

# Comments on “Reuse of Semiconductor Wastewater Using Reverse Osmosis and Metal-Immobilized Catalyst-Based Advanced Oxidation Process”

Frank-Dieter Kopinke\* and Anett Georgi

Helmholtz-Centre for Environmental Research—UFZ, Department of Environmental Engineering, D-04318 Leipzig, Germany

Sir: Recently, Choi and Chung published a research paper in this journal entitled “Reuse of Semiconductor Wastewater Using Reverse Osmosis and Metal-Immobilized Catalyst-Based Advanced Oxidation Process”.<sup>1</sup> This paper addressed a relevant issue in water treatment technologies and proposed an effective hybrid process that allows recycling of semiconductor wastewater. The core of this is an advanced oxidation process (AOP) that is based on an Fe-loaded activated carbon (AC) catalyst that activates H<sub>2</sub>O<sub>2</sub> in a Fenton-like manner. The function of this solid-phase AOP system was studied in detail in the laboratory and at the pilot scale. Its main function is a decrease of the total organic carbon (TOC) content of the treated water while using H<sub>2</sub>O<sub>2</sub> very efficiently as an oxidant. The optimization of this AOP led to the conclusion “that the optimal ratio of H<sub>2</sub>O<sub>2</sub> concentration to influent TOC concentration was 1.5”. H<sub>2</sub>O<sub>2</sub> concentrations higher than ~500 µg/L gave rise to a lower efficiency of the TOC removal.

We have serious doubts about these conclusions and the interpretation of the presented results. These doubts are based on simple stoichiometric calculations and are briefly outlined as follows. The authors claim that ~70% of the 100 µg/L TOC in the influent water can be removed by adding ~100 µg/L H<sub>2</sub>O<sub>2</sub> (see Figure 4a in the original paper<sup>1</sup>). According to the classical Fenton stoichiometry  $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH}\cdot + \text{OH}^- + \text{Fe}^{3+}$  and assuming that the formed OH radicals are the dominant oxidants ( $\text{OH}\cdot + \text{e}^- \rightarrow \text{OH}^-$ ), 1 mol of H<sub>2</sub>O<sub>2</sub> can withdraw 1 mol of electrons from the target compounds. Next, one needs to know how many electrons must be transferred in order to mineralize the wastewater TOC. Unfortunately, the chemical composition of the TOC fraction is not known in detail (see Table 3 in the original work<sup>1</sup>). The formal oxidation number of carbon ( $n_{\text{C}}$ ) in the TOC fraction can vary between  $n_{\text{C}} = -4$  (methane) to  $n_{\text{C}} = +3$  (oxalic acid), more commonly between  $n_{\text{C}} = -2$  (methanol) to  $n_{\text{C}} = +2$  (formic acid). Using the TOC and chemical oxygen demand (COD) data given in chapter 3.1 in the original paper<sup>1</sup> for a typical semiconductor wastewater (1.67 mg/L C and 5.33 mg/L O), and assuming that the COD is mainly caused by the organic fraction, an average oxidation number of  $n_{\text{C}} \approx -0.8$  can be expected. This seems to be a reasonable estimate, corresponding to that of acetaldehyde ( $n_{\text{C}} = -1.0$ ) as an “average” TOC component. In order to mineralize acetaldehyde, five electrons per carbon atom must be withdrawn ( $\text{C}_2\text{H}_4\text{O} + 10 \text{ OH}\cdot \rightarrow 2 \text{ CO}_2 + 7 \text{ H}_2\text{O}$ ). This needs 10 molecules of H<sub>2</sub>O<sub>2</sub> per molecule of acetaldehyde, corresponding to a mass ratio of H<sub>2</sub>O<sub>2</sub>:TOC =  $(10 \times 34):(2 \times 12) = 14.2$  g/g. This is approximately the 10-fold mass ratio, compared to the optimal value derived in the study of Choi and Chung.<sup>1</sup>

