Characterizing the reactivity of metallic iron upon methylene blue
discoloration in Fe\(^0\)/MnO\(_2\)/H\(_2\)O systems

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Abstract

A simple method is proposed for testing the reactivity of elemental iron materials (Fe\(^0\) materials) using methylene blue (MB) as reagent. The method is based on the oxidative reactivity of Fe\(^{II}\) for reductive dissolution of MnO\(_2\). Fe\(^{II}\) is produced in-situ by the oxidation of a Fe\(^0\) material. The in-situ formed Fe\(^{II}\) reacted with MnO\(_2\) delaying the bulk precipitation of iron corrosion products and thus MB co-precipitation (MB discoloration). For a given MnO\(_2\), the extent of MB discoloration delay is a characteristic of individual Fe\(^0\) materials under given experimental conditions. The MB discoloration method for testing the reactivity of Fe\(^0\) materials is facile, cost-effective and does not involve any stringent reaction conditions.

Keywords: Adsorption, Co-precipitation, Methylene blue, Manganese oxides, Reactivity, Zerovalent iron.

Introduction

Since the introduction of permeable reactive barriers of metallic iron for groundwater remediation (Fe\(^0\) PRB technology), various Fe\(^0\) types were tested and mostly successfully used for environmental remediation. Despite the reported successes, little progress has been made toward characterizing the variability in reactivity among Fe\(^0\) samples from different sources [1,2]. Available works attempted to relate corrosion rates to: (i) the rate of hydrogen evolution [3,4] or (ii) to the extend of contaminant removal by used Fe\(^0\) materials [1,5]. Among the reactivity parameters, the composition of the aqueous solution, the Fe\(^0\) elemental composition (alloying elements) and the surface properties (specific surface area, oxidation
state) have been largely discussed [3,6,7]. However, none of these parameters is independent
and Fe\(^0\) aqueous reactivity further depends on method of manufacture [8,9]. According to Van
Orden [8], whether a metal is cast, forged, wrought or welded are as important as the
environment in the corrosion process. One major limitation of the current material testing
procedures is that each material is used for remediation tests and the reactivity is ascertained
at the end of the possibly cost-intensive and time consuming experiments. An alternative
approach consisting in testing the reactivity of Fe\(^0\) materials in dilute EDTA
(ethylenediaminetetraacetic acid) was recently presented [2]. However, EDTA is a strong
chelating agent known to delay the process of iron hydroxide precipitation [10] at near neutral
pH which is characteristic for most natural systems.

There is a need to develop simple, reliable and cost-effective methods to test the reactivity of
Fe\(^0\) materials. Ideally such methods should (i) be performed under conditions where iron
solubility is not enhanced, and (ii) be applicable for material screening in preliminary works
to avoid analytical cost. This study proposed a simple approach to compare the reactivity of
Fe\(^0\) toward methylene blue discoloration. Four materials of known relative reactivity [2] were
tested to ascertain the efficiency of the new method. The selected materials are representative
for the large array of powdered and granular Fe\(^0\) materials used in environmental remediation.

Background of the experimental methodology

Methylene blue (MB) discoloration in the presence of Fe\(^0\) results mostly from MB co-
precipitation with in situ generated iron corrosion products [11,12]. Therefore, in a Fe\(^0\)/H\(_2\)O
system, the extend of MB discoloration should increase steadily from the start of the
experiment to the time of total discoloration. If the process of corrosion product precipitation
is delayed, the resulting MB discoloration is also delayed.

The differentiation of the reactivity of Fe\(^0\) materials in Fe\(^0\)/MB/H\(_2\)O systems is based on the
reaction of Fe\(^{II}\) with MnO\(_2\) [13,14]. Fe\(^{II}\) is generated in-situ from Fe\(^0\) oxidation. Because
liberated Fe\(^{II}\) species are used for the reductive dissolution of MnO\(_2\) (at the MnO\(_2\) surface),
they are not available for quantitative MB co-precipitation. Thus, the blue intensity of MB solution will not decreased as rapidly as in the system without MnO₂. Accordingly, for parallel experiments with a given MnO₂ and various Fe⁰ samples, the extent of MB discoloration will be a reflection of the chemical reactivity of individual Fe⁰ samples. Therefore, if a Fe⁰ sample is low reactive no or little delay of MB discoloration will be observed (assumption 1). For reactive Fe⁰ samples the more reactive the sample the more extensive the discoloration delay (assumption 2).

The used methodology for testing the reactivity of Fe⁰ in MnO₂/MB/H₂O systems consists in following the process of MB discoloration in a given MnO₂/H₂O system as influenced by various Fe⁰ while testing the validity of assumptions 1 and 2. It should be kept in mind that MB discoloration and not MB removal is discussed in this study. For the discussion of MB removal TOC measurements for instance should have been necessary to account for MB reduction to colorless leuco-methylene blue (LMB) [15] which remains in solution.

