

1 **Impact of MnO<sub>2</sub> on the efficiency of metallic iron for the removal of dissolved Cr<sup>VI</sup>, Cu<sup>II</sup>,**  
2 **Mo<sup>VI</sup>, Sb<sup>V</sup>, U<sup>VI</sup> and Zn<sup>II</sup>**

3 Noubactep C.\*<sup>(a,c)</sup>, Btatkeu K.B.D.<sup>(b)</sup>, Tchatchueng J.B.<sup>(b)</sup>

4 <sup>(a)</sup> Angewandte Geologie, Universität Göttingen, Goldschmidtstraße 3, D - 37077 Göttingen, Germany;

5 <sup>(b)</sup> ENSAI/University of Ngaoundere, BP 455 Ngaoundere, Cameroon;

6 <sup>(c)</sup> Kultur und Nachhaltige Entwicklung CDD e.V., Postfach 1502, D - 37005 Göttingen, Germany.

7 (\*) e-mail: [cnoubac@gwdg.de](mailto:cnoubac@gwdg.de); Tel. +49 551 39 3191, Fax: +49 551 399379

8 **Abstract**

9 The idea that manganese oxide (MnO<sub>2</sub>) sustains the reactivity of metallic iron (Fe<sup>0</sup>) is  
10 investigated in this study. A multi-elemental aqueous system containing Cr<sup>VI</sup>, Cu<sup>II</sup>, Mo<sup>VI</sup>, Sb<sup>V</sup>,  
11 U<sup>VI</sup>, and Zn<sup>II</sup> (each about 100 µM) was used as model solution. Non-disturbed batch  
12 experiments were performed at initial pH values 4.0 and 6.0 for one month. Three different  
13 systems were investigated: (i) MnO<sub>2</sub> alone, (ii) “Fe<sup>0</sup> + sand”, and (iii) “Fe<sup>0</sup> + MnO<sub>2</sub>”. The  
14 experimental vessels contained either: (i) no material (blank), (ii) up to 9.0 g/L of MnO<sub>2</sub>, or  
15 (iii) 5 g/L Fe<sup>0</sup> and 0 to 9.0 g/L MnO<sub>2</sub> or sand. Results clearly revealed quantitative  
16 contaminant removal (> 70 %) confirming the suitability of Fe<sup>0</sup> as a highly efficient reactive  
17 material for the removal of the 6 tested metallic ions over a pH range applicable to  
18 environmental waters. Results also corroborated the suitability of MnO<sub>2</sub> to sustain the long-  
19 term Fe<sup>0</sup> reactivity. Further studies in dynamic systems (column studies) are necessary to fine-  
20 tune the use of MnO<sub>2</sub> in Fe<sup>0</sup> filtration systems.

21 **Keywords:** Drinking water, Heavy metals, Iron filters, Manganese oxides, Zerovalent iron.

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23

## 23 **1 Introduction**

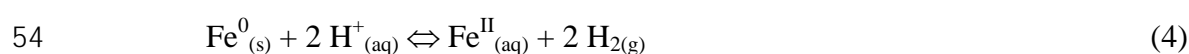
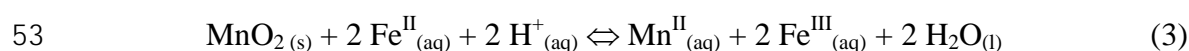
24 The use of metallic iron ( $\text{Fe}^0$ ) for the treatment of contaminated groundwater is already a  
25 standard remediation approach [1-3]. This approach has the great advantage that many classes  
26 of contaminants are removed in a single filtration operation [4]. This observation has  
27 motivated the suggestion of  $\text{Fe}^0$  as reactive agent for decentralized safe drinking water  
28 provision [5-8] in general and for household filters in particular [9,10].

29 A packed  $\text{Fe}^0$  bed is regarded as a filtration system in which contaminants are removed during  
30 aqueous iron corrosion [5-8]. In such a system, the main mechanisms of contaminant removal  
31 are: (i) adsorption onto iron corrosion products (iron oxides and hydroxides), (ii) enmeshment  
32 with precipitating iron oxides/hydroxides (co-precipitation), and (iii) adsorptive size-  
33 exclusion (straining). Adsorptive size-exclusion is improved during the service life of a filter  
34 by the in-situ formation of volumetric expansive corrosion products [11,12]. In fact, the  
35 volume of any iron corrosion product (e.g.  $\text{FeO}$ ,  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeOOH}$ ) is  
36 larger than that of the original metal ( $\text{Fe}^0$ ). The ratio between the volume of expansive  
37 corrosion product ( $V_{\text{ox}}$ ) and the volume of iron consumed in the corrosion process ( $V_{\text{Fe}}$ ) is  
38 called “rust expansion coefficient” ( $\eta$ ) and takes values between 2.08 and 6.40 [11].

$$39 \quad \eta = V_{\text{ox}}/V_{\text{Fe}} \quad (1)$$

40 The idea of using  $\text{Fe}^0$  for household filters is not new [13-16]. However, conventional  
41 household  $\text{Fe}^0$  filters were found very efficient but not sustainable as they were clogged after  
42 some weeks of operation [17]. Recent theoretical studies [9,10,18] have re-vived research on  
43 household  $\text{Fe}^0$  filters. It was shown that reducing the proportion of  $\text{Fe}^0$  in a filter (admixture  
44 with a non expansive material) is the prerequisite for long-term efficiency. Furthermore, tools  
45 to sustain the long-term reactivity were discussed. These tools included the use of bimetallic  
46 systems (e.g.  $\text{Fe}^0/\text{Ni}^0$ ,  $\text{Fe}^0/\text{Pd}^0$ ) and the use of  $\text{MnO}_2$  admixture [19].

47 The use of  $\text{MnO}_2$  to sustain iron reactivity has already been discussed in the literature for the  
48 removal of methylene blue [20], clofibrac acid [21], diclofenac [22,23], radium [24], and  
49 uranium [24,25]. The idea behind using  $\text{MnO}_2$  to sustain  $\text{Fe}^0$  reactivity is that,  $\text{Fe}^{\text{II}}$  species  
50 from  $\text{Fe}^0$  oxidation (Eq. 2) are used for the reductive dissolution of  $\text{MnO}_2$  (Eq. 3) [26,27]. For  
51 the sake of clarity, the oxidation of  $\text{Fe}^0$  by water ( $\text{H}^+$ ) and  $\text{MnO}_2$  are given by Eq. 4 and 5.



56 Chemical and electrochemical reactions likely to occur in a  $\text{Fe}^0/\text{MnO}_2/\text{H}_2\text{O}$  systems are  
57 discussed in details in ref. [27]. For the present work, it is sufficient to consider that: (i)  
58 reaction 5 is more favourable than reaction 4 ( $\text{MnO}_2$  is a stronger oxidizing agent than  $\text{H}_2\text{O}$ ),  
59 and (ii)  $\text{Fe}^{\text{II}}$  consumption (via oxidation by  $\text{MnO}_2$  to  $\text{Fe}^{\text{III}}$ ) will result in an increase in  $\text{Fe}^0$   
60 oxidation after the Le Chatelier's principle.

61 The chemical reaction between  $\text{Fe}^{\text{II}}$  and  $\text{MnO}_2$  necessarily takes place at the surface of  $\text{MnO}_2$ .  
62 In other words,  $\text{Fe}^{\text{II}}$  species are transported away from the vicinity of the  $\text{Fe}^0$  surface and are  
63 not available to form the oxide-film. The formation of the oxide-film is responsible for  $\text{Fe}^0$   
64 passivation (reactivity loss) [1,4]. Sustained  $\text{Fe}^0$  reactivity can be intuitively coupled with  
65 long-term contaminant removal. It is essential to notice that  $\text{Fe}^{\text{III}}$  species formed at the  
66 vicinity of  $\text{MnO}_2$  are not “free” to co-precipitate contaminants. Rather, they can only remove  
67 contaminant by adsorption or by improving adsorptive size-exclusion. This is the reason why  
68 a delay of contaminant removal has been reported in the presence of  $\text{MnO}_2$  in short term batch  
69 experiments [20,23,25].

