

1           **Effects of mixing granular iron with sand on the efficiency of methylene blue**  
2   **discoloration**

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7  
8           **Abstract**

9           The influence of granular sand on the efficiency of metallic iron (Fe<sup>0</sup>) for the discoloration of  
10          a methylene blue (MB) solution was investigated in the current work. The initial MB  
11          concentration was 10 mg L<sup>-1</sup> and mass loadings within the range of 0 to 90 g L<sup>-1</sup> for sand and  
12          0 to 45 g L<sup>-1</sup> for Fe<sup>0</sup> were applied. The batch reaction vessel used was a graduated essay tube  
13          containing 22.0 mL of the MB solution. Shaking intensities of 0 and 75.0 rpm were applied  
14          for experimental durations of 7, 21 and 45 days. Results provide clear evidence that both Fe<sup>0</sup>  
15          and sand were independently effective for the discoloration of MB. However, the latter  
16          material was significantly less effective, recording 54.0 % compared to 82.0 % recorded for  
17          the Fe<sup>0</sup> after 45 days in experiment with 45.0 g L<sup>-1</sup> of each material. Similarly, mixing 90 g L<sup>-1</sup>  
18          sand with 45.0 g L<sup>-1</sup> of Fe<sup>0</sup> depicted a MB discoloration efficacy of 72.0 % demonstrating  
19          that the discoloration capability of the Fe<sup>0</sup> was significantly 'masked' by the presence of sand.  
20          This observation provides clear evidence to question the common approach of using  
21          adsorbents for contaminant accumulation in the vicinity of Fe<sup>0</sup> materials in order to facilitate  
22          chemical reduction by Fe<sup>0</sup>. Further research is required to determine the relative affinity of  
23          different materials that can be used in Fe<sup>0</sup> mixtures for maximum contaminant removal  
24          efficacies.

25          **Keywords:** Dye discoloration, Fe<sup>0</sup>/sand mixtures, Methylene blue, Water treatment,  
26          Zerovalent iron.

## 27 **1 Introduction**

28 Metallic iron ( $\text{Fe}^0$ ) has been demonstrated in numerous studies to represent the best available  
29 material for subsurface permeable reactive barriers [1-5].  $\text{Fe}^0$  has also been demonstrated as a  
30 highly efficient material for wastewater treatment and safe drinking water provision [5-10]. In  
31 all these applications  $\text{Fe}^0$  is routinely mixed with inert materials. The most used additive is  
32 sand [11-15]. Reported goals of mixing sand and  $\text{Fe}^0$  are: (i) meeting design requirements  
33 (**goal 1**), (ii) saving  $\text{Fe}^0$  costs (**goal 2**), and (iii) delaying particle clogging (**goal 3**). However,  
34 actually there is no conclusive experimental evidence to demonstrate that  $\text{Fe}^0$ /sand mixtures  
35 are more or less effective than pure  $\text{Fe}^0$  systems [16].

36 The relevance of mixing iron and sand was recognized since the early phase of technology  
37 development [17]. However, the literature still contains limited information on  $\text{Fe}^0$ /sand  
38 mixtures [15]. The need for systematic work aiming at establishing the practical use of  
39  $\text{Fe}^0$ /sand mixtures has been recently theoretically discussed as summarized in ref. [18].  
40 Results concluded that, when designing a  $\text{Fe}^0$  treatment system, priority must be placed on the  
41 aforementioned goals number 1 and 3, stating that goal number 2 (low cost) is required, but  
42 not an intrinsic requirement of a  $\text{Fe}^0$  filtration system. In fact, mixing  $\text{Fe}^0$  and sand is  
43 regarded as reducing the proportion of  $\text{Fe}^0$ , and thus ‘creating’ or ‘leaving’ room for sustained  
44 iron corrosion [19,20]. In other words, theoretical studies disprove the view of Ulsamer [16].  
45 Moreover,  $\text{Fe}^0$ /sand systems are more sustainable than pure  $\text{Fe}^0$  system as a rule [18]. On the  
46 other hand, the statement of Ulsamer [16] resulted from a critical literature review, showing  
47 that available data are not univocal [15]. These data resulted mostly from columns studies  
48 [15,21,22]. While a column experiment is the most effective method to investigate the  
49 mechanisms behind the efficacy of a  $\text{Fe}^0$  filtration system, a well-designed batch experiments  
50 could be useful in fine-tuning some relevant aspects at the laboratory scale [5]. For example  
51 **goal 3** (avoiding or delaying particle clogging) can be properly investigated in batch systems  
52 using tubular vessels enabling juxtaposition of used materials at the bottom of the vessel.

