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

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

Removal Efficiency with Fe$^0$, Mg$^0$, and Zn$^0$
Nurul Amin et al. (2008) presented the results of TB removal by Fe$^0$, Mg$^0$ and Zn$^0$ as summarised in Table 1 without any further discussion. Assuming that Mg$^0$ and Zn$^0$ were of
comparative particle size and purity like Fe\(_0\), these results suggest that TB reduction by Fe\(_0\) (direct reduction, see below) may not be the major removal mechanism in the Fe\(_0\)-H\(_2\)O system. In fact, on the reduction-potential scale, Mg\(_0\) and Zn\(_0\) are more susceptible to oxidation than Fe\(_0\) (Table 1). Data from the synthetic organic chemistry support this conclusion.

Elemental metals are traditionally used in the synthetic organic chemistry as reductive agents, for example for the transformation of aromatic nitro compounds to their corresponding aromatic amines. The most classic and practical reductants are zinc (Zn\(_0\); E\(_0\) = -0.76 V), tin (Sn\(_0\); E\(_0\) = -0.14 V), or iron (Fe\(_0\); E\(_0\) = -0.44 V) in the presence of an acid (Boix and Poliakoff, 1999; Wang et al., 2003). The reactions are performed in organic solvents or in the presence of acids, which pose waste-handling problems (Wang et al., 2003). Quantitative aqueous reduction reactions are only possible at elevated temperatures. For example Boix and Poliakoff (1999) reported a selective reduction of nitroarenes to anilines using Zn\(_0\) in water at 250 °C (near-critical water) in high yields, but only 10% yield of aniline was observed from the reduction of nitrobenzene using Fe\(_0\) under the reaction conditions. The reactivity of Zn\(_0\) is superior to that Fe\(_0\), while metallic iron is non-toxic, cheap and commercially available. To perform the reduction of nitro compounds to amines with iron powder, the reaction should be carried out at higher temperature (> 250 °C) owing to the low reactivity of iron metal (Wang et al., 2003).

Clearly, aqueous reduction reactions that are quantitative with Zn\(_0\) at a given temperature should exhibit a lower yield with Fe\(_0\) under the same conditions. Under the experimental conditions of Nurul Amin et al. (2008), the yield of TB removal by Zn\(_0\) was 13%. This result suggests that the observed quantitative TB removal (100%) in the Fe\(_0\)-H\(_2\)O system is due to at
least 90% of removal agents (including reductants) other than the available amount of Fe$^0$ at
the surface of the used Fe$^0$ materials. These processes are inherent to iron corrosion.

From open literature on metal corrosion, it is well-known that the corrosion behaviour of a
metal is not a direct reflect of its standard electrode potential (E$^0$ value; Bojic et al., 2007 and
references therein). The protectiveness of the oxide layers formed on the individual metals is a
key factor in this regard. Iron has been shown to exhibit the tendency of forming oxide layers
which are not adherent to metallic iron. Therefore, generated oxide layers constantly flake off
and expose fresh iron surface for attack (Dickerson et al., 1979; Campbell, 1990).

Consequently, processes responsible for increased TB removal in the Fe$^0$-H$_2$O system are
coupled with progressive iron corrosion. In this regard TB may be (i) reduced by Fe$^0$ (direct
reduction) or secondary reductants like Fe$^{II}$, H/H$_2$ (indirect reduction), (ii) adsorbed onto
already generated corrosion products (adsorption) or (iii) co-precipitated with nascent or
recrystallizing corrosion products (co-precipitation). Note that, if TB is reduced in the
aqueous phase, the products of the reaction may equally adsorb onto or co-precipitate with
corrosion products. In considering solely direct reduction and adsorption, Nurul Amin et al.
(2008) have overseen indirect reduction and co-precipitation. Contaminant co-precipitation
through corrosion products has been shown to be the primary removal mechanism in Fe$^0$-H$_2$O
systems (Noubactep, 2007). Note that chloride ions from TB reduction may co-precipitate
with iron corrosion products. Therefore, regarding the absence of Cl$^-$ in the aqueous solution
as indication for TB adsorption is questionable.

