

1 Comments on “**Removal of thiobencarb in aqueous solution by zero valent iron**” by Md.
2 Nurul Amin et al. [Chemosphere 70 (2008) 511–515].

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9 **Introduction**

10 In a recent article entitled “Removal of thiobencarb in aqueous solution by zero valent iron”,
11 Nurul Amin and his coworkers (2008) reported the development of a cost-effective method
12 for the purification of thiobencarb-contaminated water (agricultural wastewaters) using
13 powdered elemental iron (zerovalent iron or Fe^0). For this purpose 10 mL of a 10 mg L^{-1}
14 thiobencarb (TB) solution was allowed to react with 0.05 to 2 g powdered Fe^0 [$d \leq 150 \mu\text{m}$,
15 specific surface area (SSA) = $7.0 \text{ m}^2 \text{ g}^{-1}$] at 25 °C for 1 to 24 h. Some experiments were
16 conducted with elemental magnesium and elemental zinc. As result 10 mg L^{-1} TB could be
17 almost completely removed from 10 mL solution by 0.1 g Fe^0 (mass loading: 10 g L^{-1}). TB
18 removal was accompanied by chloride ion release to the aqueous solution suggesting that
19 reduction and adsorption are the two processes responsible for TB removal.

20 The study of Nurul Amin et al. (2008) is very informative to researchers interested in the field
21 of iron technology as it relates the state-of-the-art of the technology. However, the article
22 contains areas where improvements could be made that will be discussed below.

23

24 **Removal Efficiency with Fe^0 , Mg^0 , and Zn^0**

25 Nurul Amin et al. (2008) presented the results of TB removal by Fe^0 , Mg^0 and Zn^0 as
26 summarised in Table 1 without any further discussion. Assuming that Mg^0 and Zn^0 were of

27 comparative particle size and purity like Fe^0 , these results suggest that TB reduction by Fe^0
28 (direct reduction, see below) may not be the major removal mechanism in the Fe^0 - H_2O
29 system. In fact, on the reduction-potential scale, Mg^0 and Zn^0 are more susceptible to
30 oxidation than Fe^0 (Table 1). Data from the synthetic organic chemistry support this
31 conclusion.

32
33 Elemental metals are traditionally used in the synthetic organic chemistry as reductive agents,
34 for example for the transformation of aromatic nitro compounds to their corresponding
35 aromatic amines. The most classic and practical reductants are zinc (Zn^0 ; $E^0 = -0.76 \text{ V}$), tin
36 (Sn^0 ; $E^0 = -0.14 \text{ V}$), or iron (Fe^0 ; $E^0 = -0.44 \text{ V}$) in the presence of an acid (Boix and Poliakoff,
37 1999; Wang et al., 2003). The reactions are performed in organic solvents or in the presence
38 of acids, which pose waste-handling problems (Wang et al., 2003). Quantitative aqueous
39 reduction reactions are only possible at elevated temperatures. For example Boix and
40 Poliakoff (1999) reported a selective reduction of nitroarenes to anilines using Zn^0 in water at
41 $250 \text{ }^\circ\text{C}$ (near-critical water) in high yields, but only 10% yield of aniline was observed from
42 the reduction of nitrobenzene using Fe^0 under the reaction conditions. The reactivity of Zn^0 is
43 superior to that Fe^0 , while metallic iron is non-toxic, cheap and commercially available. To
44 perform the reduction of nitro compounds to amines with iron powder, the reaction should be
45 carried out at higher temperature ($> 250 \text{ }^\circ\text{C}$) owing to the low reactivity of iron metal (Wang
46 et al., 2003).

47
48 Clearly, aqueous reduction reactions that are quantitative with Zn^0 at a given temperature
49 should exhibit a lower yield with Fe^0 under the same conditions. Under the experimental
50 conditions of Nurul Amin et al. (2008), the yield of TB removal by Zn^0 was 13%. This result
51 suggests that the observed quantitative TB removal (100%) in the Fe^0 - H_2O system is due to at

52 least 90% of removal agents (including reductants) other than the available amount of Fe^0 at
53 the surface of the used Fe^0 materials. These processes are inherent to iron corrosion.