53 Laboratory essay tubes are such vessels [23]. A survey of the literature revealed that the effect  
54 of mixing sand and  $\text{Fe}^0$  has been addressed since the early phase of research on  $\text{Fe}^0$   
55 remediation technology [24-28]. However, sand has been constantly used as inert additive  
56 which contribution to contaminant removal is related to the presence of  $\text{Fe}^0$ . For example,  
57 Song et al. [14] discussed the effect of mixing  $\text{Fe}^0$  and sand on the extent of  $\text{Cr}^{\text{VI}}$  removal in  
58 batch studies, using experimental results from Kim et al. [12].  
59 Kim et al. [12] investigated aqueous  $\text{Cr}^{\text{VI}}$  removal in batch studies, and reported that, the  $\text{Cr}^{\text{VI}}$   
60 removal efficiency after 48 hours greatly increased from about 50 % in pure  $\text{Fe}^0$  systems to 85  
61 % in  $\text{Fe}^0$ /sand systems. The authors reported that reduction products ( $\text{Cr}^{\text{III}}$  species) adsorbed  
62 onto sand which shows higher sorption affinity than  $\text{Fe}^0$ , thus “leaving a large portion of  
63 active sites of the  $\text{Fe}^0$  unblocked” [14]. This conclusion seems counter-intuitive as in  $\text{Fe}^0$ /sand  
64 mixtures, reaction rates should diminish due to the decrease in reactive surface concentration  
65 (disadvantaged mass transfer of  $\text{Cr}^{\text{III}}$  to  $\text{Fe}^0$  surface). On the other hand, the adsorption  
66 capacity of sand for Cr is limited. Therefore, coating sand with iron oxides is an established  
67 tool to sustain metal removal in sand filters [29,30]. The efficiency of iron-coated sand filters  
68 suggests that in the experiments of Kim et al. [12], in-situ generated iron oxides were  
69 adsorbed onto sand and subsequently removed  $\text{Cr}^{\text{VI}}$  or  $\text{Cr}^{\text{III}}$ . Alternatively,  $\text{Cr}^{\text{VI}}$  adsorbed onto  
70 in-situ generated iron-coated sand can be further reduced to  $\text{Cr}^{\text{III}}$  by  $\text{Fe}^{\text{II}}$  or  $\text{H}_2$  from  
71 continuous  $\text{Fe}^0$  oxidation [31,32].  
72 The conclusions of Kim et al. [12] are consistent with the view, that sand delays clogging  
73 [17,22]. Clogging delay is achieved by decreasing the proportion of reactive  $\text{Fe}^0$  which  
74 progressively fill the connected pores with expansive corrosion products having a volume 2.1  
75 to 6.4 larger than  $\text{Fe}^0$  is the metal [33]. By mixing  $\text{Fe}^0$  with inert sand, a certain pH control  
76 can also be achieved as the proportion of  $\text{Fe}^0$  inducing pH elevation is limited [15]. While the  
77 optimal proportion of  $\text{Fe}^0$  relevant for the design of  $\text{Fe}^0$  filtration systems can not be achieved  
78 in batch experiments the qualitative compaction can be observed.

79 The objective of the present communication is to provide evidence for the effect of mixing  
80  $\text{Fe}^0$  and sand on the process of aqueous contaminant removal. A commercial  $\text{Fe}^0$  material is  
81 used. Methylene blue (MB -  $10 \text{ mg L}^{-1}$ ) is used as model contaminant. The extent of MB  
82 discoloration is characterized using three different systems: (i)  $\text{Fe}^0$  alone, (ii) sand alone, and  
83 (iii) " $\text{Fe}^0$  + sand". Non-disturbed experiments and experiments shaken at 75 rpm were  
84 performed. Results are comparatively discussed.

## 85 **2 Background of the experimental methodology**

86 Methylene blue (MB) is a cationic dye which is preferentially adsorbed onto negatively  
87 charged surfaces [34,35]. The application of MB adsorption in environmental science was  
88 demonstrated affordable, applicable and rapid [34,36,37]. MB adsorption is also widely used  
89 in the context of ' $\text{Fe}^0$  for environmental remediation' (e.g. in  $\text{Fe}^0/\text{H}_2\text{O}$  systems) [37,38].

