

1 **Comment on "Oxidative degradation of organic compounds using zero-valent iron in**  
2 **the presence of natural organic matter serving as an electron shuttle"**

3 C. Noubactep

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

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

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7 In a recent study, Kang and Choi (1) investigated the oxidative degradation of 4-chlorophenol  
8 (4-CP) and clofibric acid (CA) by metallic iron ( $\text{Fe}^0$ ) as promoted by natural organic matters  
9 acting as electron shuttle to mediate electron transfer from the surface of  $\text{Fe}^0$  to dissolved  $\text{O}_2$ .  
10 Their results indicated that both humic acid (HA) and fulvic acid (FA) can serve as electron  
11 shuttle, while enhancing the production of  $\text{Fe}^{\text{II}}$  and  $\text{H}_2\text{O}_2$  that subsequently initiates the OH  
12 radical mediated oxidation of 4-CP and CA through Fenton reaction. However, there is strong  
13 evidence that the conclusion of Kang and Choi are not supported by own experimental data.

14 First, the work of Kang and Choi (1) is based on the premise that  $\text{Fe}^0$ -induced contaminant  
15 removal is "initiated by the direct electron transfer from  $\text{Fe}^0$  to substrates". This premise was  
16 already questioned or/and proven inconsistent (2, 3). In fact, organic substances (4-CP and  
17 CA) are primarily sequestered in the matrix of in-situ generated iron corrosion products and  
18 may be further reduced and or oxidized by several mechanisms. On the other hand the HA  
19 and FA can only act as electron shuttle only if the oxide-film on  $\text{Fe}^0$  is conductive (e.g.  $\text{Fe}_3\text{O}_4$   
20 – ref. 4) or rendered conductive by sequestered electron shuttle (including HA and FA).  
21 However, an electronic conductive oxide film can not be expected as the rule when the  
22 oxidant is  $\text{O}_2$ , because the quantitative oxidation to  $\text{Fe}^{\text{III}}$  species is thermodynamically  
23 favourable at non acidic pH. Note that the experiments of Kang and Choi (1) are performed at  
24 an initial pH of 2.5, suggesting that depending on the extend of  $\text{Fe}^0$  consumption (final pH  
25 value),  $\text{Fe}^{\text{II}}$  may be stable in the course of the experiment but quantitative  $\text{Fe}^{\text{III}}$  production will  
26 occur with increasing pH (5).

27 Second, the system  $\text{Fe}^0/\text{H}_2\text{O}/\text{O}_2$  and the impact of electron shuttle on it has been extensively  
28 investigated in the aeration step of the *Becher Process* (ref. 4 and references therein). The  
29 *Becher process* is an environmentally friendly, cost-effective extraction method for upgrading  
30 ilmenite ( $\text{FeTiO}_3$ ) to synthetic rutile (SR: 94 %  $\text{TiO}_2$ ). The aeration step involves agitating the  
31 reduced ilmenite (RI) in a  $\text{NH}_4\text{Cl}$  solution while air is sparged through the pulp. The metallic  
32 iron in the RI is dissolved as  $\text{Fe}^{2+}$  which is then oxidised to a variety of  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$   
33 oxide/hydroxides during the aeration reaction. The efficiency of the aeration step is limited in  
34 that there is little control over the types of iron oxides that are formed. To improve the  
35 efficiency of the aeration step, the use of various catalysts has been examined. A class of  
36 redox catalysts, based on anthraquinone derivatives was identified as being very effective. It  
37 could be shown that the addition of these reagents was able to halve reaction times without  
38 influencing the quality of the SR, and to guarantee the formation of the preferred conductive  
39 iron oxide ( $\text{Fe}_3\text{O}_4$ ) product. With other words, the system investigated by Kang and Choi (1)  
40 is not new, they should have used well-documented results from hydrometallurgy to discuss  
41 contaminant removal (and degradation).

42 Third, the chloride ion ( $\text{Cl}^-$ ) production is used to support degradation pathway (vs.  
43 adsorption). However, the results of Kang and Choi (1) showed significant differences in the  
44 kinetic and the extend of  $\text{Cl}^-$  production in the presence of HA and FA (figure 1a and 1c –  
45 only for review) but no difference in the kinetics of organic compounds removal  
46 (“degradation”). If  $\text{Cl}^-$  production was really coupled to 4-CP (or CA) degradation, the  
47 difference in the kinetics of  $\text{Cl}^-$  production should be reflected in the kinetics of contaminant  
48 degradation.

49 Fourth, Kang and Choi (1) performed their experiments with a starting pH value of 2.5 and  
50 did not record pH evolution during their experiments. Because the system was not buffered, it  
51 is likely the discussed differential behaviour in the presence of HA and FA are due to their  
52 differential impact on the pH of the system. While working at an initial pH value of 2.5, Kang

53 and Choi (1) compared their results to those of Tratnyek et al. (6) for instance. Tratnyek et al.  
54 (6) performed all their experiments in buffer systems at pH values > 5.6. Therefore,  
55 “conflicting” results are expected as the experimental conditions are largely different.  
56 Moreover, it is difficult to presage which natural systems are mimicked by Kang and Choi (1)  
57 with and initial pH value of 2.5.

