1 **Characterizing the reactivity of metallic iron upon methylene blue**

2 **discoloration in Fe$^0$/MnO$_2$/H$_2$O systems**

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6

7 **Abstract**

8 A simple method is proposed for testing the reactivity of elemental iron materials (Fe$^0$

9 materials) using methylene blue (MB) as reagent. The method is based on the oxidative

10 reactivity of Fe$^{II}$ for reductive dissolution of MnO$_2$. Fe$^{II}$ is produced in-situ by the oxidation

11 of a Fe$^0$ material. The in-situ formed Fe$^{II}$ reacted with MnO$_2$ delaying the bulk precipitation of

12 iron corrosion products and thus MB co-precipitation (MB discoloration). For a given MnO$_2$,

13 the extent of MB discoloration delay is a characteristic of individual Fe$^0$ materials under given

14 experimental conditions. The MB discoloration method for testing the reactivity of Fe$^0$

15 materials is facile, cost-effective and does not involve any stringent reaction conditions.

16 **Keywords**: Adsorption, Co-precipitation, Methylene blue, Manganese oxides, Reactivity,

17 Zerovalent iron.

18 **Introduction**

19 Since the introduction of permeable reactive barriers of metallic iron for groundwater

20 remediation (Fe$^0$ PRB technology), various Fe$^0$ types were tested and mostly successfully

21 used for environmental remediation. Despite the reported successes, little progress has been

22 made toward characterizing the variability in reactivity among Fe$^0$ samples from different

23 sources [1,2]. Available works attempted to relate corrosion rates to: (i) the rate of hydrogen

24 evolution [3,4] or (ii) to the extend of contaminant removal by used Fe$^0$ materials [1,5].

25 Among the reactivity parameters, the composition of the aqueous solution, the Fe$^0$ elemental

26 composition (alloying elements) and the surface properties (specific surface area, oxidation

27   state) have been largely discussed [3,6,7]. However, none of these parameters is independent

28   and $Fe^0$ aqueous reactivity further depends on method of manufacture [8,9]. According to Van

29   Orden [8], whether a metal is cast, forged, wrought or welded are as important as the

30   environment in the corrosion process. One major limitation of the current material testing

31   procedures is that each material is used for remediation tests and the reactivity is ascertained

32   at the end of the possibly cost-intensive and time consuming experiments. An alternative

33   approach consisting in testing the reactivity of $Fe^0$ materials in dilute EDTA

34   (ethylenediaminetetraacetic acid) was recently presented [2]. However, EDTA is a strong

35   chelating agent known to delay the process of iron hydroxide precipitation [10] at near neutral

36   pH which is characteristic for most natural systems.

37   There is a need to develop simple, reliable and cost-effective methods to test the reactivity of

38   $Fe^0$ materials. Ideally such methods should (i) be performed under conditions where iron

39   solubility is not enhanced, and (ii) be applicable for material screening in preliminary works

40   to avoid analytical cost. This study proposed a simple approach to compare the reactivity of

41   $Fe^0$ toward methylene blue discoloration. Four materials of known relative reactivity [2] were

42   tested to ascertain the efficiency of the new method. The selected materials are representative

43   for the large array of powdered and granular $Fe^0$ materials used in environmental remediation.

44   **Background of the experimental methodology**

45   Methylene blue (MB) discoloration in the presence of $Fe^0$ results mostly from MB co-

46   precipitation with in situ generated iron corrosion products [11,12]. Therefore, in a $Fe^0/H_2O$

47   system, the extend of MB discoloration should increase steadily from the start of the

48   experiment to the time of total discoloration. If the process of corrosion product precipitation

49   is delayed, the resulting MB discoloration is also delayed.