54

55 From open literature on metal corrosion, it is well-known that the corrosion behaviour of a
56 metal is not a direct reflect of its standard electrode potential (E^0 value; Bojic et al., 2007 and
57 references therein). The protectiveness of the oxide layers formed on the individual metals is a
58 key factor in this regard. Iron has been shown to exhibit the tendency of forming oxide layers
59 which are not adherent to metallic iron. Therefore, generated oxide layers constantly flake off
60 and expose fresh iron surface for attack (Dickerson et al., 1979; Campbell, 1990).
61 Consequently, processes responsible for increased TB removal in the $\text{Fe}^0\text{-H}_2\text{O}$ system are
62 coupled with progressive iron corrosion. In this regard TB may be (i) reduced by Fe^0 (*direct*
63 *reduction*) or secondary reductants like Fe^{II} , H/H_2 (*indirect reduction*), (ii) adsorbed onto
64 already generated corrosion products (*adsorption*) or (iii) co-precipitated with nascent or
65 recrystallizing corrosion products (*co-precipitation*). Note that, if TB is reduced in the
66 aqueous phase, the products of the reaction may equally adsorb onto or co-precipitate with
67 corrosion products. In considering solely direct reduction and adsorption, Nurul Amin et al.
68 (2008) have overseen indirect reduction and co-precipitation. Contaminant co-precipitation
69 through corrosion products has been shown to be the primary removal mechanism in $\text{Fe}^0\text{-H}_2\text{O}$
70 systems (Noubactep, 2007). Note that chloride ions from TB reduction may co-precipitate
71 with iron corrosion products. Therefore, regarding the absence of Cl^- in the aqueous solution
72 as indication for TB adsorption is questionable.

73

74 **Rationale for Experimental Conditions**

75 First of all, the used Fe^0 mass loadings varied from 5 to 200 g L^{-1} , corresponding to available
76 surface areas varying from 0.35 to 14 m^2 (in 10 mL solution). As the cross-section of
77 individual TB molecules is not given, the reader can not imagine whether the available

78 surface area in each reaction bottle is sufficient to realize “stoichiometric” degradation
79 (monolayer coverage of the Fe⁰ material). Ebie et al. (2001) have shown effective activated
80 carbon adsorption of TB in pores of size below 15 Å. Considering TB as a rigid sphere with a
81 radius of 7.5 Å (one half of 15 Å), the total surface occupied by the amount of TB in 10 mL
82 solution is calculated as 0.413 m² (Jia et al., 2007). This surface is purchased by 0.06 g of the
83 used Fe⁰ material (SSA = 7 m² g⁻¹). Therefore, using a mass loading of 6 g L⁻¹ would have
84 been sufficient for a “stoichiometric” TB degradation. These calculations show clearly that in
85 the majority of reported experiments, Nurul Amin et al. (2008) used large excess of Fe⁰. On
86 the other site, the molar ratio Fe⁰/TB varies from 2279 to 91150 (assuming 92% Fe in the
87 used Fe⁰ material). Therefore, the conclusion of Nurul Amin et al. (2008) that “1 kg of iron
88 powder can be applied to the treatment of 100 L TB-contaminated water with 10 µg mL⁻¹
89 concentration” (1g TB per kg Fe⁰ or 1 mg g⁻¹) may be speculated if only the numbers of
90 treatment batch systems are increased. The possibility of large scale plant is not supported by
91 any scientific criterion. Furthermore the presented “simple, easy handling and convenient
92 method with iron metal” is not compared with available technologies for TB removal such as
93 the use of activated carbon adsorption. A good decolourising activated carbon should fulfil at
94 least 200 mg g⁻¹ removal capacity for methylene for example (Attia et al., 2008 and references
95 therein). Therefore, although the present work is very informative to researchers interested in
96 the field of iron remediation technology, it is questionable whether the proposed method is
97 really affordable (1 mg g⁻¹).

98
99 The second point concerns the chosen experimental duration (treatment time). Most of the
100 experiments have been performed with a Fe⁰ mass loading of 10 g L⁻¹ for 1 to 24 h. The
101 mixing intensity is not specified. It is obvious that the extent of TB removal dictates the
102 treatment time. Figure 1 summarizes the effect of iron surface area (m²) on the TB removal
103 efficiency. It can be seen that for Fe⁰ surface area ≥ 0.7 m² (0.1 g Fe⁰) the removal efficiency

104 is larger than 97%. Therefore, it is questionable why results with essentially larger Fe^0 surface
105 areas (up to 14 m^2) are reported. Furthermore, for a purposeful discussion of the reaction
106 mechanism experiments with less Fe^0 or smaller mixing intensities could have been
107 advantageous to access the region of sharply removal efficiencies (first 3 h). The monitoring
108 of the chloride ion generation in such systems could also enable a better discussion of the
109 extent of TB reduction as relative little amount of corrosion products is available to interfere
110 with generated Cl^- . Under shaken conditions iron corrosion, and thus corrosion products
111 precipitation is accelerated. Cl^- , TB, and TB reduction products are certainly entrapped in the
112 matrix of co-precipitating iron oxides. Therefore, the absence of Cl^- in the solution is by no
113 means a hint for contaminant adsorption, as suggested by Nurul Amin et al. (2008). Since the
114 iron mass loading, the mixing intensity and the treatment time are not independent variables,
115 the mixing intensity should always be specified to enable comparison with other published
116 data.