### 90 **2.1 MB discoloration in $\text{Fe}^0/\text{H}_2\text{O}$ systems**

91 In  $\text{Fe}^0/\text{H}_2\text{O}$  systems, MB discoloration results from the synergy between (i) adsorption onto  
92 in-situ generated iron oxides and (ii) co-precipitation with nascent iron hydroxides [8,10]. It is  
93 essential to note that discoloration by a redox process ( $E^0 = 0.01 \text{ V}$  at pH 7 vs.  $E^0 = -0.44 \text{ V}$   
94 for  $\text{Fe}^{\text{II}}/\text{Fe}^0$ ) was proven insignificant as the large polar organic molecule can not  
95 quantitatively access the  $\text{Fe}^0$  surface [8,10]. The  $\text{Fe}^0$  surface is permanently covered with a  
96 multi-layered oxide scale. On the other hand, MB adsorption onto natural sand has been  
97 documented by Mitchell et al. [39]. These authors tested 65 sand samples from 45 localities  
98 from which only 6 samples (9.2 %) depicted 'low' adsorptive affinity for MB. The following  
99 observation of Mitchell et al. [39] is essential for  $\text{Fe}^0/\text{H}_2\text{O}$  systems: "sand artificially coated  
100 with  $\text{Fe}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$  adsorbed very little methylene blue". Recently, Varlikli et al. [40] tested  
101 the suitability of Sahara desert sand (SaDeS) for removing organic (cationic and anionic) dyes  
102 from aqueous solutions. They observed that MB demonstrated the strongest affinity for  
103 SaDeS with an adsorption capacity of  $11.98 \text{ mg g}^{-1}$  (initial MB concentration:  $11.2 \text{ mg L}^{-1}$ )

### 104 **2.2 MB discoloration in $\text{Fe}^0/\text{sand}/\text{H}_2\text{O}$ systems**

105 The observation of Mitchell et al. [39] that coated metal oxides impairs the adsorption of MB  
106 by sand suggests that a sand sample is a better MB adsorbent than the resulted iron oxide  
107 coated one. A  $\text{Fe}^0/\text{sand}/\text{H}_2\text{O}$  system is a dynamic system containing 100 % ‘clean’ sand only  
108 at the initial time ( $t = 0$ ). Once iron corrosion starts, sand surface is progressively coated with  
109 in-situ generated iron oxides. In other words, the adsorption capacity of sand for MB in a  
110  $\text{Fe}^0/\text{sand}/\text{H}_2\text{O}$  system is maximal at  $t = 0$ . This adsorption capacity decreases with time as a  
111 function of three key operational parameters: (i) the kinetics of  $\text{Fe}^0$  oxidation ( $\text{Fe}^0$  intrinsic  
112 reactivity), (ii) the available amount of sand, and (iii) the available amount of  $\text{Fe}^0$ .  
113 Since  $\text{Fe}^0$  alone (e.g.  $\text{Fe}^0/\text{H}_2\text{O}$  system) is efficient in decolourising aqueous MB [40,41], the  
114 effects of sand on MB discoloration in the presence of  $\text{Fe}^0$  may be summarized in two  
115 hypothesis. First, MB discoloration by  $\text{Fe}^0$  is not affected by the presence of sand  
116 (Assumption 1). Second, MB discoloration by  $\text{Fe}^0$  is significantly retarded by the presence of  
117 sand (Assumption 2). Based on the results of Mitchell et al. [39], the obvious case that sand  
118 addition may increase MB discoloration is not considered.

119 The used methodology for the investigation of the impact of sand on MB discoloration by  $\text{Fe}^0$   
120 comprises testing the validity of Assumption 1 and Assumption 2 by following the MB  
121 discoloration in the presence (absence) of sand. For this purpose, the addition of sand is tested  
122 as a tool to delay the availability of “free” corrosion products. In-situ generated iron corrosion  
123 products are adsorbed onto the sand surface, worsening its capacity of MB adsorption [39].  
124 Adsorbed corrosion products are not available to enmeshed MB in the vicinity of  $\text{Fe}^0$ .

### 125 **3 Materials and methods**

#### 126 **3.1 Solutions**

127 The used MB was of analytical grade. The working solution was  $10.0 \text{ mg L}^{-1}$ . The solutions  
128 were prepared by diluting a  $1000 \text{ mg L}^{-1}$  stock solution.