50   The differentiation of the reactivity of $Fe^0$ materials in $Fe^0/MB/H_2O$ systems is based on the

51   reaction of $Fe^{II}$ with $MnO_2$ [13,14]. $Fe^{II}$ is generated in-situ from $Fe^0$ oxidation. Because

52   liberated $Fe^{II}$ species are used for the reductive dissolution of $MnO_2$ (at the $MnO_2$ surface),

53 they are not available for quantitative MB co-precipitation. Thus, the blue intensity of MB

54 solution will not decreased as rapidly as in the system without $MnO_2$. Accordingly, for

55 parallel experiments with a given $MnO_2$ and various $Fe^0$ samples, the extent of MB

56 discoloration will be a reflection of the chemical reactivity of individual $Fe^0$ samples.

57 Therefore, if a $Fe^0$ sample is low reactive no or little delay of MB discoloration will be

58 observed (**assumption 1**). For reactive $Fe^0$ samples the more reactive the sample the more

59 extensive the discoloration delay (**assumption 2**).

60 The used methodology for testing the reactivity of $Fe^0$ in $MnO_2/MB/H_2O$ systems consists in

61 following the process of MB discoloration in a given $MnO_2/H_2O$ system as influenced by

62 various $Fe^0$ while testing the validity of assumptions 1 and 2. It should be kept in mind that

63 MB discoloration and not MB removal is discussed in this study. For the discussion of MB

64 removal TOC measurements for instance should have been necessary to account for MB

65 reduction to colorless leuco-methylene blue (LMB) [15] which remains in solution.

66 **Materials and Methods**

67 **Solutions**

68 Methylene blue (MB) is a traditionally favourite dye of choice for laboratory and technical

69 purposes [16,17]. Its molecule has a minimum diameter of approximately 0.9 nm [18] and is

70 also used as redox indicator [15]. The used initial concentration was 12 mg/L (~0.037 mM)

71 MB and it was prepared by diluting a 1000 mg/L stock solution. All chemicals were analytical

72 grade.

73 **Solid materials**

74 One scrap iron (ZVI1) and three commercially available iron materials (ZVI2 to ZVI4) have

75 been tested in the present study. Table 1 summarizes the main characteristics of these

76 materials together with their iron content. Before used ZVI4 (Tab. 1) was crushed and sieved;

77 the size fraction 1.0-2.0 mm was used without any further pretreatment. The specific surface

78 area of the materials were not available nor determined. This parameter is known as one of the

79  most important reactivity factors [20]. However, it is not the objective of this study to

80  investigated the impact of the specific surface area on the reactivity of the material, but rather

81  to compare the material in the form in which they could be used in field applications.

82  Therefore, all other materials were used as obtained. Crushing and sieving ZVI4 aimed at

83  working with materials of particle size relevant for field applications. The materials differ

84  regarding their characteristics such as content of metallic iron, additives, grain size and shape.

85  No information about the manufacture process (e.g. raw material, heat treatment) was

86  available.

87  The used $MnO_2$ is commercial sample from Merck (85 - 90% $MnO_2$; synthetic pyrulosite).

88  The powdered sample was used without any pre-treatment.

89  **Discoloration studies**

90  Batch experiments with a shaking intensity of 50 $min^{-1}$ were conducted in essay tubes for an

91  experimental duration of 6 days. The essay tubes were immobilized on a support frame. A

92  rotary shaker HS 501 D from "Janke & Kunkel", DCM Laborservice was used. The batches

93  consisted of 0 to 9.0 g/L of the synthetic pyrulosite ($MnO_2$) and 5 g/L of each $Fe^0$. A parallel

94  experiments with the $Fe^0$ materials alone was performed. The extent of MB discoloration in

95  the investigated systems was characterized by allowing 0.0 to 0.20 g of $MnO_2$ and 0.11 g of

96  each $Fe^0$ to react in sealed sample tubes containing 22.0 mL of a MB solution (12 mg/L) at

97  laboratory temperature (about $20 \pm 2$ ° C). Initial pH was ~7.8. After equilibration, up to 3 mL

98  of the supernatant solutions were carefully retrieved (no filtration) for MB measurements (no

99  dilution). Each experiment was performed in triplicate and averaged results are presented.