70 Available results [20-25] univocally showed the capability of  $\text{MnO}_2$  to sustain contaminant  
71 removal. However, apart from Burghardt and Kassahun [24] who investigated the binary

72 Ra/U system, all available data are related to single-contaminant systems. Such systems  
73 typically fail as environmental analogues. Therefore, there is a high need for multi-elemental  
74 studies for Fe<sup>0</sup> remediation to advance the design of treatment infrastructures [28].

75 The objective of the current study is to investigate the suitability of MnO<sub>2</sub> to sustain Fe<sup>0</sup>  
76 reactivity using a multi-elemental system as model solution. Tested contaminants are: Cr<sup>VI</sup>,  
77 Cu<sup>II</sup>, Mo<sup>VI</sup>, Sb<sup>V</sup>, U<sup>VI</sup>, and Zn<sup>II</sup> (each about 100 μM). These elements are known for their  
78 different affinity to Fe hydroxides and their different redox properties (Table 1) [29]. The  
79 experiments were performed under non-disturbed conditions at pH 4.0 and 6.0 for up to 60  
80 days in three different systems: “MnO<sub>2</sub> alone”, Fe<sup>0</sup> + MnO<sub>2</sub>”, Fe<sup>0</sup> + sand”. The results are  
81 comparatively discussed.

## 82 **2 Materials and methods**

### 83 **2.1 Chemicals**

84 All chemicals (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, CuSO<sub>4</sub>·5H<sub>2</sub>O, Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, K(SbO)C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>,  
85 ZnSO<sub>4</sub>) used in this study were of analytical grade. All solutions were prepared using a spring  
86 water. The used spring water was from the Lausebrunnen in Krebeck (administrative district  
87 of Göttingen). Spring water was used as proxy for natural water. Its average composition (in  
88 mg/L) was: Cl<sup>-</sup>: 9.4; NO<sub>3</sub><sup>-</sup>: 9.5; SO<sub>4</sub><sup>2-</sup>: 70.9; HCO<sub>3</sub><sup>-</sup>: 95.1; Na<sup>+</sup>: 8.4; K<sup>+</sup>: 1.0; Mg<sup>2+</sup>: 5.7; Ca<sup>2+</sup>:  
89 110.1; and pH 7.8. pH adjustment to values of 4.0 and 6.0 was performed with diluted NaOH  
90 and HNO<sub>3</sub> solutions. These initial pH values were selected to uncover the pH value of natural  
91 waters [29].

92 Table 1 summarizes some characteristics of the six tested metals which are important in  
93 discussing their removal from the aqueous solution [30]. The chemicals were weighed to yield  
94 an initial concentration of 0.10 mM (100 μM) corresponding to concentrations varying  
95 between 5.2 and 23.8 mg/L (Tab. 1). The operational initial concentration was determined  
96 from the so-called blank experiment (72 to 99 μM). Deriving initial concentration from the

97 blank experiments enabled the consideration of all possible factors affecting the decrease of  
98 metal concentration. These factors include adsorption onto the walls of the essay tubes,  
99 common ion effect and precipitation. The initial concentration (100  $\mu\text{M}$ ) was selected to ease  
100 discussion on the molar basis. The resulting weight concentrations (Tab. 1) uncover the  
101 concentration range tested for environmental remediation [28,29,31].

## 102 **2.2 Solid materials**

103 **Fe<sup>0</sup> material:** The used Fe<sup>0</sup> material is a readily available scrap iron. Its elemental  
104 composition was determined by X-Ray Fluorescence Analysis and was found to be: C:  
105 3.52%; Si: 2.12%; Mn: 0.93%; Cr: 0.66%. The material was fractionated by sieving. The  
106 fraction 1.6 - 2.5 mm was used. The sieved Fe<sup>0</sup> was used without any further pre-treatment.

107 **Manganese oxide:** A natural manganese nodule was used as source of MnO<sub>2</sub>. The sample  
108 was collected from the deep sea, crushed and sieved. An average particle size of 1.5 mm was  
109 used. Its elemental composition was determined by X-Ray Fluorescence Analysis and was  
110 found to be: Mn: 41.8%; Fe: 2.40%; Si: 2.41%; Ni: 0.74%; Zn: 0.22%; Ca: 1.39%; Cu:  
111 0.36%. These manganese nodules originated from the pacific ocean (Guatemala basin: 06°30  
112 N, 92°54 W and 3670 m deep). The target chemically active component is MnO<sub>2</sub>, which  
113 occurs naturally mainly as birnessite and todorokite [32-34]. Generally, natural manganese  
114 oxides exhibit marked variability of key structural parameters (e.g. porosity, degree of  
115 hydration, average manganese oxidation state) that influence their chemical reactivity. The  
116 used MnO<sub>2</sub> was proven reactive in previous works [25].

117 **Sand:** The used sand was a commercial material for aviculture ("Papagaiensand" from RUT –  
118 Lehrte/Germany). Papagaiensand was used as received without any further pre-treatment nor  
119 characterization. This sand was the operational reference non-adsorbing material.

120 Materials selected for study were known to be effective for adsorbing metallic ions ( $\text{Fe}^0$ ,  
121  $\text{MnO}_2$ , sand), delaying the availability of iron corrosion products in  $\text{Fe}^0/\text{H}_2\text{O}$  systems ( $\text{MnO}_2$ )  
122 [20-25], or as admixing agent (sand).

### 123 **2.3 Experimental methodology**

124 Batch experiments without shaking were conducted in essay tubes containing 22.0 mL of the  
125 model solution (about 100  $\mu\text{M}$   $\text{Cr}^{\text{VI}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Mo}^{\text{VI}}$ ,  $\text{Sb}^{\text{V}}$ ,  $\text{U}^{\text{VI}}$  and  $\text{Zn}^{\text{II}}$ ). Two sets of experiments  
126 were performed: Experiment 1 ( $\leq 33$  days) and experiment 2 (60 days).

127 **Experiment 1:** The essay tubes containing weighted solid materials were left further  
128 undisturbed for 1 to 33 d. At pre-selected times, 22 ml of the model solution was added to  
129 three tubes to yield the wished experimental duration one day after the last solution addition.  
130 The time “one day after the last solution addition” (end of the experiment) was the date of the  
131 measurement of the pH value and the preparation of solutions (dilutions) for metal analysis.  
132 The batches consisted of 0 to 9.0  $\text{g L}^{-1}$  of  $\text{MnO}_2$  or 5  $\text{g L}^{-1}$   $\text{Fe}^0$  and 0 to 9.0  $\text{g L}^{-1}$   $\text{MnO}_2$  or  
133 sand. The extent of metal removal and the pH value in each system was characterized at the  
134 end of the experiment. At this date, up to 200  $\mu\text{L}$  of the supernatant solutions were carefully  
135 retrieved (no filtration) and diluted for concentration measurements.

136 **Experiment 2:** The essay tubes containing the model solution and (i) 0 to 9.0  $\text{g L}^{-1}$  of  $\text{MnO}_2$   
137 or (ii) 5  $\text{g L}^{-1}$   $\text{Fe}^0$  and 0 to 9.0  $\text{g L}^{-1}$   $\text{MnO}_2$  or sand were left undisturbed for 60 d, 200  $\mu\text{L}$  of  
138 the supernatant solutions were retrieved and diluted (no filtration) for concentration  
139 measurements and the pH value of the remaining solution was measured.