#### 129 **3.2 Solid materials**

##### 130 **3.2.1 Metallic iron ( $\text{Fe}^0$ )**

131 The used Fe<sup>0</sup> material was purchased from iPutech (Rheinfelden, Germany). The material is  
132 available as fillings with a particle size between 0.3 and 2.0 mm. Its average elemental  
133 composition as specified by iPutech was: C: 3.52 %; Si: 2.12 %; Mn: 0.93 %; Cr: 0.66 %. The  
134 material was used without any pre-treatment. Fe<sup>0</sup> was proven a powerful discoloration agent  
135 for MB. In particular, discoloration agents are progressively generated in-situ [41,42].  
136 Therefore, the discoloration capacity of used Fe<sup>0</sup> can not be exhausted within the  
137 experimental duration ( $\leq 42$  days).

### 138 **3.2.2 Sand**

139 The used sand was a commercial material for aviculture (“Papagaiensand” from RUT –  
140 Lehrte/Germany). Papagaiensand was used as received without any further pre-treatment nor  
141 characterization. The particle size was between 2.0 and 4.0 mm. Sand was used as an  
142 adsorbent because of its worldwide availability and its common use as admixing agent in  
143 Fe<sup>0</sup>/H<sub>2</sub>O systems. The adsorption capacity of various sand samples for MB has been largely  
144 documented in the literature [39,40,43,44]. Unlike Fe<sup>0</sup>, the adsorption capacity of sand for  
145 MB can be exhausted within the experimental duration.

## 146 **3.3 MB discoloration**

### 147 **3.3.1 Non-disturbed batch experiments**

148 Batch experiments without shaking were conducted in essay tubes for an experimental  
149 duration of 21 and 42 days. The batches consisted of 0.0 to 2.0 g of sand, 0.0 to 1.0 g of Fe<sup>0</sup>  
150 and 22 mL of a 10 mg L<sup>-1</sup> MB solution. A reaction time of 21 d was selected to allow a MB  
151 discoloration efficiency larger than 50 % in the system with Fe<sup>0</sup> alone. The extent of MB  
152 discoloration in investigated systems was characterized at laboratory temperature (about 22°  
153 C). Initial pH was ~8.2. After equilibration, up to 3 mL of the supernatant solutions was  
154 carefully retrieved (no filtration) for MB measurement (no dilution).

### 155 **3.3.2 Shaken batch experiments**

156 The assay tubes were amended with materials and MB solution as described above and  
157 allowed to equilibrate on a rotary shaker at 75 rpm for 7 days.

158 Each experiment was performed in triplicate and averaged results are presented.

### 159 **3.4 Analytical methods**

160 MB aqueous concentrations were determined by a Cary 50 UV-Vis spectrophotometer  
161 (Varian) at a wavelength of 664.5 nm. Cuvettes with 1 cm light path were used. The  
162 spectrophotometer was calibrated for MB concentrations  $\leq 15 \text{ mg L}^{-1}$ . The pH value was  
163 measured by combined glass electrodes (WTW Co., Germany).

### 164 **3.5 Expression of experimental results**

165 After the determination of the residual MB concentration (C) in batch studies, the  
166 corresponding percent MB discoloration was calculated according to the following equation  
167 (Eq. 1):

$$168 \quad P = [1 - (C/C_0)] * 100\% \quad (1)$$

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

## 175 **4 Results and Discussion**

176 The initial pH value of the MB solution was 8.2. The final pH value varies between 7.9 and  
177 8.8 for all investigated systems (results not shown). With a variation of only one pH unit, the  
178 process of MB discoloration depends primarily on the availability (and amount) of  $\text{Fe}^0$  and  
179 sand. MB discoloration as used in this work is not interchangeable with MB removal as the  
180 DOC values were not characterized. However, from a pure thermodynamic perspective MB is  
181 not redox sensitive in  $\text{Fe}^0/\text{H}_2\text{O}$  systems [41,42] (see section 2).