100  **Analytical methods**

101  MB concentrations were determined by a Cary 50 UV-Vis spectrophotometer at a wavelength

102  of 664.5 nm using cuvettes with 1 cm light path. The pH value was measured by combined

103  glass electrodes (WTW Co., Germany). Electrodes were calibrated with five standards

104    following a multi-point calibration protocol in agreement with the current IUPAC

105    recommendation [21].

**Expression of experimental results**

107    After the determination of the residual MB concentration (C) the corresponding percent MB

108    discoloration was calculated according to the following equation (Eq. 1):

109    $$P = [1 - (C/C_0)] * 100\% \tag{1}$$

110    where $C_0$ is the initial aqueous MB concentration (about 12 mg/L), while C gives the MB

111    concentration after the experiment. The operational initial concentration ($C_0$) for each case

112    was acquired from a triplicate control experiment without additive material (so-called blank).

113    This procedure was to account for experimental errors during dilution of the stock solution,

114    MB adsorption onto the walls of the reaction vessels and all other possible side reaction

115    during the experiments.

**Results and Discussion**

**Effect of $MnO_2$ on the process MB discoloration in $Fe^0/H_2O$ systems**

118    Figure 1 compares the extent of MB discoloration in the three investigated systems: (i) 0 to

119    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

120    $MnO_2$ (System III). From Figure 1a it can be seen that System II is more efficient at

121    discolouring MB at all tested material loadings. This observation is consistent with the

122    intrinsic nature of both materials. $MnO_2$ acts mostly as an absorbent with limited adsorption

123    capacity. $Fe^0$ and its oxidation products can adsorb MB. Oxidation products of $Fe^0$ include

124    $Fe(OH)_2$, $Fe(OH)_3$, FeOOH, $Fe_2O_3$, $Fe_3O_4$, and green rust [22-24]. Their role in the

125    mechanisms of aqueous contaminant removal is yet to be properly characterized [24,25]. It is

126    certain that, during their precipitation corrosion products sequestrate MB in their structure

127    [11]. Therefore, in a $Fe^0/MB/H_2O$ system, MB discoloration may occur via adsorption and co-

128    precipitation. Reduction to colourless LMB is also likely to occur. Whatever the actual MB

129    discoloration mechanisms in $Fe^0/H_2O$ systems are, the addition of various amounts of $MnO_2$

130 to 5 g/L $Fe^0$ should have increased the extend of MB discoloration relative to the experiment

131 with 5 g/L $Fe^0$ alone as represented in Fig. 1a. Accordingly, the discoloration extend of 52 %

132 with 5 g/L $Fe^0$ in the absence of $MnO_2$ should increase with increasing $MnO_2$ loading to reach

133 95 % discoloration at 9.0 g/L $MnO_2$. This theoretical prediction (Fig. 1a) could not be verified

134 experimentally as shown in Fig. 1b. Instead of increasing with increasing $MnO_2$ loading, the

135 discoloration extent decreased from 52 % at 0 g/L $MnO_2$ to 40 % for $MnO_2$ loadings > 2 g/L.

136 This observation is compatible with MB co-precipitation as main discoloration mechanism.

137 The observed discoloration extent of 40 % for $MnO_2$ loadings > 2 g/L corresponds to the

138 discoloration in: (i) system I ($MnO_2$ alone) for $MnO_2$ loadings > 6.5 g/L or (ii) system II ($Fe^0$

139 alone) for $Fe^0$ loadings > 2.0 g/L. This observation suggests that mixing 5 g/L $Fe^0$ with 0 to

140 9.0 g/L $MnO_2$ results in a system less efficient at discolouring MB than a system with only

141 2.5 g/L $Fe^0$. Note that if MB was acting as redox indicator, the discoloration extend should

142 have steadily increased with increasing $MnO_2$ loading. This observation corroborates the

143 prediction that iron hydroxides sequestrate MB while precipitating.