Materials and Methods

Solutions

Methylene blue (MB) is a traditionally favourite dye of choice for laboratory and technical purposes [16,17]. Its molecule has a minimum diameter of approximately 0.9 nm [18] and is also used as redox indicator [15]. The used initial concentration was 12 mg/L (~0.037 mM) MB and it was prepared by diluting a 1000 mg/L stock solution. All chemicals were analytical grade.

Solid materials

One scrap iron (ZVI1) and three commercially available iron materials (ZVI2 to ZVI4) have been tested in the present study. Table 1 summarizes the main characteristics of these materials together with their iron content. Before used ZVI4 (Tab. 1) was crushed and sieved; the size fraction 1.0-2.0 mm was used without any further pretreatment. The specific surface area of the materials were not available nor determined. This parameter is known as one of the
most important reactivity factors [20]. However, it is not the objective of this study to
investigated the impact of the specific surface area on the reactivity of the material, but rather
to compare the material in the form in which they could be used in field applications.
Therefore, all other materials were used as obtained. Crushing and sieving ZVI4 aimed at
working with materials of particle size relevant for field applications. The materials differ
regarding their characteristics such as content of metallic iron, additives, grain size and shape.
No information about the manufacture process (e.g. raw material, heat treatment) was
available.
The used MnO$_2$ is commercial sample from Merck (85 - 90% MnO$_2$; synthetic pyrulosite).
The powdered sample was used without any pre-treatment.

**Discoloration studies**
Batch experiments with a shaking intensity of 50 min$^{-1}$ were conducted in essay tubes for an
experimental duration of 6 days. The essay tubes were immobilized on a support frame. A
rotary shaker HS 501 D from “Janke & Kunkel”, DCM Laborservice was used. The batches
consisted of 0 to 9.0 g/L of the synthetic pyrulosite (MnO$_2$) and 5 g/L of each Fe$^0$. A parallel
experiments with the Fe$^0$ materials alone was performed. The extent of MB discoloration in
the investigated systems was characterized by allowing 0.0 to 0.20 g of MnO$_2$ and 0.11 g of
each Fe$^0$ to react in sealed sample tubes containing 22.0 mL of a MB solution (12 mg/L) at
laboratory temperature (about 20 ± 2 °C). Initial pH was ~7.8. After equilibration, up to 3 mL
of the supernatant solutions were carefully retrieved (no filtration) for MB measurements (no
dilution). Each experiment was performed in triplicate and averaged results are presented.

**Analytical methods**
MB concentrations were determined by a Cary 50 UV-Vis spectrophotometer at a wavelength
of 664.5 nm using cuvettes with 1 cm light path. The pH value was measured by combined
glass electrodes (WTW Co., Germany). Electrodes were calibrated with five standards
following a multi-point calibration protocol in agreement with the current IUPAC recommendation [21].

Expression of experimental results

After the determination of the residual MB concentration (C) the corresponding percent MB discoloration was calculated according to the following equation (Eq. 1):

\[
P = [1 - (C/C_0)] \times 100\%
\]  

(1)

where \( C_0 \) is the initial aqueous MB concentration (about 12 mg/L), 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 reaction during the experiments.