Rationale for Experimental Conditions

First of all, the used Fe$^0$ mass loadings varied from 5 to 200 g L$^{-1}$, corresponding to available
surface areas varying from 0.35 to 14 m$^2$ (in 10 mL solution). As the cross-section of
individual TB molecules is not given, the reader can not imagine whether the available
surface area in each reaction bottle is sufficient to realize “stoichiometric” degradation (monolayer coverage of the Fe\(^0\) material). Ebie et al. (2001) have shown effective activated carbon adsorption of TB in pores of size below 15 Å. Considering TB as a rigid sphere with a radius of 7.5 Å (one half of 15 Å), the total surface occupied by the amount of TB in 10 mL solution is calculated as 0.413 m\(^2\) (Jia et al., 2007). This surface is purchased by 0.06 g of the used Fe\(^0\) material (SSA = 7 m\(^2\) g\(^{-1}\)). Therefore, using a mass loading of 6 g L\(^{-1}\) would have been sufficient for a “stoichiometric” TB degradation. These calculations show clearly that in the majority of reported experiments, Nurul Amin et al. (2008) used large excess of Fe\(^0\). On the other site, the molar ratio Fe\(^0\)/TB varies from 2279 to 91150 (assuming 92% Fe in the used Fe\(^0\) material). Therefore, the conclusion of Nurul Amin et al. (2008) that “1 kg of iron powder can be applied to the treatment of 100 L TB-contaminated water with 10 μg mL\(^{-1}\) concentration” (1g TB per kg Fe\(^0\) or 1 mg g\(^{-1}\)) may be speculated if only the numbers of treatment batch systems are increased. The possibility of large scale plant is not supported by any scientific criterion. Furthermore the presented “simple, easy handling and convenient method with iron metal” is not compared with available technologies for TB removal such as the use of activated carbon adsorption. A good decolourising activated carbon should fulfil at least 200 mg g\(^{-1}\) removal capacity for methylene for example (Attia et al., 2008 and references therein). Therefore, although the present work is very informative to researchers interested in the field of iron remediation technology, it is questionable whether the proposed method is really affordable (1 mg g\(^{-1}\)).

The second point concerns the chosen experimental duration (treatment time). Most of the experiments have been performed with a Fe\(^0\) mass loading of 10 g L\(^{-1}\) for 1 to 24 h. The mixing intensity is not specified. It is obvious that the extent of TB removal dictates the treatment time. Figure 1 summarizes the effect of iron surface area (m\(^2\)) on the TB removal efficiency. It can be seen that for Fe\(^0\) surface area ≥ 0.7 m\(^2\) (0.1 g Fe\(^0\)) the removal efficiency
is larger than 97%. Therefore, it is questionable why results with essentially larger Fe$^0$ surface areas (up to 14 m$^2$) are reported. Furthermore, for a purposeful discussion of the reaction mechanism experiments with less Fe$^0$ or smaller mixing intensities could have been advantageous to access the region of sharply removal efficiencies (first 3 h). The monitoring of the chloride ion generation in such systems could also enable a better discussion of the extent of TB reduction as relative little amount of corrosion products is available to interfere with generated Cl$^-$. Under shaken conditions iron corrosion, and thus corrosion products precipitation is accelerated. Cl$^-$, TB, and TB reduction products are certainly entrapped in the matrix of co-precipitating iron oxides. Therefore, the absence of Cl$^-$ in the solution is by no means a hint for contaminant adsorption, as suggested by Nurul Amin et al. (2008). Since the iron mass loading, the mixing intensity and the treatment time are not independent variables, the mixing intensity should always be specified to enable comparison with other published data.

**Conclusions**

Nurul Amin et al. (2008) certainly showed the capacity of Fe$^0$ to quantitatively remove TB from aqueous solutions (e.g., agricultural wastewaters in general). However, their experimental conditions may not be pertinent to enable traceable conclusions. Because the formulated criticisms are valid for the majority of works dealing with the process of contaminant removal in Fe$^0$-H$_2$O systems, an unified procedure for the investigation of processes in Fe$^0$-H$_2$O systems is needed.

The discussion above also shows that the well-established premise that contaminants are removed from the Fe$^0$-H$_2$O systems under field and laboratory conditions (T ≤ 35 °C) by direct reduction is partly a contradiction of good data from synthetic organic chemistry.
Therefore, a close investigation of the processes of contaminant removal in Fe\(^0\)-H\(_2\)O systems is necessary to access the long-term stability of removed contaminants.

References


**Table 1**: Characteristics of elemental metals and their percent removal of thiobencarb (P) from aqueous solution. n.s.= not specified.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E^\circ$ (V)</th>
<th>d (μm)</th>
<th>S ($m^2 g^{-1}$)</th>
<th>P (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^0$</td>
<td>-2.2</td>
<td>n.s.</td>
<td>n.s.</td>
<td>60</td>
</tr>
<tr>
<td>Zn$^0$</td>
<td>-0.76</td>
<td>n.s.</td>
<td>n.s.</td>
<td>13</td>
</tr>
<tr>
<td>Fe$^0$</td>
<td>-0.44</td>
<td>&lt; 150</td>
<td>7.0</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 1: The effect of iron surface area (m$^2$) on the thiobencarb (TB) removal efficiency from the aqueous solution. Data from Table 1 in Nurul Amin et al. (2008). The lines are not fitting functions, they simply connect points to facilitate visualization.