117

118 **Conclusions**

119 Nurul Amin et al. (2008) certainly showed the capacity of Fe^0 to quantitatively remove TB
120 from aqueous solutions (e.g., agricultural wastewaters in general). However, their
121 experimental conditions may not be pertinent to enable traceable conclusions. Because the
122 formulated criticisms are valid for the majority of works dealing with the process of
123 contaminant removal in Fe^0 - H_2O systems, an unified procedure for the investigation of
124 processes in Fe^0 - H_2O systems is needed.

125

126 The discussion above also shows that the well-established premise that contaminants are
127 removed from the Fe^0 - H_2O systems under field and laboratory conditions ($T \leq 35 \text{ }^\circ\text{C}$) by
128 direct reduction is partly a contradiction of good data from synthetic organic chemistry.

129 Therefore, a close investigation of the processes of contaminant removal in $\text{Fe}^0\text{-H}_2\text{O}$ systems
130 is necessary to access the long-term stability of removed contaminants.

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156

157 **Table 1:** Characteristics of elemental metals and their percent removal of thiobencarb (P)

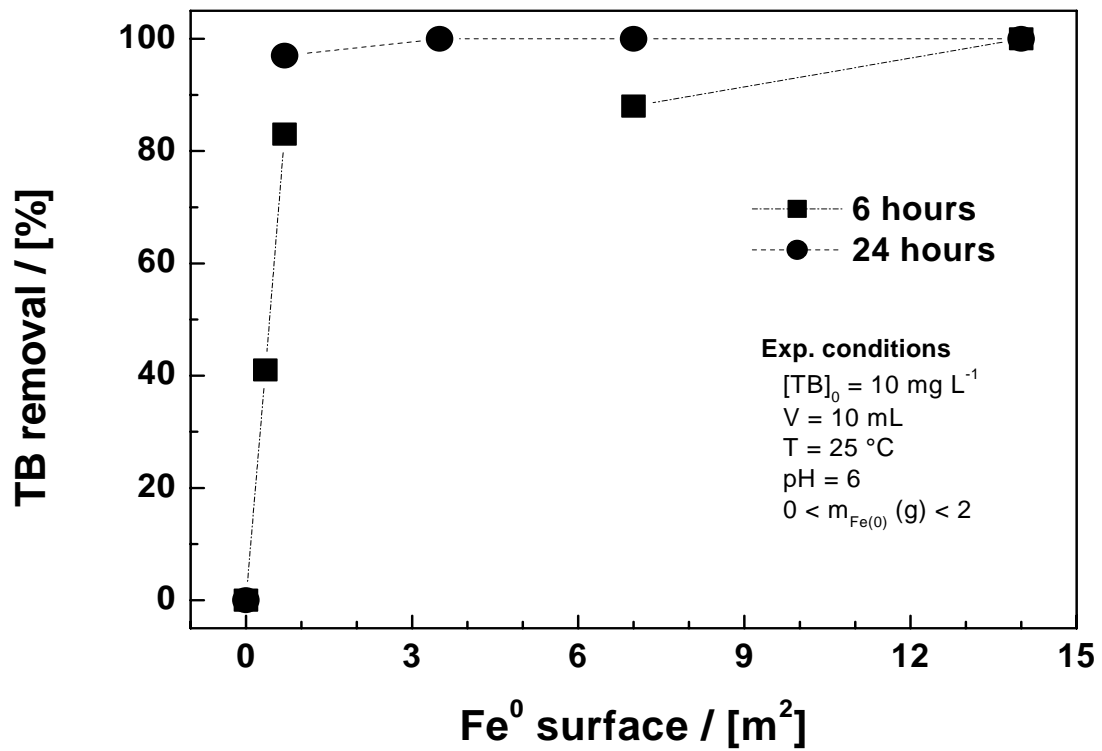
158 from aqueous solution. n.s.= not specified.

159

Material	E°	d	S	P
	(V)	(μm)	($\text{m}^2 \text{g}^{-1}$)	(%)
Mg^0	-2.2	n.s.	n.s.	60
Zn^0	-0.76	n.s.	n.s.	13
Fe^0	-0.44	< 150	7.0	100

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161



162 **Figure 1:** The effect of iron surface area (m²) on the thiobencarb (TB) removal efficiency
 163 from the aqueous solution. Data from Table 1 in Nurul Amin et al. (2008). The lines are not
 164 fitting functions, they simply connect points to facilitate visualization.
 165