Results and Discussion

Effect of MnO\(_2\) on the process MB discoloration in Fe\(^0\)/H\(_2\)O systems

Figure 1 compares the extent of MB discoloration in the three investigated systems: (i) 0 to 9.0 g/L MnO\(_2\) (System I), (ii) 0 to 9.0 g/L Fe\(^0\) (System II) and (iii) 5 g/L Fe\(^0\) and 0 to 9.0 g/L MnO\(_2\) (System III). From Figure 1a it can be seen that System II is more efficient at discoloring MB at all tested material loadings. This observation is consistent with the intrinsic nature of both materials. MnO\(_2\) acts mostly as an absorbent with limited adsorption capacity. Fe\(^0\) and its oxidation products can adsorb MB. Oxidation products of Fe\(^0\) include Fe(OH)\(_2\), Fe(OH)\(_3\), FeOOH, Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), and green rust [22-24]. Their role in the mechanisms of aqueous contaminant removal is yet to be properly characterized [24,25]. It is certain that, during their precipitation corrosion products sequestrate MB in their structure [11]. Therefore, in a Fe\(^0\)/MB/H\(_2\)O system, MB discoloration may occur via adsorption and co-precipitation. Reduction to colourless LMB is also likely to occur. Whatever the actual MB discoloration mechanisms in Fe\(^0\)/H\(_2\)O systems are, the addition of various amounts of MnO\(_2\)
to 5 g/L Fe\(^0\) should have increased the extend of MB discoloration relative to the experiment
with 5 g/L Fe\(^0\) alone as represented in Fig. 1a. Accordingly, the discoloration extend of 52 %
with 5 g/L Fe\(^0\) in the absence of MnO\(_2\) should increase with increasing MnO\(_2\) loading to reach
95 % discoloration at 9.0 g/L MnO\(_2\). This theoretical prediction (Fig. 1a) could not be verified
experimentally as shown in Fig. 1b. Instead of increasing with increasing MnO\(_2\) loading, the
discooloration extent decreased from 52 % at 0 g/L MnO\(_2\) to 40 % for MnO\(_2\) loadings > 2 g/L.
This observation is compatible with MB co-precipitation as main discoloration mechanism.
The observed discoloration extent of 40 % for MnO\(_2\) loadings > 2 g/L corresponds to the
discooloration in: (i) system I (MnO\(_2\) alone) for MnO\(_2\) loadings > 6.5 g/L or (ii) system II (Fe\(^0\)
alone) for Fe\(^0\) loadings > 2.0 g/L. This observation suggests that mixing 5 g/L Fe\(^0\) with 0 to
9.0 g/L MnO\(_2\) results in a system less efficient at discolouring MB than a system with only
2.5 g/L Fe\(^0\). Note that if MB was acting as redox indicator, the discoloration extend should
have steadily increased with increasing MnO\(_2\) loading. This observation corroborates the
prediction that iron hydroxides sequestrate MB while precipitating.
**Effect of various Fe\(^0\) on the process of MB discoloration**
Figure 2 compares the extent of MB discoloration by tested Fe\(^0\) materials in the presence and
in the absence of MnO\(_2\). From Fig. 2a the following order of efficiency can be observed:
ZVI3 < ZVI1 ≅ ZVI4 < ZVI2. This order of efficiency was the same than that obtained by
Noubactep et al. [2] while testing the same materials for U\(^{VI}\) removal and for Fe dissolution in
0.02 M EDTA ( see also Tab. 2). These results suggest that MB discoloration in Fe\(^0\)/H\(_2\)O
systems is a simple method to differentiate the reactivity of materials. However, due to the
diversity of possible discoloration mechanisms, it was important to make sure that Fe\(^0\)
oxidative dissolution is evidenced. For this purpose MnO\(_2\) is added to the systems to evidence
the effects of in-situ generated Fe\(^{II}\). Fig. 2b summarises the results. The same order of
reactivity was found (ZVI3 < ZVI1 ≅ ZVI4 < ZVI2). A close consideration of Fig. 2b reveals
that ZVI3 is low reactive (assumption 1: no delay of MB discoloration) because unlike for the
three other materials no initial discoloration decrease was observed upon MnO$_2$ addition. All other materials are more reactive than ZVI3 (assumption 2: *the more extensive the discoloration delay the more reactive the sample*). Powdered ZVI2 was the most reactive material. The increased MB discoloration efficiency with ZVI2 is due to the increased Fe$^0$ surface area resulting in a better solid/H$_2$O contact. Again granular ZVI1 and ZVI4 showed very close reactivity, suggesting that the MB discoloration method is as powerful as the two other tests but essentially simpler. The reactivity of used materials is also reflected by the final pH value (Eq. 2). According to Eq. 2 ($H^+$ production), the more reactive a material, the lower the final pH value (Tab. 2).

$$\text{2 Fe}^{2+} + \text{MnO}_2 + 2 \text{H}_2\text{O} \Rightarrow 2 \text{FeOOH} + \text{Mn}^{2+} + 2 \text{H}^+$$

(2)

The verification of assumptions 1 and 2 validates the efficiency of MB discoloration for testing the reactivity of Fe$^0$ materials in Fe$^0$/MnO$_2$/H$_2$O systems.

**Conclusions**

Methylene blue has been used for the characterization of the reactivity of Fe$^0$ materials. The proposed method is simple and does not involve any stringent reaction conditions. This method is a good alternative for reported costly instrumental procedures [2]. The proposed method has been successfully applied to differentiate the reactivity of four Fe$^0$ materials of known relative reactivity. This method can be used for material screening prior to cost-intensive investigations. Moreover, the test can be further developed to yield a characteristic parameter for Fe$^0$ materials similar to iodine number or methylene blue number for the characterization of activated carbons [16,18].

**Acknowledgments**

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**References**


Table 1: Main characteristics and iron content of the four tested Fe⁰ materials. The material code ("code") are from the author, the given form is as supplied; d (μm) is the diameter of the supplied material and the Fe content is given in % mass.