#### 182 **4.1 Non-disturbed batch experiments**

183 Figure 1 summarizes the results of non-disturbed batch experiments for 21 and 45 days. Fig.  
184 1a compares the extent of MB discoloration by sand ( $\leq 90 \text{ g L}^{-1}$ ) and  $\text{Fe}^0$  ( $\leq 45 \text{ g L}^{-1}$ ) after 21  
185 days. It is seen that, based on the used masses,  $\text{Fe}^0$  is a more efficient MB discoloration agent  
186 than sand. MB discoloration is levelled at about 60 % in the pure  $\text{Fe}^0$  system and at about 45  
187 % in the pure sand system. In both systems, a pseudo-equilibrium is observed due to the  
188 slowness of MB diffusion to the surface of the adsorbing material at the bottom of the essay  
189 tubes. In the pure sand system, the adsorption capacity might be achieved for a long enough  
190 experimental duration. In  $\text{Fe}^0$ -containing systems on the contrary, the adsorption capacity can  
191 not be exhausted at the laboratory scale, because completed depletion of  $\text{Fe}^0$  should be  
192 achieved.

193 Fig. 1b shows that mixing  $90 \text{ g L}^{-1}$  sand to  $\text{Fe}^0$  significantly increased the efficiency of the  
194 system only for low  $\text{Fe}^0$  loading ( $< 6 \text{ g L}^{-1}$ ). For these  $\text{Fe}^0$  loadings the surfaces of  $\text{Fe}^0$  and  
195 sand compete for MB discoloration and the amount of in-situ produced iron oxides has not  
196 significantly impaired the affinity of the sand surface for MB molecules [39]. For higher  $\text{Fe}^0$   
197 mass loadings, sand addition even impaired the process of MB discoloration. Thus,  
198 Assumption 2 (MB discoloration by  $\text{Fe}^0$  is significantly retarded by the presence of sand) is  
199 validated. This observation is rationalized at first glance by the fact that sand is a good  
200 adsorbent for MB [39,40,43,44]. Adsorption on sand occurs with a more rapid kinetics than  
201  $\text{Fe}^0$  oxidation which produced MB scavengers. This seemingly surprising observation was  
202 further investigated. Results from Fig. 1a clearly disproves Assumption 1 (“MB discoloration  
203 by  $\text{Fe}^0$  is not affected by the presence of sand”).

204 Fig. 1b also shows that lengthening the reaction time from 21 to 45 days yield to increased  
205 MB discoloration. MB discoloration is now levelled to about 80 % for both systems. It is  
206 essential to recall that the systems were not shaken and that the reactive mixture was located  
207 at the bottom of the essay tubes. In this manner, gravitational diffusion was the sole driving



208 force for MB transport from the bulk solution to the adsorptive particles. Gravitational  
209 diffusion is induced by concentration gradient due to MB adsorption and/or co-precipitation at  
210 the bottom of the essay tubes. In the pure Fe<sup>0</sup> systems particle cementation was observed at  
211 the end of the experiments both after 21 and 45 days, with the cake after 45 days being more  
212 harder than that after 21 days. In Fe<sup>0</sup>/sand system not such cementation was observed. These  
213 observation suggested that the pure Fe<sup>0</sup> system was already at a pseudo-steady state while the  
214 Fe<sup>0</sup>/sand system was still progressing to such a stage. Accordingly, it can be postulated that  
215 for longer experimental duration, Fe<sup>0</sup>/sand systems will be more efficient than pure sand  
216 systems. However, this will not result from MB adsorption onto sand but to continuous Fe<sup>0</sup>  
217 corrosion and scavengers generation. Accordingly, mixing Fe<sup>0</sup> and sand is an efficient tool to  
218 sustain Fe<sup>0</sup> corrosion [10,15].

219 The last important feature from Fig. 1 is that while using essay tubes in non-disturbed batch  
220 experiments, no pseudo-equilibrium was achieved even after 45 days. Accordingly, no effort  
221 was made to model the results using available equilibrium models (e.g. Freundlich, Langmuir,  
222 Temkin). Efforts to model Fe<sup>0</sup> removal results by these models are faulty because Fe<sup>0</sup> is  
223 supposed to react until complete depletion. Therefore, any equilibrium model should take the  
224 intrinsic reactivity of used Fe<sup>0</sup> and its reaction kinetics into account. No such a study could be  
225 found in the literature. In contrary, the literature contain many studies characterizing Fe<sup>0</sup>  
226 materials by their adsorption capacity (e.g. in mg contaminant per g Fe<sup>0</sup>) based on result of  
227 short term batch experiments [1,5]. Usually these experiments are performed under mixing  
228 conditions (mixing type, mixing intensity) which are no relevant for experimental situations  
229 [45]. Recent works have shown that while using the experimental design of the present study,  
230 the shaking intensity should not exceed 50 rpm [23,41,42] to be relevant for field situations.  
231 The next section presents results of experiments obtained when the systems presented above  
232 were shaken at 75 rpm for 7 days (1 week). This shaking intensity (> 50 rpm) was selected to  
233 increase the probability to observe difference with non-disturbed conditions within 7 days.