### 140 **2.4 Analytical methods**

141 Analysis for Cr, Cu, Fe, Mn, Mo, Sb, U and Zn was performed by inductively coupled plasma  
142 mass spectrometry (ICP-MS) at the Department of Geochemistry (Centre of Geosciences,  
143 University of Göttingen). All chemicals used for experiments and analysis were of analytical  
144 grade. The pH value was measured by combination glass electrodes (WTW Co., Germany).

145 The electrodes were calibrated with five standards following a multi-point calibration  
146 protocol [35] and in agreement with the new IUPAC recommendation [36].

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

### 148 **3 Results and Discussion**

#### 149 **3.1 pH variation**

150 Figure 1a depicts the time-dependant evolution of the pH value for the experiment with an  
151 initial pH of 4.0.  $\text{MnO}_2$  has no impact on the pH of the system. The pH increases in both  
152 systems containing  $\text{Fe}^0$  this is attributed to iron corrosion (Eq. 2) [37,38]. Three days after the  
153 start of the experiments, the pH in both  $\text{Fe}^0$  systems (Eq. 2 and Eq. 5) was larger than 5.0  
154 suggesting that quantitative contaminant removal by adsorption and co-precipitation was  
155 likely to occur [39,40]. In fact, metal removal mostly occurs by adsorption and co-  
156 precipitation. Even chemically transformed metal species (e.g.  $\text{Cr}^{\text{III}}$ ,  $\text{Mo}^{\text{III}}$ ,  $\text{U}^{\text{IV}}$ ) must be  
157 removed by one of these mechanisms which are all coupled with iron oxide precipitation.  
158 Quantitative iron precipitation take place only when the pH value is larger than 4.0 to 4.5  
159 [37,38,41]. For  $\text{pH} < 4.0$ , the solubility of iron is high and iron precipitation is not  
160 quantitative. A classical example is that of Cr [42-44]. Soluble  $\text{Cr}^{\text{VI}}$  is reduced at pH 2.0-3.5  
161 to soluble  $\text{Cr}^{\text{III}}$  and the pH is raised to a value above 6.0 where  $\text{Cr}^{\text{III}}$  is essentially less soluble.  
162 Clearly, quantitative aqueous contaminant removal by  $\text{Fe}^0$  is only expected at  $\text{pH} > 4.5$ .  
163 Metals are then fixed selectively according to factors like their atomic radii [30], their charges  
164 at a given pH value, their oxidation state (Tab. 1).

165 It is interesting to notice that the pH value was levelled to a value of 6.0 in the system " $\text{Fe}^0$  +  
166 sand" after 10 days. The pH further increases to 9.0 in the system " $\text{Fe}^0$  +  $\text{MnO}_2$ " after 21  
167 days. The greater pH increase in the presence of  $\text{MnO}_2$  is a strong experimental evidence for  
168 the suitability of  $\text{MnO}_2$  to sustain the reactivity of  $\text{Fe}^0$  at the long-term ([19] and ref. cited  
169 therein). In fact, iron corrosion leading to elevated pH values is sustained by  $\text{MnO}_2$  (Eq. 5).

170 It should be kept in mind that slow kinetics of the involved multi-steps heterogeneous  
171 reactions provides a continuing source of powerfully hydrous ferric oxides for contaminant  
172 removal and is thus advantageous as such systems are designed to function for years [1,45].

173 Figure 1b compares the extent of pH increase in both systems with  $\text{Fe}^0$  for the experiment at  
174 initial pH 6.0 ( $t \leq 33$  d). A clear difference between systems “ $\text{Fe}^0 + \text{sand}$ ” and “ $\text{Fe}^0 + \text{MnO}_2$ ”  
175 is observed at this time. This difference is a reflect of the discussed sustained  $\text{Fe}^0$  reactivity by  
176  $\text{MnO}_2$ . According to Eq. 4 and Eq. 5, this difference in at first glance the reflect of the higher  
177 oxidative capacity of  $\text{MnO}_2$  compared to  $\text{H}_2\text{O}$ . However, it should be kept in mind that Eq. 5  
178 is not likely to quantitatively occur in a single step, even under acidic conditions [27].

### 179 **3.2 Iron release**

180 Figure 2 summarizes the time-dependant evolution the iron concentration for the investigated  
181 systems at pH 6.0 (initial pH). It is seen that the iron concentration first increased from 0  $\mu\text{M}$   
182 at  $t = 0$  to about 150  $\mu\text{M}$  at  $t = 8$  d and then monotonically decreased to a value of 20 to 30  
183  $\mu\text{M}$  in the system “ $\text{Fe}^0 + \text{sand}$ ”. This iron profile is compatible with the process of oxide-film  
184 formation and the accompanying decreased corrosion kinetics [37,38,46].

185 Figure 2 also shows that, in system “ $\text{Fe}^0 + \text{MnO}_2$ ” dissolved Fe is maximal at  $t = 3$  days and  
186 (about 35  $\mu\text{M}$ ) decreased to 7  $\mu\text{M}$  at  $t = 30$  d. This observation is compatible with recent  
187 findings from Pan and van Duin [47,48] who reported on a three-stages iron oxidation based  
188 on the generated species and oxidation speed. Accordingly, early iron oxides are rather mixed  
189 and instable, whereas the later oxides are more organized and stable. The oxidation speed is  
190 significantly reduced. Moreover generated  $\text{Fe}^{\text{II}}$  species are partly adsorbed onto crystallized  
191 iron oxides and are not present in the aqueous phase. Therefore, despite sustained reactivity of  
192  $\text{Fe}^0$ , Fe is not quantitatively released into the solution. Fe concentration remained very low but  
193 never decreased to undetectable levels. As discussed in section 3.1 the impact of  $\text{MnO}_2$  on pH  
194 increased was still measured two months after the start of the experiments.



### 195 **3.3 Manganese release**

196 Figure 3 compares the extent of Mn release in the three systems at pH 6.0 (initial pH). It is  
197 seen that the “Fe<sup>0</sup> + MnO<sub>2</sub>” is the sole system releasing Mn. The Mn concentration first  
198 increased from 0 μM at t = 0 to about 120 μM at t = 7 d. The concentration is then levelled to  
199 about 80 μM through the end of the experiment. This levelled Mn concentration ([Mn] ≠ 0  
200 μM) corroborated sustained Fe<sup>0</sup> reactivity (Eq. 4). It should be noticed that in the system  
201 “MnO<sub>2</sub> alone”, Mn concentration was constantly lower than 20 μM. It is known that MnO<sub>2</sub> is  
202 very stable in water under ambient conditions [32-35,49].

### 203 **3.4 Metal removal**

#### 204 **3.4.1 Initial pH = 4.0**

205 Figure 4a summarizes the residual metal concentration at day 33 as a function of the MnO<sub>2</sub>  
206 loading in system “Fe<sup>0</sup> + MnO<sub>2</sub>”. It is clearly shown that the extent of contaminant removal  
207 was negligible although the final pH was larger than 5.0 (section 3.1). Fig. 4b shows that  
208 systems with lower MnO<sub>2</sub> loadings exhibited higher Fe concentration. This observation is  
209 consistent with the above discussed sustainability of Fe<sup>0</sup> reactivity by MnO<sub>2</sub> (Eq. 4). In fact,  
210 larger MnO<sub>2</sub> loadings are coupled with greater extent of Fe<sup>0</sup> corrosion, yielding larger pH  
211 values and decreased Fe solubility [38].