<table>
<thead>
<tr>
<th>Supplier (a)</th>
<th>Supplier denotation</th>
<th>code</th>
<th>form</th>
<th>d (μm)</th>
<th>Fe (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAZ, mbH</td>
<td>Sorte 69 (b)</td>
<td>ZVI1</td>
<td>fillings</td>
<td>-</td>
<td>93 (c)</td>
</tr>
<tr>
<td>G. Maier GmbH</td>
<td>FG 0000/0080</td>
<td>ZVI2</td>
<td>powder</td>
<td>≤ 80</td>
<td>92 (d)</td>
</tr>
<tr>
<td>Würth</td>
<td>Hartgussstrahlmittel</td>
<td>ZVI3</td>
<td>spherical</td>
<td>1200</td>
<td>n.d. (e)</td>
</tr>
<tr>
<td>ISPAT GmbH</td>
<td>Schwammeisen</td>
<td>ZVI4</td>
<td>spherical</td>
<td>9000</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

(a) List of suppliers: MAZ (Metallaufbereitung Zwickau, Co) in Freiberg (Germany); Gotthart Maier Metallpulver GmbH (Rheinfelden, Germany), ISPAT GmbH, Hamburg (Germany), Connelly GPM Inc. (USA), (b) Scrap iron material; (c) Mbudi et al. [19]; (d) average values from material supplier, (e) not determined.
Table 2: Extent of MB discoloration ($P_{MB}$) at a $Fe^0$ mass loading of 9.0 g/L, decrease of the percent MB discoloration ($\Delta P_{MB}$), and final pH value in the presence of 5 g/L $Fe^0$ as the MnO$_2$ loading varied from 0 to 1.1 g/L. For ZVI3 no decrease ($\Delta P_{MB} = 3.5\%$) was observed under the experimental conditions (50 min$^{-1}$ for 6 days). Data for the rate of iron dissolution in a 2 mM EDTA solution ($a_{EDTA}$) and the percent uranium removal ($P_{U}$) are presented for comparison.

<table>
<thead>
<tr>
<th>Material</th>
<th>$P_{MB}$ (%)</th>
<th>$\Delta P_{MB}$ (%)</th>
<th>$pH_{final}$</th>
<th>$a_{EDTA}^{(a)}$ (μM/h)</th>
<th>$P_{U}^{(a)}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZVI1</td>
<td>48.8</td>
<td>-4.8</td>
<td>7.8</td>
<td>1.95</td>
<td>81.0</td>
</tr>
<tr>
<td>ZVI2</td>
<td>100.0</td>
<td>-38.4</td>
<td>7.4</td>
<td>2.65</td>
<td>100.0</td>
</tr>
<tr>
<td>ZVI3</td>
<td>31.9</td>
<td>3.5</td>
<td>8.6</td>
<td>1.54</td>
<td>63.1</td>
</tr>
<tr>
<td>ZVI4</td>
<td>49.1</td>
<td>-8.7</td>
<td>7.9</td>
<td>1.86</td>
<td>87.0</td>
</tr>
</tbody>
</table>

$^{(a)}$Values according to Noubactep et al. [2].
Figure 1

(a) theoretical 5 g/L Fe$^0$ + MnO$_2$

(b) experiment

- t = 6 days
- N = 50 min$^{-1}$
- Fe$^0$ = ZVI11

MB removal / [%]

MnO$_2$
Fe$^0$
Fe$^0$ + MnO$_2$

material / [g/L]

0 2 4 6 8
Figure 2

(a) MB removal [%] vs Fe\(^0\) [g/L] for ZVI3, ZVI4, ZVI1, ZVI2. 

(b) MB removal [%] vs MnO\(_2\) [g/L] for ZVI1, ZVI2, ZVI3, ZVI4.
**Figure Captions**

**Figure 1**: Methylene blue discoloration by MnO₂, Fe⁰, and “Fe⁰ + MnO₂” for 6 days as a function of the material loading (Fe⁰, MnO₂). ZVI1 is the used Fe⁰ source. In Fig 1a the theoretical discoloration extent assuming additive removal of Fe⁰ (5 g/L) and varying amount of MnO₂ is represented. Fig. 1b represents experimental results for the three systems together with the line corresponding to MB discoloration by 5 g/L Fe⁰ (no MnO₂ addition). All lines are not fitting functions, they simply connect points to facilitate visualization.

**Figure 2**: Methylene blue discoloration by the individual Fe⁰ materials (a) and 5 g/L each material and varying amounts of MnO₂ (b). The experiments were performed for 6 days while shaking at 50 min⁻¹. The lines are not fitting functions, they simply connect points to facilitate visualization.