

1 Comments on “**Sorption of triazoles to soil and iron minerals**” by Y. Jia et al.
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4 C. Noubactep

5 Angewandte Geologie, Universität Göttingen, Goldschmidtstraße 3, D - 37077 Göttingen,
6 Germany.

7 e-mail: cnoubac@gwdg.de; Tel. +49 551 39 3191, Fax: +49 551 399379

8

9 **Abstract**

10 This letter suggests possible improvements on the discussion of the adsorptive removal of
11 triazoles by iron minerals which are possible corrosion products of elemental iron materials
12 (Fe^0) in a recent article by Y. Jia and his co-workers. Also recalled is the importance of the
13 adsorption of organics by iron corrosion products which is not properly addressed in the iron
14 technology literature when the contaminants are redox-sensitive.

15

16 **Keywords:** Adsorption; Elemental Iron; Iron Corrosion; Iron Oxhydroxides; Triazoles.

17

18 **Introduction**

19 In a recent article entitled “Sorption of triazoles to soil and iron minerals” Jia and his
20 coworkers (2007) discussed the adsorption of triazoles to soil, iron minerals and elemental
21 iron (Fe^0 or zerovalent iron) in order to better understand the fate and transport of these highly
22 mobile and recalcitrant compounds in the subsurface. For this purpose benzotriazole (BTA)
23 and methylbenzotriazole (MeBTA) were used as model contaminants. Among other results,
24 Jia et al. (2007) found out: (i) negligible MeBTA adsorption onto Fe_2O_3 ; (ii) considerable
25 MeBTA adsorption onto ferrihydrites; (iii) strong BTA and MeBTA adsorption onto
26 elemental iron (Fe^0). It was concluded that using elemental iron permeable reactive barriers

27 can be an effective technology to mitigate the migration of highly mobile triazoles in the
28 subsurface.

29 The present communication aims at (i) optimising the discussion of the mechanism of
30 triazoles removal by elemental iron materials based on the chemistry of iron corrosion and (ii)
31 discussing the consequence of the results of Jia et al. (2007) for the reactive wall technology.

32

33 **Concerning the Mechanism of Triazoles Removal by Elemental Iron**

34 Jia et al. (2007) mostly considered elemental iron (Fe^0) in their discussion as pure adsorbent
35 although they observed Fe^0 oxidation for experimental duration > 48 h. This basic assumption
36 led to the conclusion that adsorption to Fe^0 seems to be controlled by multi-layer coverage.
37 The time dependence of contaminant removal is not shown. It could have been interesting to
38 discuss whether there is a relation between iron oxidation ($t > 48$ h) and increased
39 contaminant removal. Even though triazoles are iron corrosion inhibitors (Yao et al., 2003), a
40 100 % inhibition can not be awaited. Jia et al. (2007) implicitly recognized that triazoles will
41 not stop iron corrosion in suggesting Fe^0 materials as reactive media for the mitigation of
42 triazoles migration at contaminated sites. However, the dynamic nature of the process of iron
43 corrosion is not properly addressed. The suggested multi-layer Fe^0 surface coverage is not
44 consistent with the progression of Fe^0 oxidation.

45 Table 1 gives a general overview of reactants pertinent to contaminant removal in the
46 presence of ferrihydrite, hematite, magnetite and metallic iron. For the discussion of the
47 results of Jia et al. (2007), redox processes (here reduction) should be ignored because
48 investigated triazoles are not redox-sensitive. From table 1 it can be seen that beside
49 ferrihydrite, hematite and magnetite several other adsorbents may exist in the $\text{Fe}^0\text{-H}_2\text{O}$
50 system (Roh et al., 2000, Schmuki 2002). Iron oxhydroxides are progressively generated in
51 $\text{Fe}^0\text{-H}_2\text{O}$ system. In all other systems on the contrary, the total amount of adsorbent is present
52 at the start of the experiment. Assuming for simplicity that no mineral dissolution occurs, the