## 234 **4.2 Shaken batch experiments**

235 Figure 2 summarizes the results of MB discoloration in the three investigated systems, shaken  
236 at 75 rpm for 7 days. Figure 2 clearly shows that the pure  $\text{Fe}^0$  system was the most efficient,  
237 followed by the “ $\text{Fe}_i^0 + \text{sand}$ ” system. The observation that MB is continuously adsorbed and  
238 co-precipitated by iron corrosion products is confirmed by the course of the line “ $\text{Fe}_i^0$ ”. The  
239 least efficient system was “ $\text{Fe}^0 + \text{sand}_i$ ”. This corresponds to the system with the smallest  $\text{Fe}^0$   
240 loading ( $5 \text{ g L}^{-1}$ ) and the largest sand loading (up to  $90 \text{ g L}^{-1}$ ). It is important to notice that  
241 parallel “ $\text{Fe}_i^0$ ” and “ $\text{sand} + \text{Fe}_i^0$ ” systems contained exactly the same amount of  $\text{Fe}^0$  but “ $\text{sand}$   
242 +  $\text{Fe}_i^0$ ” additionally contains  $90 \text{ g L}^{-1}$  sand. For  $\text{Fe}^0$  mass loadings larger than  $11 \text{ g L}^{-1}$ , “ $\text{Fe}^0$ ”  
243 was more efficient than “ $\text{sand} + \text{Fe}_i^0$ ”. Thus the validity of Assumption 2 is confirmed by  
244 shaken experiments.

245 These results from Fig. 2 clearly show that the presence of sand impairs the accessibility of  
246 MB to the vicinity of  $\text{Fe}^0$  particle where absorption and co-precipitation occurs. It should be  
247 kept in mind that in-situ iron oxide coating at the surface of sand impair MB discoloration in  
248 two ways: (i) decreasing the affinity of sand surface for MB [39], and (ii) consuming “free”  
249 corrosion products which would have co-precipitated MB. At the end of the experiment minor  
250 compaction was observed in some reaction vessels for the  $\text{Fe}^0/\text{sand}$  system. As a rule, when  
251 compaction becomes significant the access of sand and  $\text{Fe}^0$  surface is limited and MB  
252 discoloration is impaired. Accordingly, while mixing  $\text{Fe}^0$  and sand a balance must be found  
253 between (i) “decreased reactive surface” because of sand addition and (ii) “sustained  $\text{Fe}^0$   
254 reactivity” by virtue of sand addition.

## 255 **4.3 Removal mechanisms**

256 The use of adsorbing agents to accumulate reducible species in the vicinity of  $\text{Fe}^0$  media has  
257 been extensively reported in the literature [5]. However, the driving force for the transfer of  
258 adsorbed species to the  $\text{Fe}^0$  surface has not been identified/reported [46]. The discussion  
259 above has recalled that in-situ coating of the  $\text{Fe}^0$  surface can even impair adsorptive

260 accumulation. However, when accumulation is favourable, adsorbed species are more or less  
261 attached to the adsorbents (including sand and iron oxides). Adsorbed reducible species will  
262 not readily migrate to the  $\text{Fe}^0$  surface, but could be easily chemically transformed in the  
263 adsorbed state by  $\text{Fe}^{\text{II}}$  and  $\text{H}_2$  from continue iron corrosion. Reduction by  $\text{Fe}^{\text{II}}$  and  $\text{H}_2$  is a  
264 chemical reaction while reduction by  $\text{Fe}^0$  is an electrochemical reaction [47]. In other words,  
265 although iron corrosion is an electrochemical process, contaminant reduction in  $\text{Fe}^0/\text{H}_2\text{O}$   
266 system is not induced by electrons from the metal body ( $\text{Fe}^0$ ). This has been demonstrated for  
267 example by Odziemkowski et al. [48], Lavine et al. [49], Jiao et al. [50] and Ghauch et al.  
268 [51]. Therefore, the reported efficiency of  $\text{Fe}^0/\text{sand}$  system for contaminant reduction  
269 corroborates the adsorption co-precipitation concept [46,52-54], arguing that direct reduction  
270 (electrons from  $\text{Fe}^0$ ) does not play any significant role in the process of contaminant  
271 reduction.