144 **Effect of various $Fe^0$ on the process of MB discoloration**

145 Figure 2 compares the extent of MB discoloration by tested $Fe^0$ materials in the presence and

146 in the absence of $MnO_2$. From Fig. 2a the following order of efficiency can be observed:

147 ZVI3 < ZVI1 $\cong$ ZVI4 < ZVI2. This order of efficiency was the same than that obtained by

148 Noubactep et al. [2] while testing the same materials for $U^{VI}$ removal and for Fe dissolution in

149 0.02 M EDTA ( see also Tab. 2). These results suggest that MB discoloration in $Fe^0/H_2O$

150 systems is a simple method to differentiate the reactivity of materials. However, due to the

151 diversity of possible discoloration mechanisms, it was important to make sure that $Fe^0$

152 oxidative dissolution is evidenced. For this purpose $MnO_2$ is added to the systems to evidence

153 the effects of in-situ generated $Fe^{II}$. Fig. 2b summarises the results. The same order of

154 reactivity was found (ZVI3 < ZVI1 $\cong$ ZVI4 < ZVI2). A close consideration of Fig. 2b reveals

155 that ZVI3 is low reactive (assumption 1: *no delay of MB discoloration*) because unlike for the

156   three other materials no initial discoloration decrease was observed upon $MnO_2$ addition. All

157   other materials are more reactive than ZVI3 (assumption 2: *the more extensive the*

158   *discoloration delay the more reactive the sample*). Powdered ZVI2 was the most reactive

159   material. The increased MB discoloration efficiency with ZVI2 is due to the increased $Fe^0$

160   surface area resulting in a better solid/$H_2O$ contact. Again granular ZVI1 and ZVI4 showed

161   very close reactivity, suggesting that the MB discoloration method is as powerful as the two

162   other tests but essentially simpler. The reactivity of used materials is also reflected by the

163   final pH value (Eq. 2). According to Eq. 2 ($H^+$ production), the more reactive a material, the

164   lower the final pH value (Tab. 2).

165   $$2\,Fe^{2+} + MnO_2 + 2\,H_2O \Rightarrow 2\,FeOOH + Mn^{2+} + 2\,H^+ \qquad (2)$$
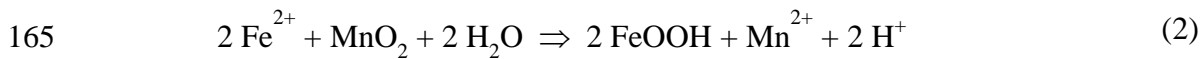
166   The verification of assumptions 1 and 2 validates the efficiency of MB discoloration for

167   testing the reactivity of $Fe^0$ materials in $Fe^0/MnO_2/H_2O$ systems.

168   **Conclusions**

169   Methylene blue has been used for the characterization of the reactivity of $Fe^0$ materials. The

170   proposed method is simple and does not involve any stringent reaction conditions. This

171   method is a good alternative for reported costly instrumental procedures [2]. The proposed

172   method has been successfully applied to differentiate the reactivity of four $Fe^0$ materials of

173   known relative reactivity. This method can be used for material screening prior to cost-

174   intensive investigations. Moreover, the test can be further developed to yield a characteristic

175   parameter for $Fe^0$ materials similar to iodine number or methylene blue number for the

176   characterization of activated carbons [16,18].

177   **Acknowledgments**

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248

248 **Table 1**: Main characteristics and iron content of the four tested $Fe^0$ materials. The material code

249 ("code") are from the author, the given form is as supplied; d (μm) is the diameter of the supplied

250 material and the Fe content is given in % mass.

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

251    (a) List of suppliers: MAZ (Metallaufbereitung Zwickau, Co) in Freiberg (Germany); Gotthart Maier

252       Metallpulver GmbH (Rheinfelden, Germany), ISPAT GmbH, Hamburg (Germany), Connelly GPM Inc.

253       (USA), [b]Scrap iron material; [c] Mbudi et al. [19]; [d] average values from material supplier, [e]not

254       determined.