The actual demand for H<sub>2</sub>O<sub>2</sub> can be expected to be much higher, because of the fact that only a fraction of H<sub>2</sub>O<sub>2</sub> is decomposed, according to the Fenton stoichiometry, and only a small fraction of the generated OH radicals is used for oxidation of the target compounds.<sup>2,3</sup> A large portion will be quenched by reactions with the surface of the AC. As an example, Huling et al.<sup>4</sup> regenerated AC loaded with 0.02 wt % of methyl *tert*-butyl ether (MTBE) with a similar Fenton system. They achieved a 90% MTBE destruction after application of 3000–6000 g of H<sub>2</sub>O<sub>2</sub> per gram of decomposed (not mineralized) MTBE. This oxidation efficiency is 3–4 orders of magnitude lower than that derived by Choi and Chung from their results.<sup>1</sup>

The degree of OH radical utilization is expected to be smaller at lower concentrations of the target compounds in the water (TOC) and, consequently, lower loadings of the AC. A TOC concentration of 100 µg/L can be considered to be a very low target concentration. Hence, the chances for its efficient oxidation in competition with the carbon surface are even worse.

One could argue that some contaminants will be only partially oxidized in the proposed solid-phase AOP reactor. This would be sufficient to explain their removal from the treated water, and thus it would not be justified to calculate with high electron transfer numbers. However, the TOC concentration as a key parameter does not distinguish between less-oxidized organics and highly oxidized organics. It only distinguishes between organic carbon and inorganic carbon, the latter being CO<sub>2</sub> or carbonate ( $n_{\text{C}} = +4$ ), whose formation requires mineralization of the target compounds.

The removal of organic contaminants by means of a catalytically active AC bed is usually performed by means of a combination of sorption and chemical reactions. The study of Choi and Chung<sup>1</sup> does not mention any blank experiments (e.g., without H<sub>2</sub>O<sub>2</sub> feeding) or data that allow us to distinguish between the two processes or even to quantify their contributions. Nevertheless, it might be useful to consider the behavior of some individual TOC components, which are summarized in Table 3 in the original paper by Choi and Chung.<sup>1</sup> Some of them are removed completely; other compounds run through the catalyst bed. Let us consider two examples in more detail: (1) chloroform is removed completely, and (2) acetaldehyde runs through the reactor. Looking at the characteristic sorption and reactivity properties of these two compounds, it becomes obvious that chloroform is a better candidate for sorption ( $K_{\text{OW, chloroform}}/K_{\text{OW, acetaldehyde}} \approx 30$ ),<sup>5</sup> whereas acetaldehyde is more easily oxidized

Published: November 19, 2014

( $k_{\text{OH,acetaldehyde}}/k_{\text{OH,chloroform}} \approx 150$ ).<sup>6</sup>  $K_{\text{OW},i}$  is the octanol–water partition coefficient as a measure of the hydrophobicity of compound  $i$  and  $k_{\text{OH},i}$  is the second-order rate coefficient for the attack of OH radicals on these compounds, according to  $\text{OH}\cdot + i \rightarrow \text{products}$ . It is obvious that the presented examples do favor sorption as an explanation, rather than oxidation, as the dominant removal process—at least for some of the TOC components.

One could argue that the sorption capacity of an AC bed is not sufficient to explain the observed removal efficiencies ( $\sim 70\%$  up to 180 d) under long-term conditions, as presented in Figure 6a in the original paper.<sup>1</sup> The breakthrough time of a sorbent bed can be approximated by means of the formula

$$t_{\text{breakthrough}} = \frac{K_F \times C_{\text{influent}}^{1/(n-1)}}{\text{SV}}$$

where  $K_F$  is the Freundlich sorption coefficient,  $1/n$  the Freundlich exponent,  $C_{\text{influent}}$  the sorbate influent concentration, and SV the space velocity (expressed in terms of  $\text{h}^{-1}$ ) of the water flow (given in units of  $\text{m}^3/\text{h}$ ) through the sorbent bed (given in units of  $\text{m}^3$ ). Assuming reasonable values for the various parameters, including  $\text{SV} = 6 \text{ h}^{-1}$ , as applied in the study, this predicts a breakthrough time on the order of  $10^4$ – $10^6 \text{ h}$ , which is longer than the observation time applied in the study of Choi and Chung<sup>1</sup> ( $180 \text{ d} \approx 10^{3.6} \text{ h}$ ). Consequently, sorption cannot be excluded as the dominant contaminant removal process under the applied conditions. The long lifetime of the sorbent filter is simply due to the very low TOC concentration in the influent water ( $10^{-7} \text{ kg/L}$ ).