## 272 **5 Concluding remarks**

273 This study has investigated the effect of mixing granular iron with sand for methylene blue  
274 (MB) discoloration. Three ranges of sand mass loading were tested: (i) absence of sand (pure  
275  $\text{Fe}^0$ ), (ii) limited amount of sand ( $11 < [\text{sand}] (\text{g L}^{-1}) < 45$ , (iii) abundance of sand ( $> 50 \text{ g L}^{-1}$ ).  
276 Results showed that the kinetics of mass transfer, the relative amounts of  $\text{Fe}^0$  and sand all  
277 affect the efficiency of  $\text{Fe}^0/\text{sand}$  mixtures for MB discoloration. The results achieved herein  
278 are purely qualitative and suggest that more research it needed with other contaminants in  
279 batch and column experiments before accumulated data can be converted into useful  
280 knowledge for the further development of the  $\text{Fe}^0$  technology. For example, based of the  
281 findings that (i) anionic (e.g. Acid Orange-7, Congo Red, Eriochrome Black T, Rose Bengal)  
282 and cationic (e.g. Janus Green, Rhodamine 6G, Toluidine Blue) dyes exhibit very different  
283 adsorption affinity for iron oxides [40,55] and (ii) metal oxide coated sands are worse  
284 adsorbents for MB than ‘virgin’ sands [39], working in parallel with organic anionic and

285 cationic dyes will enable a rapid characterization of sand on contaminant removal in Fe<sup>0</sup>/H<sub>2</sub>O  
286 systems.

287 This study clearly shows that in delaying particle compaction, Fe<sup>0</sup> “dilution” with sand is  
288 certainly beneficial for the long-term efficiency of Fe<sup>0</sup> remediation systems. Accordingly, for  
289 the long term, mass transfer limitations are compensated by sustained reactivity. Practitioners  
290 of Fe<sup>0</sup> technology have already taken advantage of this phenomenon [1,2,11,13]. However,  
291 available data were gained in a very pragmatic approach. With the recent establishment of the  
292 equation of a Fe<sup>0</sup> bed [20] and the proper consideration of the volumetric expensive nature of  
293 iron corrosion [19,56,57], more research is needed to determine more precisely the conditions  
294 for a non site specific Fe<sup>0</sup>/sand system design. The present study has not attempted to  
295 introduce any mathematical model of the investigated systems which could account for  
296 example for the mass of material. Rather, the study is regarded as preliminary guidelines for  
297 the optimisation of filtration Fe<sup>0</sup>/H<sub>2</sub>O systems.