53 $\text{Fe}^0\text{-H}_2\text{O}$ system is the single system with varying adsorbent amounts. The in-situ generation
54 of adsorbents alone is a strong argument for strong triazoles adsorption in the $\text{Fe}^0\text{-H}_2\text{O}$
55 system. The adsorptive characteristics of the individual iron oxides depends mostly on three
56 factors (Anderson and Benjamin 1985, Axe and Trivedi 2002, Cornell and Schwertmann
57 2003, Coughlin and Stone 1995, Martin 2005): (i) specific surface area (abundance of binding
58 sites), (ii) porosity and pore size distribution (accessibility of binding sites), and (iii)
59 crystallinity (reactivity of binding sites). As metastable minerals amorphous iron oxides are
60 transformed to more stable crystalline forms upon ageing. The ageing process is known to be
61 retarded by adsorption of inorganic and organic species (Axe and Trivedi 2002 and references
62 therein). As a result, hydrous amorphous iron oxides are persistent in $\text{Fe}^0\text{-H}_2\text{O}$ systems.
63 Consequently, the reactivity of the $\text{Fe}^0\text{-H}_2\text{O}$ system is variable and depends on the relative
64 abundance of amorphous iron oxides. The aging process for high porous amorphous
65 oxyhydroxides is usually accompanied by dehydration and conversion to a less porous
66 structure. For example, Anderson and Benjamin (1985) reported a typical specific surface
67 area of $500 \text{ m}^2/\text{g}$ for fresh generated ferrihydrites and only $30\text{-}50 \text{ m}^2/\text{g}$ for goethite. It can be
68 anticipated that in the initial stage of Fe^0 corrosion pertinent to the experimental conditions of
69 Jia et al. (2007), high amounts of high porous amorphous iron oxides (e.g. ferrihydrites) are
70 generated and was responsible for the observed removal efficiency of Fe^0 materials.
71 The discussed evolution in the reactivity of iron corrosion products with increasing stability
72 (ferrihydrites \gg hematite and magnetite) by Jia et al. (2007) is consistent with the
73 observations from table 1. Therefore, under the experimental conditions of Jia et al. (2007),
74 triazoles may have been mostly removed by iron corrosion products and not by multi-layer
75 adsorption onto the bare Fe^0 surface. While the Fe^0 specific surface area is known (or can be
76 determined) and is certainly determinant for the materials reactivity (e.g. Johnson et al. 1996),
77 it should not be used in discussing the results of triazoles removal. The reactive transient
78 states (table 1) that certainly play an important role in the process of triazoles removal are

79 difficult to characterize (porosity, surface area, crystallinity) and their characteristics change
80 with increasing experimental duration. These transient states also acts as adsorbents for
81 primary corrosion products (Fe^{II} , H/H_2). The adsorption of Fe^{II} on mineral surfaces yields
82 structural Fe^{II} ($\text{Fe}^{\text{II}}_{(\text{s})}$, table 1) which is a stronger reducing agent than aqueous Fe^{II} (White and
83 Peterson 1996).

84 Porous and amorphous transient state corrosion products adsorb contaminant strongly
85 (relative high binding strength) and can entrapped them in their matrix during their
86 agglomeration (coprecipitation) or their crystallisation (Crawford et al., 1993; Füredi-
87 Milhofer, 1981). The distinction between adsorption and coprecipitation is not always clear.
88 Contaminant adsorption processes can occur whenever a solid substrate surface (iron
89 corrosion products) is present. That is the solid substrate is pre-formed prior to addition of the
90 contaminant to be removed from solution. Coprecipitation processes are subtly different to
91 adsorption processes. In the case of coprecipitation the solid substrate is formed in the
92 presence of the contaminant to be removed from solution (Crawford et al., 1993). In a
93 dynamic Fe^0 - H_2O system, some contaminant molecules will be adsorbed on already available
94 stable corrosion products (hematite or magnetite) while some others will co-precipitated with
95 transient states (ferrihydrites, green rusts...).

96 Few studies directly compare the efficiency of adsorption and coprecipitation processes
97 (Crawford et al., 1993 and references therein), it is believed that coprecipitation will enhance
98 the removal efficiency to a greater extent than that of simple adsorption. This further
99 enhancement either could be due to a greater binding strength for a co-precipitate surface
100 (having multiple surface site types) over a simple precipitate surface (having a single surface
101 type) or may simply be due to an effective increase in surface area for adsorption as colloidal
102 particles are formed (Crawford et al., 1993). The results of Jia et al. (2007) support this belief.
103 Moreover, the increased adsorption of triazoles by Fe^0 is more likely due to the combination
104 of adsorption and coprecipitation by in-situ generated and ageing corrosion products.

105 A Fe⁰-H₂O system may be considered as a complex mixture of adsorptive species of different
106 reactivity. The overall reactivity of the system for a given contaminant depends on the
107 properties of the contaminants and the relative proportion of high reactive species in the
108 system. For instance, in the early stage of the iron wall life, the proportion of porous
109 amorphous oxyhydroxides is high and the contaminant removal capacity of the system is high.
110 Depending on the geochemical conditions, the reactivity may decrease with time as suggested
111 by Jia et al. (2007) or may progress to a pseudo steady state, for example if a groundwater
112 contains high level of species as Cl⁻ for instance that may sustain iron corrosion (Kim et al.,
113 2007).