212 The main feature from Fig. 4 is that Fe<sup>0</sup> is not suitable for water treatment when the pH is  
213 lower than 5.0 (e.g. acid mine drainage). For such situations alternatives should be used or the  
214 pH will be first increased. Another important feature from Fig. 4a is that the concentration of  
215 Cu and Cr were partly higher than that of the working initial solution. This result is  
216 compatible with the fact that these elements were leached from MnO<sub>2</sub> [33]. In fact, while the  
217 Cr content of the used MnO<sub>2</sub> was not measured, the Cu was 0.36 % as indicated in section  
218 2.2.

#### 219 **3.4.2 Initial pH = 6.0**

220 Figure 5 summarizes the evolution of the residual metal concentration ( $\mu\text{M}$ ) for the three  
221 systems at initial pH 6.0. It is shown from Fig. 5a that metal removal by  $\text{MnO}_2$  is minimal. In  
222 the presence of  $\text{Fe}^0$ , the removal of  $\text{Cr}^{\text{VI}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Sb}^{\text{V}}$ ,  $\text{U}^{\text{VI}}$  and  $\text{Zn}^{\text{II}}$  is quantitative ( $> 90\%$ ) for  
223 33 d contact time. However, the removal extent of these species is significantly influenced  
224 by the presence of  $\text{MnO}_2$  (" $\text{Fe}^0 + \text{sand}$ " vs. " $\text{Fe}^0 + \text{MnO}_2$ " systems).  $\text{Mo}^{\text{VI}}$  is the sole ion  
225 which removal extent has never reached 90% under tested experimental conditions (Tab. 2).  
226 Table 3 comparatively quantifies the extent of metal removal in the " $\text{Fe}^0 + \text{sand}$ " and " $\text{Fe}^0 +$   
227  $\text{MnO}_2$ " systems. Negative  $\delta_1$  and  $\delta_2$  values clearly demonstrated the delay of metal removal  
228 due to the presence of  $\text{MnO}_2$ . Positive  $\Delta'$  values indicate an overall progression of the process  
229 of metal removal despite delay due to the presence of  $\text{MnO}_2$ . The ability of  $\text{MnO}_2$  to sustain  
230  $\text{Fe}^0$  reactivity is delineated.

231 In system " $\text{Fe}^0 + \text{sand}$ ",  $\text{Mo}^{\text{VI}}$  removal is not quantitative (Tab. 2, Fig. 5b). In system " $\text{Fe}^0 +$   
232  $\text{MnO}_2$ ",  $\text{Sb}^{\text{V}}$  and  $\text{Mo}^{\text{VI}}$  removal are not quantitative (Tab. 2, Fig. 5c). This result corroborates  
233 the view that metals are removed by "free" iron corrosion products [21,22,23,25] since both  
234 elements exhibit the lowest affinity for iron oxides ([28,29] and references cited therein). It is  
235 very important to notice that the surface charge of the adsorbent alone is not sufficient for the  
236 discussion of the removal behaviour. In fact, Tab. 1 shows that only Zn and Cu are present as  
237 positively charged species (cations) which are readily adsorbed by negatively charged iron  
238 oxides [29]. However, U and Cr were also available as negatively charged species (anions).  
239 Furthermore, in  $\text{Fe}^0/\text{H}_2\text{O}$  systems,  $\text{Cr}^{\text{VI}}$  can be readily reduced (e.g. by  $\text{Fe}^{\text{II}}$  species) to less  
240 soluble  $\text{Cr}^{\text{III}}$  while reduction of soluble  $\text{U}^{\text{VI}}$  to less soluble  $\text{U}^{\text{IV}}$  is less favourable.  
241 Nevertheless, Cr and U exhibited very similar removal behaviours. It should be kept in mind  
242 that iron oxides and hydroxides are in-situ generated and are in permanent transformation  
243 such that contaminant removal is not performed by a well-defined adsorbing agent [39,40].

244 The experiments at initial pH 6.0 were duplicated for 60 d (Experiment 2) to access the  
245 evolution of the “Fe<sup>0</sup> + MnO<sub>2</sub>” system. The results are presented in Tab. 2 and Tab. 3. Results  
246 showed a continuous decrease of the concentration for all elements. For example, the removal  
247 extent of Mo<sup>VI</sup> increased from 70.0 % after 1 month to 83.7 % after 2 months in the “Fe<sup>0</sup> +  
248 sand” system ( $\Delta_{1,2}$  value = 13.7 %). In the “Fe<sup>0</sup> + MnO<sub>2</sub>” system, the extent of Mo<sup>VI</sup> removal  
249 increased from 60.3 to 74.7 % ( $\Delta'_{1,2}$  value = 14.4 %). Tab. 2 shows the following variations  
250 for  $\Delta_{1,2}$  and  $\Delta'_{1,2}$  values:  $0.4 \leq \Delta_{1,2} \leq 13.7$  ;  $1.3 \leq \Delta'_{1,2} \leq 16.3$ . The highest  $\Delta$  values  
251 correspond to elements (Mo, Sb and Zn) with the lowest affinity to iron oxides in the  
252 investigated pH range (pH > 6.0). Note that, in the “Fe<sup>0</sup> + sand” system, further contaminant  
253 removal beyond 33 d was only significant (> 3 %) for Mo (13.7 %) and Zn (3.8 %) (Tab. 2).  
254 Table 3 shows that the impact of MnO<sub>2</sub> on the extent of metal removal was higher after 1  
255 month ( $\delta_1 > \delta_2$ ). The increasing order of  $\delta_1$  value was: Cr < Mo < Cu < Zn < Sb < U. The  
256 increasing order of element covalent radius (Tab. 1) is: Cu = Zn < Cr < Mo = Sb < U. The  
257 increasing order of element atomic mass (Tab. 1) is: Cr < Cu < Zn < Mo < Sb < U. A survey  
258 of these three series suggests that, similar to the charge of the species, none of the criteria is  
259 really relevant to rationalize the interaction of tested element with in-situ generated iron  
260 corrosion products. Tested metals ions have permanent or variable oxidation state (Tab. 1)  
261 and possibly participate in redox processes. All these properties determine their removal from  
262 the aqueous phase [29] .

#### 263 **4 Concluding remarks**

264 The suitability of Fe<sup>0</sup> for the removal of dissolved Cr<sup>VI</sup>, Cu<sup>II</sup>, Mo<sup>VI</sup>, Sb<sup>V</sup>, U<sup>VI</sup>, and Zn<sup>II</sup> is  
265 accessed in this communication. Results corroborated the view that tested contaminants are  
266 removed by in-situ generated iron corrosion products. A non-reducible species (Zn<sup>II</sup>), two less  
267 adsorbable species (Mo<sup>VI</sup>, Sb<sup>V</sup>) and three other elements with slightly different affinity to iron

268 corrosion products are all quantitatively removed for sufficient long experimental durations (>  
269 1 month).

270 The suitability of  $\text{MnO}_2$  to sustain  $\text{Fe}^0$  reactivity for the contaminant removal is also  
271 confirmed. The importance of this latter aspect has been recently presented in theoretical  
272 works on the suitability of  $\text{MnO}_2$  to sustain the efficiency of household water filters [19].  
273 While  $\text{MnO}_2$  has been proved to delay the kinetics of contaminant removal in short term batch  
274 experiments, it has been postulated that the main benefit of  $\text{MnO}_2$  is to sustain  $\text{Fe}^0$  corrosion.  
275 In fact, in  $\text{Fe}^0$  filters, sustained  $\text{Fe}^0$  corrosion produces iron (hydr)oxides at different depths  
276 for quantitative contaminant removal. Future works should investigate this aspect for a proper  
277 design of sustainable  $\text{Fe}^0$  filtration systems at all scales (household filters, subsurface reactive  
278 walls). A recently presented tool for the design of laboratory column experiments for better  
279 results comparability [50] could support these efforts.