58 In conclusion the work of Kang and Choi (1) is an illustration of the quality of published  
59 works on the topic of “remediation with Fe<sup>0</sup>” in so many peer-reviewed scientific journals.  
60 Are member of the Fe<sup>0</sup> remediation community matured enough to admit the evidence (or the  
61 possibility) that their work has followed a wrong direction, since the seminal works of  
62 Matheson and Tratnyek (7) and Weber (8)? This maturity is the premise to rectify the made  
63 errors and quickly achieve progresses in understanding this proven effective technology.  
64 Beside the inconsistent premise on the mechanism of contaminant removal in Fe<sup>0</sup>/H<sub>2</sub>O  
65 systems, it is evident that neither available results from hydrometallurgy nor the complex pH  
66 dependence behaviour of iron species (reactivity of oxides, solubility of individual species)  
67 were properly considered by Kang and Choi (1). Furthermore, a proper analysis of  
68 investigated system is missed: the rationale for the used pH is not given and the evolution of  
69 the pH during the experiment is not considered in the discussion.

70 Considering the nature of the problem, it can be presumed that some environmental scientists  
71 are overwhelmed with understanding the subtlety and scientific diversity of the physical and  
72 chemical processes which are involved in iron oxidative dissolution (iron corrosion)  
73 depending on their background. To solve this problem a unified experimental procedure for  
74 contaminant removal experiments should be introduced. This is a problem which cannot be  
75 resolved by a few research groups. The developed experimental procedure should be  
76 presented in public panels.

77 **Literature Cited**

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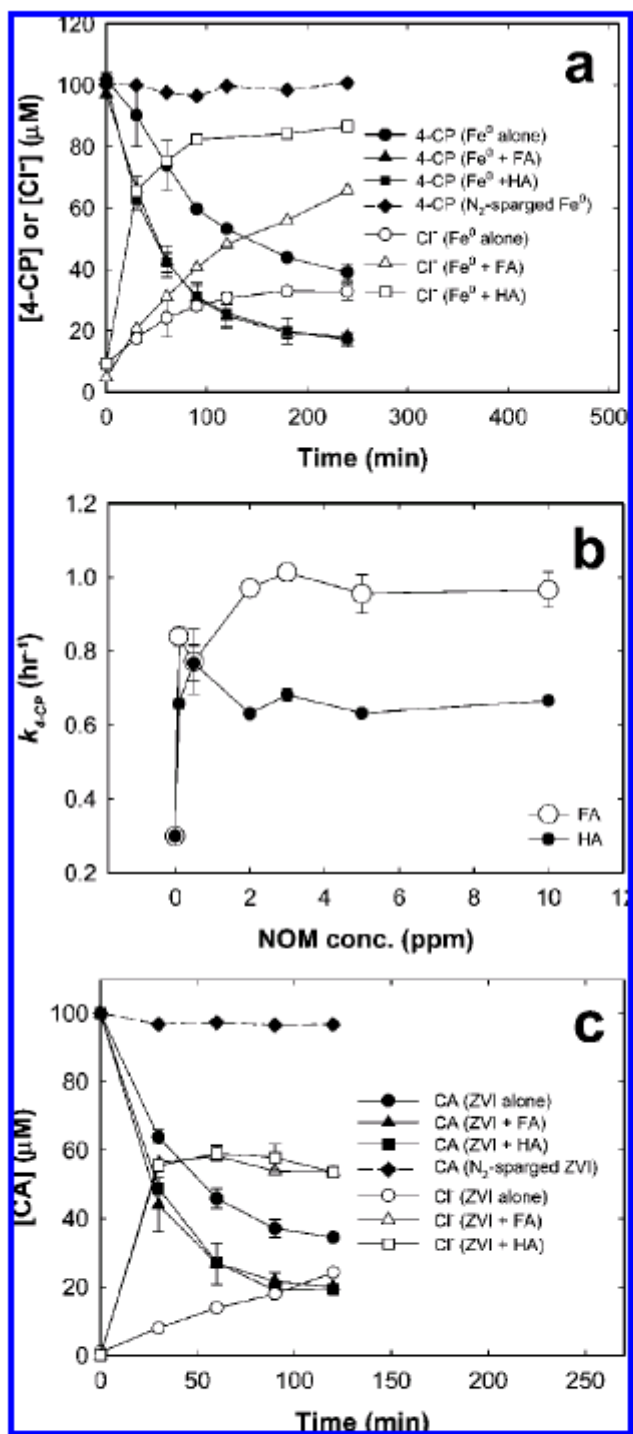


FIGURE 1. (a) Degradation of 4-CP and Cl<sup>-</sup> production in ZVI slurry in the presence or absence of 0.5 ppm HA (or 0.5 ppm FA). (b) Effect of the concentration of HA and FA on the degradation rate of 4-CP. (c) Degradation of clofibric acid (CA) and Cl<sup>-</sup> production in ZVI slurry in the presence or absence of 0.5 ppm HA (or 0.5 ppm FA). Other reaction conditions: [ZVI] = 1.0 g/L; [4-CP]<sub>0</sub> = 100 μM; [CA]<sub>0</sub> = 100 μM; pH<sub>i</sub> = 2.5.