in Table 5, the variability of the operational conditions is a major issue and the significance of results of solid phase characterization is questionable. In fact, as seen in Table 6, a myriad of characterization tools were used to “confirm” the reducing properties of Fe$_0$ for dyes$^{43}$. In such studies species like methylene blue$^{43}$ used herein as a ‘tracer’ of reactivity or arsenic$^{43}$, and proven to be non-reducible in Fe$_0$/H$_2$O systems are quantitatively removed. The first merit of the MB method is to uncover these controversial views without solid phase analysis.

The conclusion of Seng et al.$^{44}$ supports the view presented herein that the relative kinetics of Fe$_0$ and Fe$_{S_2}$ oxidation determine the preponderance of processes in Fe$_0$/Fe$_{S_2}$/H$_2$O systems$^{46}$. However, the reported selectivity of the process is questionable as sand and other natural minerals are also covered with FeCPs under similar conditions$^{47–49}$. As an example, Song et al.$^{47}$ reported on increased Cr(VI) reduction in Fe$_0$/sand/H$_2$O systems compared to Fe$_0$/H$_2$O ones. The extent of coating of each aggregate (e.g. gravel, peat, pyrite, sand) depends on both the intrinsic reactivity of used Fe$_0$ and the relative proportion of available materials. In the light of the kinetic arguments given herein, a re-evaluation of published works is possible, for example, the data of Sheba et al.$^{46}$ discussing the extent of degradation of chlorinated organic compounds (ROC) by Fe$_0$/Fe$_{S_2}$/H$_2$O systems and reporting on differential mechanisms at different Fe$_0$/Fe$_{S_2}$ ratios. The discussion given herein clearly suggests that if there are differential removal mechanisms, it is due to the differential extent of pH shift. Future research should be designed based on the chemistry of the systems$^{49}$.

Concluding remarks
The concept that adsorption and co-precipitation are the fundamental mechanisms of contaminant removal in Fe$_0$/H$_2$O systems is consistent with many experimental observations. In particular, quantitative dye discoloration was only observed for pH values corresponding to iron precipitation (hydroxide formation) (pH > 4.5, Fig. 3b), while selective dye discoloration promoted adsorptive removal. Further, while the role of the redox-mediated reactions in the discoloration of both dyes can only be speculatively discussed based on one's results, it is established that the role of Fe$_0$ is as follows: (i) shifting the pH to more acidic values, and (ii) enhancing contaminant removal by adsorption and co-precipitation during the subsequent pH increase by virtue of iron corrosion. Finally, negatively charged methyl orange (MO) showed no significant increase in discoloration relative to positively charged methylene blue (MB). Both MB and MO have a similar molecular size. This observation is consistent with the role of Fe$_0$ as a generator of contaminant scavengers, and not as a reducing agent. This observation could explain why various As (As$^{(3)}$ and As$^{(5)}$)$^{90}$ or Se (Se$^{(V)}$ and Se$^{(VI)}$)$^{91}$ species are quantitatively removed in Fe$_0$/H$_2$O systems, but not by aged iron oxides. Further research is needed to investigate the phenomena highlighted in the current study using a wide range of contaminants commonly occurring in drinking water and wastewaters.
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Author contribution
X.C., M.X. and C.N. conceived the presented idea and developed the theory. X.C. and M.X. carried out the experiment. R.H. and C.N. supervised this work. W.G. supervised the redaction of the first draft by X.C. and M.X. All authors discussed the results and contributed to the final manuscript.

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The authors declare no competing interests.

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