## 280 **Acknowledgments**

281 Thoughtful comments provided by Angelika Schöner (FSU Jena - Germany) on the revised  
282 manuscript are gratefully acknowledged. The used scrap iron was kindly purchased by the  
283 branch of the Metallaufbereitung Zwickau, (MAZ) in Freiberg. The manuscript was improved  
284 by the insightful comments of anonymous reviewers from the Chemical Engineering Journal.

## 285 **References**

286 [1] R.W. Gillham, Development of the granular iron permeable reactive barrier technology  
287 (good science or good fortune). In "Advances in environmental geotechnics :  
288 proceedings of the International Symposium on Geoenvironmental Engineering in  
289 Hangzhou, China, September 8-10, 2009"; Y. Chen, X. Tang, L. Zhan (Eds); Springer  
290 Berlin/London (2010) 5–15.

- 291 [2] S. Comba, A. Di Molfetta, R. Sethi, A Comparison between field applications of nano-,  
292 micro-, and millimetric zero-valent iron for the remediation of contaminated aquifers,  
293 *Water Air Soil Pollut.* 215 (2011) 595–607.
- 294 [3] M. Gheju, hexavalent chromium reduction with zero-valent iron (ZVI) in aquatic systems,  
295 *Water Air Soil Pollut.* (2011) doi 10.1007/s11270-011-0812-y.
- 296 [4] A.D. Henderson, A.H. Demond, Long-term performance of zero-valent iron permeable  
297 reactive barriers: a critical review, *Environ. Eng. Sci.* 24 (2007) 401–423.
- 298 [5] C. Noubactep, A. Schöner, P. Wofo, Metallic iron filters for universal access to safe  
299 drinking water, *Clean: Soil, Air, Water* 37 (2009) 930–937.
- 300 [6] C. Noubactep, Metallic iron for safe drinking water worldwide, *Chem. Eng. J.* 165 (2010)  
301 740–749.
- 302 [7] C. Noubactep, A. Schöner, Metallic iron: dawn of a new era of drinking water treatment  
303 research? *Fresen. Environ. Bull.* 19 (2010) 1661–1668.
- 304 [8] C. Noubactep, Metallic iron for safe drinking water production, *Freiberg Online Geology*,  
305 vol. 27 (2011) 38 pp. ISSN 1434-7512. ([www.geo.tu-freiberg.de/fog](http://www.geo.tu-freiberg.de/fog)).
- 306 [9] C. Noubactep, S. Caré, Enhancing sustainability of household water filters by mixing  
307 metallic iron with porous materials, *Chem. Eng. J.* 162 (2010) 635–642.
- 308 [10] C. Noubactep, S. Caré, F. Togue-Kamga, A. Schöner, P. Wofo, Extending service life  
309 of household water filters by mixing metallic iron with sand, *Clean – Soil, Air, Water* 38  
310 (2010) 951–959.
- 311 [11] C. Anstice, C. Alonso, F.J. Molina, Cover cracking as a function of bar corrosion: part I-  
312 experimental test, *Materials and structures* 26 (1993) 453–464.
- 313 [12] S. Caré, Q.T. Nguyen, V. L’Hostis, Y. Berthaud, Mechanical properties of the rust layer  
314 induced by impressed current method in reinforced mortar, *Cement and Concrete*  
315 *Research* 38 (2008) 1079–1091.

- 316 [13] A.H. Khan, S.B. Rasul, A.K.M. Munir, M. Habibuddowla, M. Alauddin, S.S. Newaz, A.  
317 Hussam, Appraisal of a simple arsenic removal method for groundwater of Bangladesh,  
318 J. Environ. Sci. Health A 35 (2000) 1021–1041.
- 319 [14] A. Hussam, A.K.M. Munir, A simple and effective arsenic filter based on composite iron  
320 matrix: Development and deployment studies for groundwater of Bangladesh, J.  
321 Environ. Sci. Health A 42 (2007) 1869–1878.
- 322 [15] T.K.K. Ngai, R.R. Shrestha, B. Dangol, M. Maharjan, S.E. Murcott, Design for  
323 sustainable development – Household drinking water filter for arsenic and pathogen  
324 treatment in Nepal, J. Environ. Sci. Health A 42 (2007) 1879–1888.
- 325 [16] H. Chiew, M.L. Sampson, S. Huch, S. Ken, B.C. Bostick, Effect of groundwater iron and  
326 phosphate on the efficacy of arsenic removal by iron-amended biosand filters, Environ.  
327 Sci. Technol. 43 (2009) 6295–6300.
- 328 [17] A. Hussam, Contending with a Development Disaster: SONO Filters Remove Arsenic  
329 from Well Water in Bangladesh, Innovations 4 (2009) 89–102.
- 330 [18] C. Noubactep, S. Caré, Dimensioning metallic iron beds for efficient contaminant  
331 removal, Chem. Eng. J. 163 (2010) 454–460.
- 332 [19] C. Noubactep, S. Caré, K.B.D. Btatkeu, C.P. Nansu-Njiki, Enhancing the sustainability  
333 of household Fe<sup>0</sup>/sand filters by using bimetallics and MnO<sub>2</sub>, Clean – Soil, Air, Water  
334 38 (2011) xy–zt.
- 335 [20] C. Noubactep, Characterizing the discoloration of methylene blue in Fe<sup>0</sup>/H<sub>2</sub>O systems, J.  
336 Hazard. Mater. 166 (2009) 79–87.
- 337 [21] A. Ghauch, H. Abou Assi, A. Tuqan, Investigating the mechanism of clofibric acid  
338 removal in Fe<sup>0</sup>/H<sub>2</sub>O systems, J. Hazard. Mater. 176 (2010) 48–55.
- 339 [22] A. Ghauch, H. Abou Assi, S. Bdeir, Aqueous removal of diclofenac by plated elemental  
340 iron: Bimetallic systems, J. Hazard. Mater. 182 (2010) 64–74.

- 341 [23] A. Ghauch, H. Abou Assi, H. Baydoun, A.M. Tuqan, A. Bejjani, Fe<sup>0</sup>-based trimetallic  
342 systems for the removal of aqueous diclofenac: Mechanism and kinetics, *Chem. Eng. J.*  
343 (2011) 1033–1044.
- 344 [24] D. Burghardt, A. Kassahun, Development of a reactive zone technology for simultaneous  
345 in situ immobilisation of radium and uranium, *Environ. Geol.* 49 (2005) 314–320.
- 346 [25] C. Noubactep, G. Meinrath, J.B. Merkel, Investigating the mechanism of uranium  
347 removal by zerovalent iron materials, *Environ. Chem.* 2 (2005), 235–242.
- 348 [26] D.F.A. Koch, Kinetics of the reaction between manganese dioxide and ferrous ion, *Aust.*  
349 *J. Chem* 10 (1957) 150–159.
- 350 [27] M.Sh. Bafghi, A. Zakeri, Z. Ghasemi, M. Adeli, Reductive dissolution of manganese ore  
351 in sulfuric acid in the presence of iron metal. *Hydrometallurgy* 90 (2008) 207–212.
- 352 [28] T.B. Scott, I.C. Popescu, R.A. Crane, C. Noubactep, Nano-scale metallic iron for the  
353 treatment of solutions containing multiple inorganic contaminants, *J. Hazard. Mater.*  
354 186 (2011) 280–287.
- 355 [29] Y.N. Vodyanitskii, The role of iron in the fixation of heavy metals and metalloids in  
356 soils: a review of publications, *Eurasian Soil Sci.* 43 (2010) 519–532.
- 357 [30] J.C. Slater, Atomic Radii in Crystals. *J. Chem. Phys.* 41 (1964) 3199–3205.
- 358 [31] K.J. Cantrell, D.I. Kaplan, T.W. Wietsma, Zero-valent iron for the in situ remediation of  
359 selected metals in groundwater, *J. Hazard. Mater.* 42 (1995) 201–212.
- 360 [32] J.E. Post, Manganese oxide minerals: Crystal structures and economic and environmental  
361 significance, *Proc. Natl. Acad. Sci. USA* 96 (1999), 3447–3454.
- 362 [33] A. Mukherjee, A.M. Raichur, K.A. Natarajan, J.M. Modak, Recent developments in  
363 processing ocean manganese nodules – A critical review, *Mineral Processing &*  
364 *Extractive Metall. Rev.* 25 (2004) 91–127.