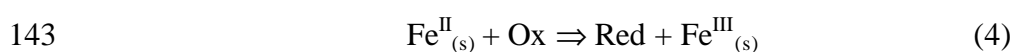
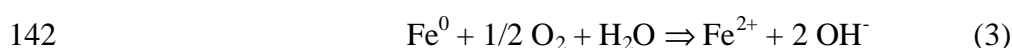
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115 **Importance of Organics Adsorption in Fe⁰-H₂O Systems**

116 The results of Jia et al. (2007) are thought-provoking impulses for the importance of the
117 adsorption (and coprecipitation) as independent organic contaminant (organics) removal
118 mechanism in Fe⁰-H₂O systems. In fact, when organic are redox-sensitive, it is generally
119 considered that, under anoxic conditions, the oxide-film on Fe⁰ acts as electron-shuttle
120 (Johnson et al., 1998; Scherer et al., 1999) to mediate contaminant reduction through
121 electrons from the bulk metal (direct reduction). This assumption is of purely thermodynamic
122 origin as it is based on the low redox potential of the couple Fe^{II}/Fe⁰ (Matheson and Tratnyek
123 1994). The validity of the premise of direct contaminant reduction has not been demonstrated
124 (Noubactep 2007a). The situation is exacerbated by the use of non-appropriated experimental
125 conditions (Noubactep 2007b, 2007c).

126 Although redox reactions in the oxide-film are known (Battaglia and Newman, 1995;
127 Stratmann and Müller, 1994) and have been shown to contribute to the contaminant removal
128 in Fe⁰-H₂O systems (Mielczarski et al., 2005), even recent works addressing the role of
129 oxide-film on the process of contaminant reduction implicitly neglect the importance of
130 indirect reduction, e.g. through structural Fe^{II}. In fact, Matheson and Tratnyek (1994)

131 proposed three pathways of reduction of chlorinated hydrocarbons (reductants: Fe⁰, Fe^{II} and
132 H₂). Using 4-aminoazobenzene as probe molecule, Weber (1996) reported that Fe⁰ surface
133 plays a decisive role in the reduction process and is responsible for observed high reduction
134 rate. Elemental iron was then used for the direct reduction of numerous organic pollutants
135 (Mielczarski et al., 2005 and references therein). For all of these pollutants a reduction
136 reactions similar to reaction (1) is assumed. Clearly, uniquely the reduction reaction with Fe⁰
137 as electron donor (Eq. 1) is usually written/given together with the oxidation of iron through
138 water (Eq. 2) or through dissolved oxygen (Eq. 3). However, Fe^{II}-species may act as
139 reductants (Eq. 4) and the reaction may be thermodynamically more favourable than Eq. 1.



144 Where Ox is the oxidized form of the contaminant and red its reduced form.

145 White and Peterson (1996) found that the half-cell potential of the solid state system Fe^{III}/Fe^{II}
146 ranges from -0.34 to -0.65 V making structural Fe^{II} in some circumstances (E_H < -0.44 V) a
147 more stronger reductant than Fe⁰ (-0.44 V). The additional fact that Fe^{II}_(s) is more accessible
148 to contaminants than the underlying Fe⁰ surface is a strong argument for possible quantitative
149 indirect reduction in Fe⁰-H₂O systems.

150 The fact that Fe⁰ is always covered by an oxide-film which is not necessarily electronic
151 conductive and that indirect reduction may be more favourable than direct reduction suggests
152 that direct reduction (Eq. 1) is not necessarily the major contaminant reduction pathway even
153 under anoxic conditions. Furthermore, the work of Jia et al. (2007) reiterates that iron oxides
154 are good adsorbents also for organics (Brown et al. 1999, Martin 2005, Vikesland et al. 2007).
155 Thus, redox-insensitive organic contaminants are successfully removed in Fe⁰-H₂O systems
156 by pure adsorption (and subsequent precipitation). Therefore, there is no reason to assume

157 that redox sensitive organics should quantitatively be reduced in such systems by direct
158 reduction. Moreover, observed reduction may be the results of indirect reduction (reduction
159 by secondary reductants) or microbial activity. Clearly, the well-established premise, that
160 redox-sensitive organic contaminants are reduced in $\text{Fe}^0\text{-H}_2\text{O}$ systems by electrons from the
161 bulk Fe^0 (Eq. 1) is instable. This statement is additionally supported by data from Stratmann
162 and Müller (1994) showing clearly that nearly Fe^{II} free oxide-films completely loosed their
163 ability to reduce molecular oxygen, suggesting that Fe^{II} species and not Fe^0 may be the
164 primary reductants in $\text{Fe}^0\text{-H}_2\text{O}$ systems. This suggestion is supported to some extend by the
165 results of Huang and Zhang (2005) showing that the addition of external Fe^{II} to a $\text{Fe}^0\text{-H}_2\text{O}$
166 system enhances nitrate reduction.

