

Interactive comment on “Natural manganese deposits as catalyst for decomposing hydrogen peroxide” by A. H. Knol et al.

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Authors comment to Mr. K. Chon

Thank you very much for your comment. We agree that the manuscript will benefit from your comment. We propose the following corrections in the manuscript, regarding the commentary: Abstract: 1. Please use capital letters only for abbreviations and 1st letter of each sentence. We agree and propose to adjust it.

Introduction: 1. Does global warming strongly contribute to increases of organic micropollutants in surface water? Different studies predict that the amount and concentration of OMPs will increase. One of the studies (Wuijts e.a., 2013) connect the increase to global warming. From the abstract: “In all locations in the Netherlands where surface

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water is abstracted for drinking water production (abstraction points), the water quality is under pressure because of climate change. The quality of water deteriorates during dry periods of low river discharge. This is because the effect of spills from sewage water treatment plants is much larger due to less dilution of polluting substances”.

P2, line 25: We propose to add “(Wuijts e.a., 2013)”. P10, We propose to add the following reference: Wuijts, S., van der Grinten, E., Meijers, E., Bak-Eijsberg, C.I., Zwolsman, J.J.G., Impact of climate change on surface water as a resource for drinking water: From problem areas to measures, Dutch Ministry of Infrastructure and Environment, 2013.

2. A thorough literature review on removal of organic micropollutants by AOPs and a role of natural manganese as catalytic scavengers of hydrogen peroxide has to be additionally included in the introduction section.

The removal of OMPs is not the scope but the result of the manuscript. It is expected that more companies will apply AOP and in many cases it is necessary to decompose the excessive hydrogen peroxide to prevent negative effects in connected (treatment) processes. P 2, line 24: We propose to add “(Houtman, 2010)”.

P4, line 10: We propose to add: “However, (Miller e.a., 1999) reported decomposition of hydrogen peroxide in the presence of sandy material from an aquifer and riverbed. The sand was naturally coated with metal oxides, from which manganese oxide was most active. It was known that dissolved manganese in surface and groundwater deposits as natural manganese oxide compounds on grains in sand filters of drinking water treatment plants. (Merkle e.a., 1996) measured a high specific surface area of naturally coated filter material, which increase with the amount of manganese coating. Decomposing hydrogen peroxide with existing or waste filter material for will contribute to a sustainable society. As a proof of principle, 1% hydrogen peroxide solution was add to grains of a full-scale double layer sand filter of a drinking water treatment plant. Microscopic examination yielded promising results: (oxygen)bubbles were formed at

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the surface of the grains”.

P10: We propose to add: Miller, C.M., Valentine, R.L., Mechanistic studies of surface catalyzed H₂O₂ Decomposition and contaminant degradation in the presence of sand, *Wat. Res.* Vol. 33, No. 12, pp. 2805-2816, 1999.

P10: We propose to add: Merkle, P.B., Knocke, W., Gallagher, D., Junta-Rosso, J., Solberg, T., Characterizing filter media mineral coatings, *Journal AWWA*, pp. 62-72, December 1996.

P4, line 10, 11 & 12: We propose to remove: “However, it was known that dissolved manganese in surface and groundwater deposits as manganese oxide compounds on grains in sand filters. Microscopic examination yielded promising results: at pre-treatment plant, (oxygen)bubbles were formed at the surface of grains of a full-scale double layer sand filter after adding 1% hydrogen peroxide solution”.

Materials and methods: 1. Please provide more detailed information on manganese coated filter materials, such as effective surface area (m²/g), which is a key factor affecting the decomposing rates of the excessive hydrogen peroxide.

We agree that surface area is a key factor for catalytic processes. However, this material is not used before for decomposition application and no specifications about the surface area were available. We know the grain size of the catalysts. We know the specific gravity. We know the manganese content. We did not (let) determine the surface areas (by for example automated cryogenic N₂ adsorption). We recognize that as a shortcoming.

Results and discussion: 1. Did the authors conduct any experiments to investigate effects of temperature and pH on the decomposition of hydrogen peroxide by GAC and manganese coated filter materials? It is expected that these parameters also provide an strong influence on the decomposition of hydrogen peroxide.

We agree that temperature and pH are key factors in the decomposition of hydrogen

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peroxide. For GAC we showed the influence of a difference of about 10 °C in Figure 8. For manganese coated filter material we do not have these data. The pH of the treated water, rapid sand filtrate of Meuse river water, is quite stable over the year. The difference between the lowest and highest measured value is approximately 0.5 pH-units. That is the reason that pH was not a subject for investigation.

2. I would recommend the authors to divide the section 3.2 (Manganese coated filter material) into three subsections according to the major types of factors influencing the decomposition of hydrogen peroxide by manganese coated filter materials to easier for readers.

The authors agree that the manuscript will benefit by dividing section 3.2 in three sections. We propose the following subsection titles: 3.2.1: Specifications (containing: manganese content, size distribution, specific gravity). 3.2.2: Decomposition rate (containing: contact time, rate constants in down flow) 3.2.3: Mode of operation (containing: up flow operation and water temperature) The relevant text, included line 21-24, page 5, will be assigned to the three subsections.

3. The results on the role of manganese coated filter materials as a catalytic scavenger of hydrogen peroxide are insufficiently discussed and poorly compared with the literature available on the topic. P7, line 11: We propose to add: “Possibly a part of the manganese oxides in MCFgw are enclosed and did not contribute to the decomposition or the surface area of MCFsw is larger (not determined)”. P8, line 2: We propose to add: “The presence of ramsdellite, in combination of the high manganese content and small grain size, probably contributed to the high conversion rate. (Páez e.a., 2011) reported high conversion rate constants with synthesized nano-needle particals ramsdellite ($\varnothing = 10$ nm, L = 180 nm). In batch operation a conversion rate constant was measured of 0.015 s⁻¹ after addition of only 0.374 gL⁻¹ particles. The conversion rate constant of 0.015 s⁻¹ of MCFsw is in line with the reported conversion rate constant of 0.007 s⁻¹ during column experiments with sandy aquifer material with different metal deposits (Miller e.a., 1995). Manganese appeared to have the biggest contribution to

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the decomposition: by lowering the manganese content of 250 mg/kg to 60 mg/kg by dissolving manganese in acid, the conversion rate constant decreased with a factor 10”.

P 10: We propose to add: Páez, C.A., Liquet D.Y., Calberg, C., Lambert, S.D., Willems, I., Germeau, A., Pirard, J.P., Heinrichs, B., Study of photocatalytic decomposition of hydrogen peroxide over ramsdellite-MnO₂ by O₂-pressure monitoring, *Catalysis Communications* 15 (2011) 132–136. P10: We propose to add: Miller C. M. and Valentine R. L., Hydrogen peroxide decomposition and quinoline degradation in the presence of aquifer material. *Water Res.*, Volume 29, Issue 10, October 1995, 2353-2359.

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