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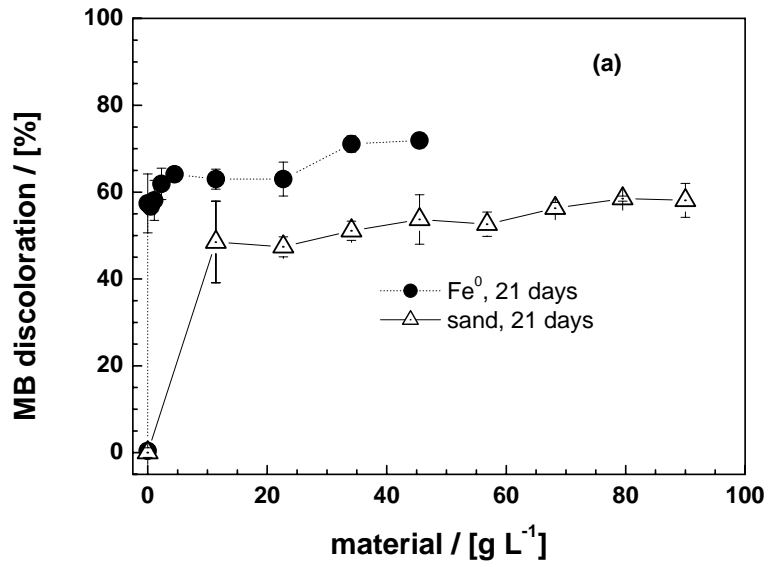
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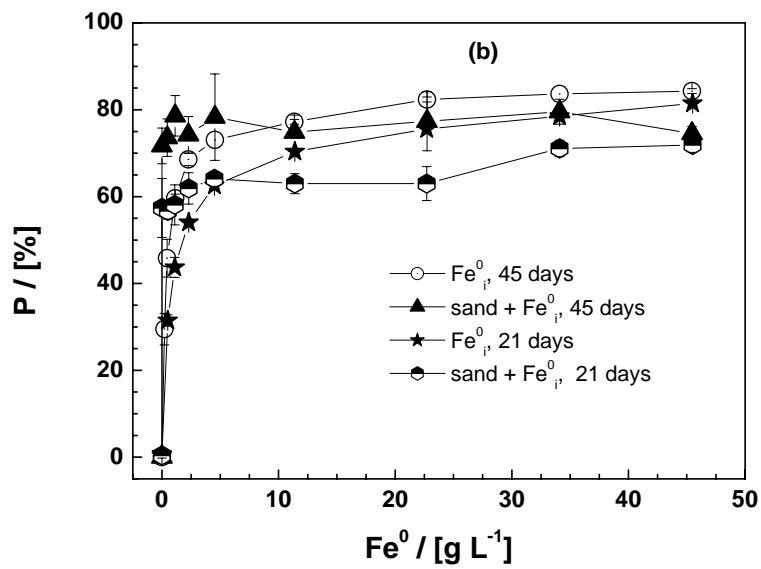
443 **Figure 1**

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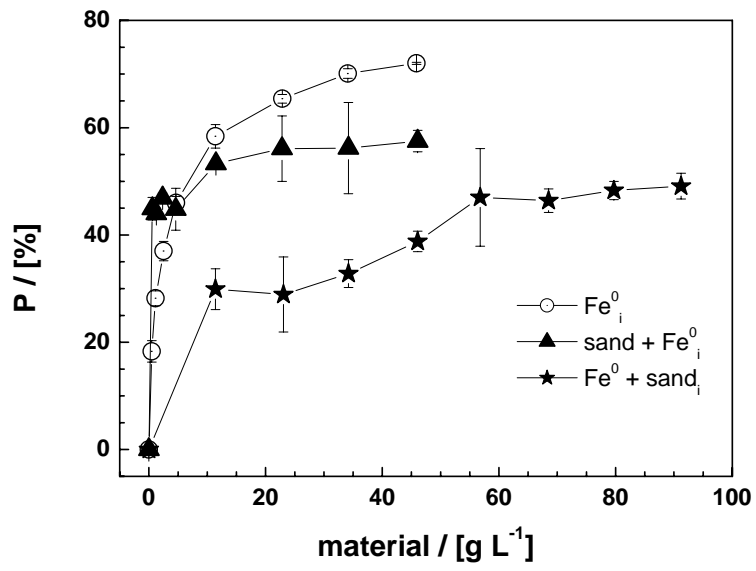


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448 **Figure 2**

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451 **Figure Captions**

452

453 **Figure 1:** Evolution of the methylene blue (MB) discoloration (P in %) as a function of  
454 material loading in non-disturbed batch experiments for 21 and 45 days: (a) pure Fe<sup>0</sup> and sand  
455 systems, (b) Fe<sup>0</sup> and Fe<sup>0</sup>/sand systems. The Fe<sup>0</sup>/sand systems (Fig. 1b) content 90 g L<sup>-1</sup> of  
456 sand and variable amounts of Fe<sup>0</sup>. The experiments were conducted with a 10 mg L<sup>-1</sup> MB  
457 solution in graduated essay tubes containing of 22 mL of the MB solution. The lines are not  
458 fitting functions, they simply connect points to facilitate visualization.

459

460 **Figure 2:** Evolution of the methylene blue (MB) discoloration (P in %) as a function of  
461 material loading in shaken batch experiments (75 rpm) for 7 days. The experiments were  
462 conducted with a 10 mg L<sup>-1</sup> MB solution in graduated essay tubes containing of 22 mL of the  
463 MB solution. The subscript “i” designates the material which mass loading varied. The other  
464 material is present in constant amount (5 g L<sup>-1</sup> for Fe<sup>0</sup> and 90 g L<sup>-1</sup> for sand). The lines are not  
465 fitting functions, they simply connect points to facilitate visualization.

466