255

255  **Table 2**: Extent of MB discoloration ($P_{MB}$) at a $Fe^0$ mass loading of 9.0 g/L, decrease of the

256  percent MB discoloration ($\Delta P_{MB}$), and final pH value in the presence of 5 g/L $Fe^0$ as the

257  $MnO_2$ loading varied from 0 to 1.1 g/L. For ZVI3 no decrease ($\Delta P_{MB}$ = 3.5 %) was observed

258  under the experimental conditions (50 $min^{-1}$ for 6 days). Data for the rate of iron dissolution

259  in a 2 mM EDTA solution ($a_{EDTA}$) and the percent uranium removal ($P_U$) are presented for
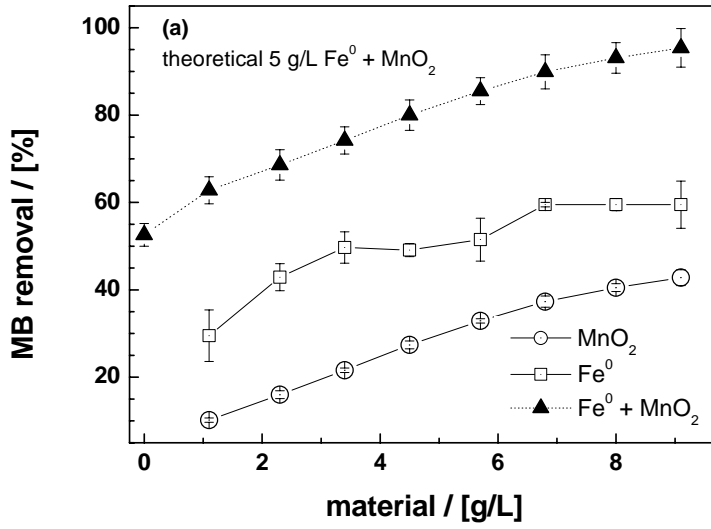
260  comparison.

| Material | $P_{MB}$ | $\Delta P_{MB}$ | $pH_{final}$ | $a_{EDTA}$ [a] | $P_U$ [a] |
|----------|----------|-----------------|--------------|----------------|-----------|
|          | (%)      | (%)             |              | ($\mu$M/h)     | (%)       |
| **ZVI1** | 48.8     | -4.8            | 7.8          | 1.95           | 81.0      |
| **ZVI2** | 100.0    | -38.4           | 7.4          | 2.65           | 100.0     |
| **ZVI3** | 31.9     | 3.5             | 8.6          | 1.54           | 63.1      |
| **ZVI4** | 49.1     | -8.7            | 7.9          | 1.86           | 87.0      |

261  [a] Values according to Noubactep et al. [2].
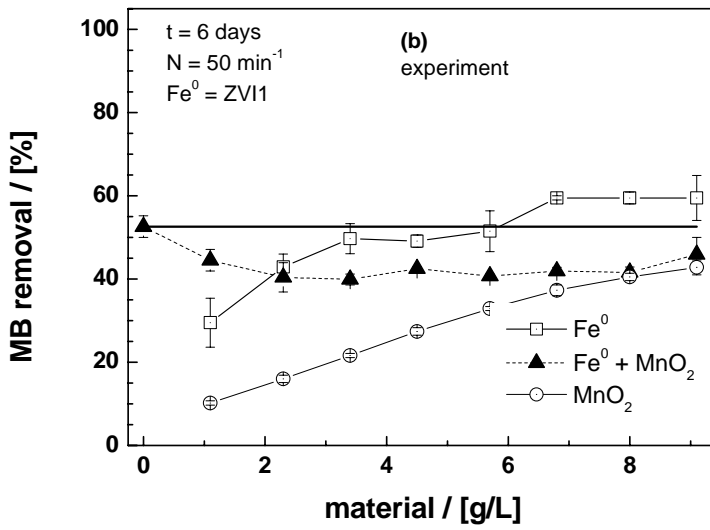
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262    **Figure 1**