In summary, we have reasonable doubts about the efficiency of the proposed solid-phase AOP system based on Fe-doped activated carbon and the interpretation of the results published by Choi and Chung.<sup>1</sup> In particular, the claimed very high oxidation efficiency ( $m_{\text{H}_2\text{O}_2}:m_{\text{TOC}} \approx 1.5$ ) seems implausible to us and is not actually covered by the presented data. We suggest considering Fe-doped zeolites as a promising alternative to AC as a sorbent and catalyst for the oxidation of polar, low-molecular-weight wastewater constituents.<sup>7–11</sup> Zeolites have the inherent advantage of being chemically inert, even under aggressive oxidizing conditions.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: frank-dieter.kopinke@ufz.de.

### Notes

The authors declare no competing financial interest.

## REFERENCES

- (1) Choi, J.; Chung, J. Reuse of semiconductor wastewater using reverse osmosis and metal-immobilized catalyst-based advanced oxidation process. *Ind. Eng. Chem. Res.* **2014**, *53*, 11167–11175.
- (2) Huling, S. G.; Hwang, S. Iron amendment and Fenton oxidation of MTBE-spent granular activated carbon. *Water Res.* **2010**, *44*, 2663–2671.
- (3) Georgi, A.; Kopinke, F.-D. Interaction of adsorption and catalytic reactions in water decontamination processes. Part 1: Oxidation of organic contaminants with hydrogen peroxide catalyzed by activated carbon. *Appl. Catal., B* **2005**, *58*, 9–18.
- (4) Huling, S. G.; Jones, P. K.; Ela, W. P.; Arnold, R. G. Fenton-driven chemical regeneration of MTBE-spent GAC. *Water Res.* **2005**, *39*, 2145–2153.

(5) Sangster, J. *Octanol–Water Partition Coefficients: Fundamentals and Physical Chemistry*; Wiley Series in Solution Chemistry, Vol. 2; John Wiley & Sons: Chichester, U.K., 1997.

(6) NIST Chemical Kinetics Database, <http://kinetics.nist.gov/kinetics/index.jsp>.

(7) Shabazi, A.; Georgi, A.; Gonzalez-Olmos, R.; Kopinke, F.-D.; Zarabadi-Poor, P. Natural and synthetic zeolites in adsorption/oxidation processes to remove surfactant molecules from water. *Sep. Purific. Technol.* **2014**, *127*, 1–9.

(8) Gonzalez-Olmos, R.; Kopinke, F.-D.; Mackenzie, K.; Georgi, A. Hydrophobic Fe-zeolites for removal of MTBE from water: Combination of adsorption and oxidation. *Environ. Sci. Technol.* **2013**, *47*, 2353–2360.

(9) Gonzalez-Olmos, R.; Martin, M. J.; Georgi, A.; Kopinke, F.-D.; Oller, I.; Malato, S. Fe-zeolites in heterogeneous photo-Fenton processes to degrade organic compounds in water at neutral pH using solar light. *Appl. Catal., B* **2012**, *125*, 51–58.

(10) Georgi, A.; Gonzalez-Olmos, R.; Koehler, R.; Kopinke, F.-D. Fe-zeolites as catalysts for wet peroxide oxidation of organic groundwater contaminants: Mechanistic studies and applicability tests. *Sep. Sci. Technol.* **2010**, *45*, 1579–1586.

(11) Gonzalez-Olmos, R.; Roland, U.; Toufar, H.; Kopinke, F.-D.; Georgi, A. Fe-zeolites as catalysts for chemical oxidation of MTBE in water with  $\text{H}_2\text{O}_2$ . *Appl. Catal., B* **2009**, *89*, 356–364.