167

168 **Conclusions**

169 The work of Jia et al. (2007) and the discussion above unequivocally reiterate that iron
170 oxihydroxides (iron corrosion products) are strong adsorbents for organic contaminants
171 (Brown et al., 1999, Vikesland et al., 2007). This evidence suggests that contaminant are
172 primarily removed from $\text{Fe}^0\text{-H}_2\text{O}$ systems through adsorption and coprecipitation. Whether a
173 subsequent reduction occurs or not depends on the local geochemical conditions, in particular
174 on the characteristics of the generated oxide-film (conductivity, porosity, mineralogical
175 composition, thickness) and the availability of secondary reductants ($\text{Fe}^{\text{II}}/\text{H}_2$) within the film.
176 With other words, the well-established premise of direct quantitative contaminant reduction in
177 $\text{Fe}^0\text{-H}_2\text{O}$ systems (Eq. 1) is instable.

178 There are at least four reasons showing that the role of corrosion products in the process of
179 contaminant removal in $\text{Fe}^0\text{-H}_2\text{O}$ systems is not always properly addressed: (i) investigations
180 have been and are currently performed with acid pre-treated Fe^0 materials; (ii) complexing
181 agents (e.g. EDTA) are commonly used to avoid the formation of corrosion products and
182 enable surface accessibility, (iii) direct reduction is assumed as major contaminant pathway

183 for redox sensitive species, and (iv) the normalization of experimental results are often related
184 to the Fe^0 specific surface area (e.g. k_{SA}). As discussed here on the light of the work of Jia et
185 al. (2007) contaminant adsorption onto corrosion products is the primary stage of the removal
186 process in Fe^0 - H_2O systems.

187 The present communication reiterates that: (i) contaminant adsorption onto corrosion products
188 and reduction are not each other exclusive, (ii) contaminant reduction do not necessarily occur
189 by electrons from Fe^0 (direct reduction), and (iii) adsorbed contaminants are not necessarily
190 further reduced. These conclusions are supported by (i) the well-known adsorptive properties
191 of iron oxides (Brown et al., 1999, Cornell and Schwertmann 2003, Vikesland et al., 2007),
192 (ii) the reported quantitative removal of electrochemically non-reducible species like zinc
193 (Ludwig and Jekel, 2007) in Fe^0 - H_2O systems. Even biological agents are removed from
194 aqueous phases in Fe^0 - H_2O systems (You et al., 2005).

195

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271

271 **Table 1:** Overview of reactants pertinent to aqueous contaminant removal in the presence of
 272 ferrihydrite ($\text{Fe}_5\text{O}_3(\text{OH})_9$), hematite (Fe_2O_3), magnetite (Fe_3O_4) and metallic iron
 273 (Fe^0). The possible contaminant removal mechanisms are given. The generation of
 274 corrosion products is a dynamic process in the course of which contaminant can be
 275 entrapped in the mass of precipitating/ageing iron oxyhydroxides (coprecipitation).
 276 In the Fe^0 - H_2O system, Fe^0 is considered as primary reductant whereas H/H_2 , $\text{Fe}^{\text{II}}_{(\text{aq})}$
 277 and $\text{Fe}^{\text{II}}_{(\text{s})}$ are secondary reductants. Therefore, secondary reductants are primary
 278 iron corrosion products (H_2 and Fe^{II}).

279

system	reactants	primary	secondary	reactivity
		mechanism	mechanism	
$\text{Fe}_5\text{O}_3(\text{OH})_9$-$\text{H}_2\text{O}$	$\text{Fe}_5\text{O}_3(\text{OH})_9$	adsorption	-	constant
Fe_2O_3-H_2O	Fe_2O_3	adsorption	-	constant
Fe_3O_4-H_2O	Fe_3O_4	adsorption	-	constant
	Fe^0 , H/H_2 , $\text{Fe}^{\text{II}}_{(\text{aq})}$, $\text{Fe}^{\text{II}}_{(\text{s})}$,	reduction	-	
Fe^0-H_2O	$\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, Fe_2O_3 , Fe_3O_4 ,	adsorption	coprecipitation	variable
	FeOOH , $\text{Fe}_5\text{O}_3(\text{OH})_9$, green rusts.	adsorption	coprecipitation	

280