- 365 [34] I. Saratovsky, P.G. Wightman, P.A. Pasten, J.F. Gaillard, K.R. Poepelmeier, Manganese  
366 oxides: Parallels between abiotic and biotic structure, *J. Am. Chem. Soc.* 128 (2006)  
367 11188–11198.
- 368 [35] G. Meinrath, P. Spitzer, Uncertainties in determination of pH, *Mikrochem. Acta* 135  
369 (2000) 155–168.
- 370 [36] R.P. Buck, S. Rondinini, A.K. Covington, F.G.K. Baucke, C.M.A. Brett, M.F. Camoes,  
371 M.J.T. Milton, T. Mussini, R. Naumann, K.W. Pratt, P. Spitzer, G.S. Wilson,  
372 Measurement of pH. Definition, standards, and procedures (IUPAC Recommendations  
373 2002), *Pure Appl. Chem.* 74 (2002) 2169–2200.
- 374 [37] A.Y. Aleksanyan, A.N. PodobaeV, I.I. Reformatskaya, Steady-state anodic dissolution of  
375 iron in neutral and close-to-neutral media, *Protection of Metals* 43 (2007) 66–69.
- 376 [38] S. Nestic, Key issues related to modelling of internal corrosion of oil and gas pipelines –  
377 A review, *Corros. Sci.* 49 (2007) 4308–4338.
- 378 [39] C. Noubactep, The fundamental mechanism of aqueous contaminant removal by metallic  
379 iron, *Water SA* 36 (2010) 663–670.
- 380 [40] C. Noubactep, Aqueous contaminant removal by metallic iron: Is the paradigm shifting?  
381 *Water SA* 37 (2011) 419–426.
- 382 [41] G.W. Whitman, R.P. Russel, V.J. Altieri, Effect of hydrogen-ion concentration on the  
383 submerged corrosion of steel, *Indust. Eng. Chem.* 16 (1924) 665–670.
- 384 [42] L.-Y. Chang, Alternative chromium reduction and heavy metal precipitation methods for  
385 industrial wastewater, *Environ. Prog.* 22 (2003) 174–182.
- 386 [43] L.-Y. Chang, Chromate reduction in wastewater at different pH levels using thin iron  
387 wires - A laboratory study. *Environ. Prog.* 24 (2005) 305–316.



- 388 [44] M. Gheju, I. Balcu, Removal of chromium from Cr(VI) polluted wastewaters by  
389 reduction with scrap iron and subsequent precipitation of resulted cations. *J. Hazard.*  
390 *Mater.* (2011), doi:10.1016/j.jhazmat.2011.09.002.
- 391 [45] D.E. Giles, M. Mohapatra, T.B. Issa, S. Anand, P. Singh, Iron and aluminium based  
392 adsorption strategies for removing arsenic fromwater, *J. Environ. Manage.* 92 (2011)  
393 3011–3022.
- 394 [46] P. Schmuki, From Bacon to barriers: a review on the passivity of metals and alloys, *J.*  
395 *Solid State Electrochem.* 6 (2002) 145–164.
- 396 [47] T. Pan, A.C.T. van Duin, Passivation of steel surface: An atomistic modeling approach  
397 aided with X-ray analyses, *Mater. Lett.* 65 (2011) 3223–3226.
- 398 [48] T. Pan, Quantum chemistry-based study of iron oxidation at the iron–water interface: An  
399 X-ray analysis aided study, *Chem. Phys. Lett.* 511 (2011) 315–321.
- 400 [49] D. Postma, C.A.J. Appelo, Reduction of Mn-oxides by ferrous iron in a flow system:  
401 column experiment and reactive transport modelling, *Geochim. Cosmochim. Acta* 64  
402 (2000) 1237–1247.
- 403 [50] C. Noubactep, S. Caré, Designing laboratory metallic iron columns for better result  
404 comparability, *J. Hazard. Mater.* 189 (2011) 809–813.

405

406

406 **Table 1:** Some characteristics of iron, manganese and the six tested metals. R is the  
 407 empirically element covalent radius (in picometers - pm) after Slater [30]. M (g/mol) is the  
 408 element atomic mass. DO is the degree of oxidation. The used DO is bold-marked and  
 409 underlined.  $C_0$  is the element initial concentration in  $\mu\text{M}$  and mg/L (ppm). It is seen that for  
 410 the same molar concentration (100  $\mu\text{M}$ ) the mass concentration varies from 5.2 ppm for Cr to  
 411 23.8 ppm for U.  $C_{0,\text{eff}}$  is the operational initial concentration for the experiment at pH 6.0 (see  
 412 text). The most likely species of tested element at pH 6.0 to 9.0 is given [29].

413

<b>X</b>	<b>R</b>	<b>M</b>	<b>DO</b>	$C_0$	$C_0$	$C_{0,\text{eff}}$	Speciation
	(pm)	(g/mol)	(-)	( $\mu\text{M}$ )	(mg/L)	( $\mu\text{M}$ )	(-)
Cr	140	51.996	III, <b><u>VI</u></b>	100	5.2	98.9	$\text{HCrO}_4^-$
Cu	135	63.546	<b><u>II</u></b>	100	6.4	86.8	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
Fe	140	55.847	<b><u>0</u></b> , II, III	0.0	0.0	0.0	-
Mn	140	54.938	II, III, <b><u>VI</u></b>	0.0	0.0	0.0	-
Mo	145	95.94	IV, <b><u>VI</u></b>	100	9.6	98.5	$\text{MoO}_4^{2-}$
Sb	145	121.75	III, <b><u>V</u></b>	100	12.2	72.1	$\text{Sb}(\text{OH})_6^-$
U	175	238.029	IV, <b><u>VI</u></b>	100	23.8	79.2	$[\text{UO}_2(\text{CO}_3)_3]^{4-}$
Zn	135	65.38	<b><u>II</u></b>	100	6.5	87.3	$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

414

415

415 **Table 2:** Comparison of the extent of metal removal (in %) in the “Fe<sup>0</sup> + sand” and “Fe<sup>0</sup> +  
 416 MnO<sub>2</sub>” systems after 1 and 2 months. C<sub>0</sub> is the operational initial concentration (see text). Δ is  
 417 the different of the removal extent after 1 month and 2 months.