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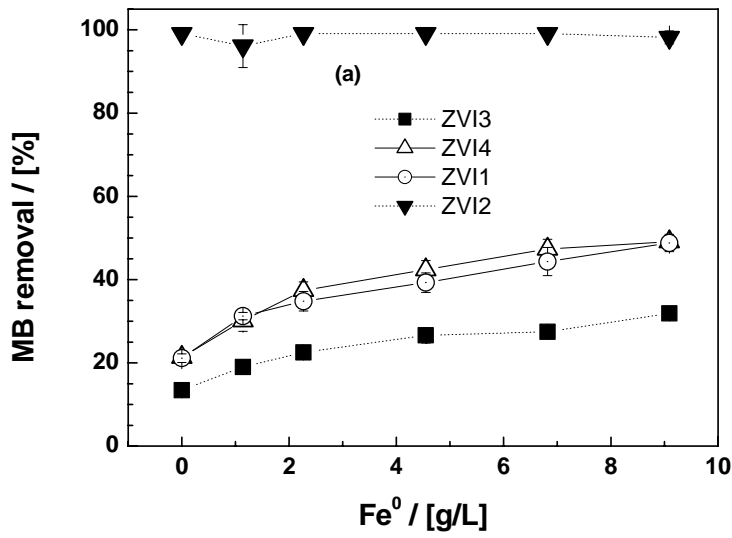


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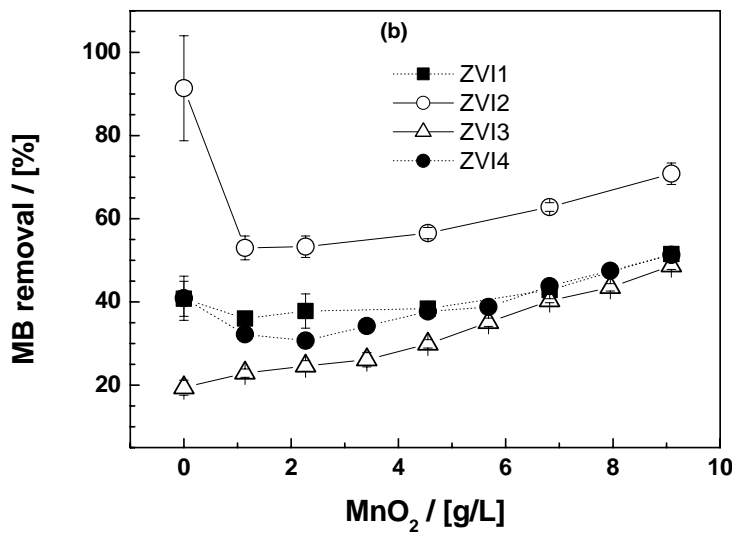
267    **Figure 2**

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**Figure Captions**

279

280 **Figure 1**: Methylene blue discoloration by $MnO_2$, $Fe^0$, and "$Fe^0$ + $MnO_2$" for 6 days as a

281        function of the material loading ($Fe^0$, $MnO_2$). ZVI1 is the used $Fe^0$ source. In Fig

282        1a the theoretical discoloration extent assuming additive removal of $Fe^0$ (5 g/L)

283        and varying amount of $MnO_2$ is represented. Fig. 1b represents experimental

284        results for the three systems together with the line corresponding to MB

285        discoloration by 5 g/L $Fe^0$ (no $MnO_2$ addition). All lines are not fitting functions,

286        they simply connect points to facilitate visualization.

287 **Figure 2**: Methylene blue discoloration by the individual $Fe^0$ materials (a) and 5 g/L each

288        material and varying amounts of $MnO_2$ (b). The experiments were performed for 6

289        days while shaking at 50 $min^{-1}$. The lines are not fitting functions, they simply

290        connect points to facilitate visualization.