418

419

Element	C <sub>0</sub> (μM)	Fe <sup>0</sup> + sand			Fe <sup>0</sup> + MnO <sub>2</sub>		
		1 month	2 months	Δ <sub>1,2</sub>	1 month	2 months	Δ' <sub>1,2</sub>
Cr	98.9	98.5	98.9	0.4	98.1	99.4	1.3
Cu	86.8	93.7	96.4	2.7	83.1	91.3	8.3
Mo	98.5	70.0	83.7	13.7	60.3	74.7	14.4
Sb	72.1	92.8	95.2	2.4	77.1	93.4	16.3
U	79.2	96.2	97.1	0.9	72.2	83.2	11.0
Zn	87.3	92.9	96.7	3.8	79.8	94.3	14.5

420

421

421 **Table 3:** Impact of MnO<sub>2</sub> on the extent of metal removal by Fe<sup>0</sup>.  $\delta_i$  is the difference between  
 422 the extent of metal removal in system “Fe<sup>0</sup> + MnO<sub>2</sub>” (P'<sub>i</sub>) and “Fe<sup>0</sup> + sand” (P<sub>i</sub>) after i months  
 423 ( $\delta_i = P'_i - P_i$ ).  $\Delta' = \delta_2 - \delta_1$ .

424

Element	Fe <sup>0</sup> + sand		Fe <sup>0</sup> + MnO <sub>2</sub>		$\delta_1$	$\delta_2$	$\Delta'$
	P <sub>1</sub>	P <sub>2</sub>	P' <sub>1</sub>	P' <sub>2</sub>	(%)	(%)	(%)
Cr	98.5	98.9	98.1	99.4	-0.4	0.4	0.8
Cu	93.7	96.4	83.1	91.3	-10.6	-5.1	5.5
Mo	70.0	83.7	60.3	74.7	-9.7	-9.0	0.7
Sb	92.8	95.2	77.1	93.4	-15.8	-1.8	13.9
U	96.2	97.1	72.2	83.2	-24.0	-13.9	10.1
Zn	92.9	96.7	79.8	94.3	-13.1	-2.4	10.7

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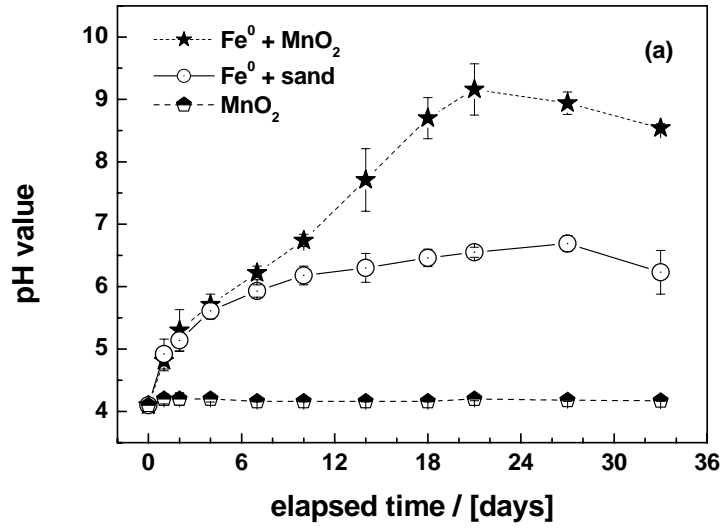
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427 **Figure 1**

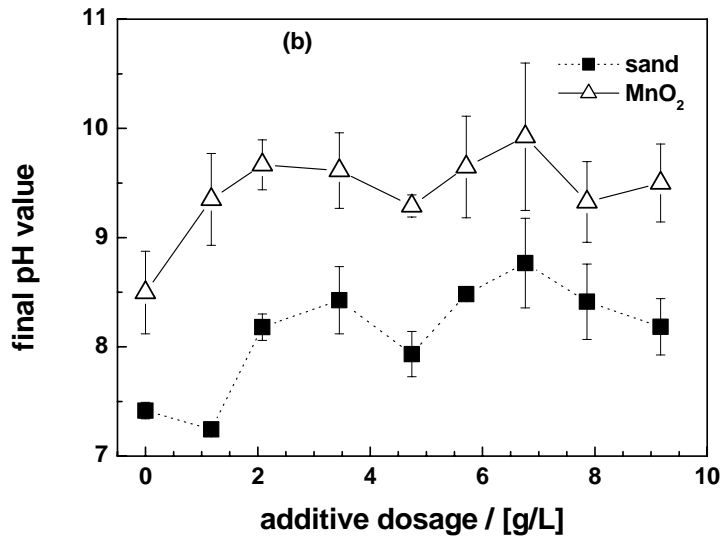
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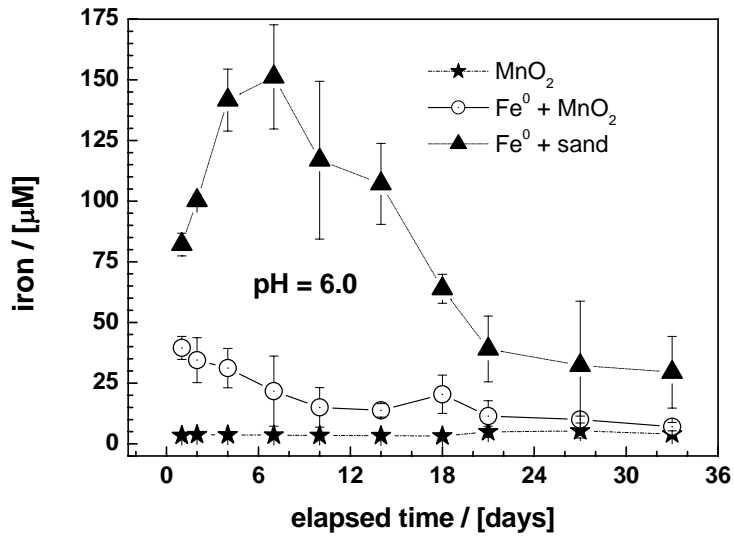
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436 **Figure 2**

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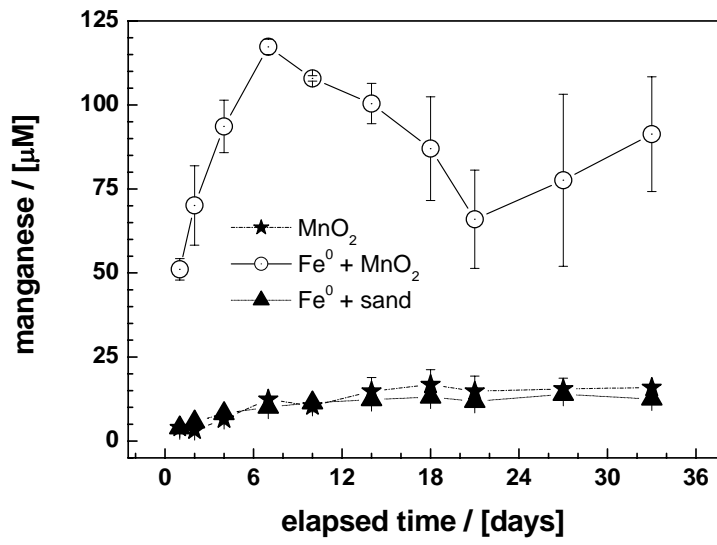


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439 **Figure 3**

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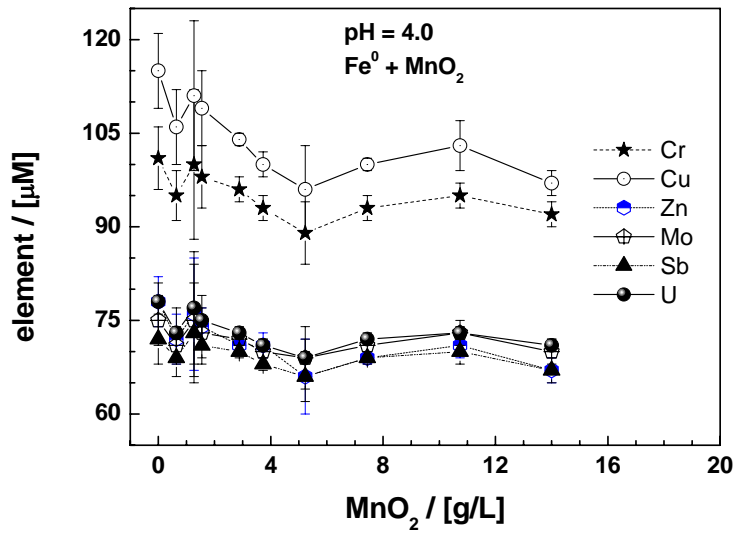


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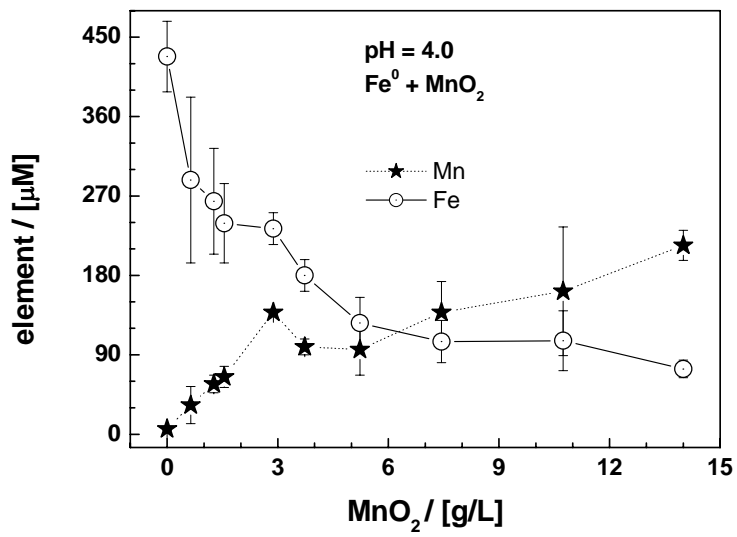
442 **Figure 4**

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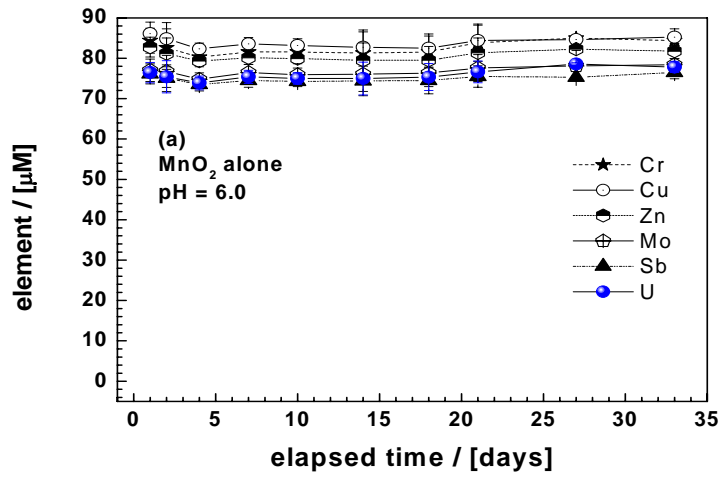
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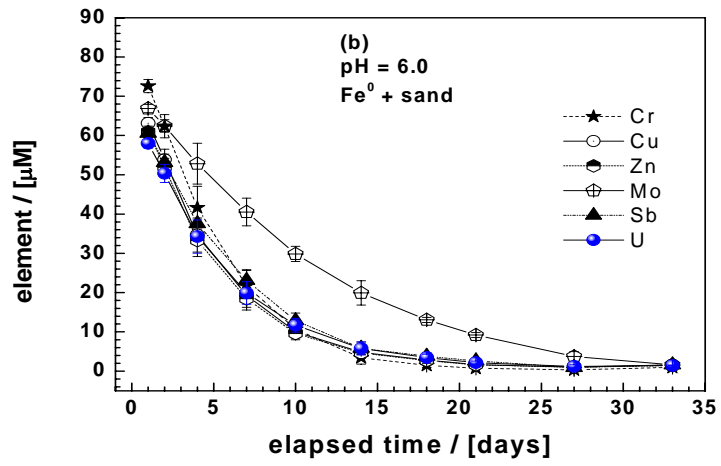
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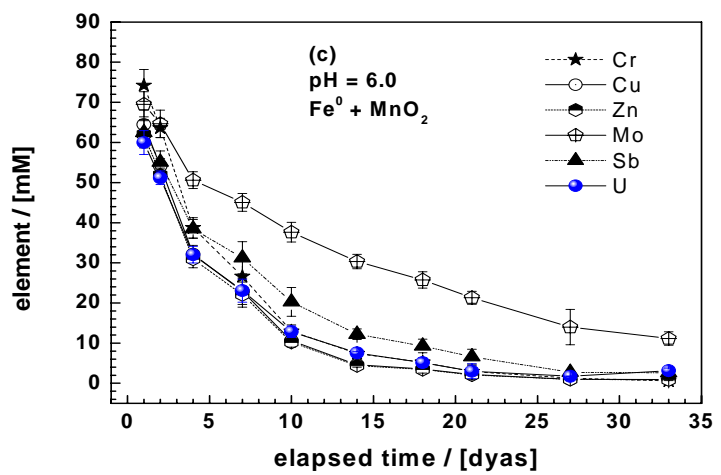
448 **Figure 5**



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### Figure Captions

453 **Figure 1:** Variation of the pH value in the investigated systems. (a) time-dependant evolution  
454 for the first 33 days, and (b) variation with additive loading after 60 days. The used Fe<sup>0</sup> and  
455 additive (MnO<sub>2</sub> or sand) loadings are 5.0 and 2.5 g/L respectively. The lines simply connect  
456 points to facilitate visualization.

457

458 **Figure 2:** Time-dependant evolution of the iron concentration for the first 33 days in the  
459 experiments at pH 6.0 with the three investigated systems. The used Fe<sup>0</sup> and additive (MnO<sub>2</sub>  
460 or sand) loadings are 5.0 and 2.5 g/L respectively. The lines simply connect points to facilitate  
461 visualization.

462

463 **Figure 3:** Time-dependant evolution of the manganese concentration for the first 33 days in  
464 the experiments at pH 6.0 with the three investigated systems. The used Fe<sup>0</sup> and additive  
465 (MnO<sub>2</sub> or sand) loadings are 5.0 and 2.5 g/L respectively. The lines simply connect points to  
466 facilitate visualization. The lines simply connect points to facilitate visualization.

467

468 **Figure 4:** Evolution of the concentration of dissolved metals as function of the additive mass  
469 loading for the experiment with “Fe<sup>0</sup> + MnO<sub>2</sub>” and pH 4.0 as initial value: (a) aqueous metal  
470 removal, and (b) metal removal from Fe<sup>0</sup> and MnO<sub>2</sub>. The used Fe<sup>0</sup> mass loading is 5.0 g/L.  
471 The lines simply connect points to facilitate visualization.

472

473 **Figure 5:** Time-dependant evolution of the concentration of dissolved metals for the  
474 experiment with pH 6.0 as initial value: (a) system “MnO<sub>2</sub> alone”, (b) “Fe<sup>0</sup> + sand” and (c)  
475 “Fe<sup>0</sup> + MnO<sub>2</sub>”. The used Fe<sup>0</sup> and additive (MnO<sub>2</sub> or sand) loadings are 5.0 and 2.5 g/L  
476 respectively. The lines simply connect points to facilitate visualization.