Letter to the Editor

What are the active species in the photocatalytic disinfection of water?

Recently, Teng et al. published an article on "Edge-functionalized g-C_3N_4 nanosheets as a highly efficient metal-free photocatalyst for safe drinking water" in this journal.[1] The article describes a new photo-catalyst and its application for water disinfection on the basis of a broad portfolio of experimental and theoretical methods. This comment aims at clarifying some discrepancies in the presented kinetic data and their mechanistic interpretation.

We found that the various numbers given in the article to characterize the kinetics of the disinfection process are not consistent. The kinetics of disinfection is described by Teng et al. as extents of bacteria deactivation vs. irradiation time, e.g. ≥99.9999% after 60 min irradiation time. From these data, the authors derive "first-order disinfection rate (k) was 0.068 min^{-1}" (p. 5). On page 14, the reader finds the definition of these k-values, which are from Chick's law: $\ln(C/C_0) = -k \cdot t$. Chick's law is simply the integrated form of a general first-order kinetics rate law. In this frame k is a rate constant (or coefficient) rather than a rate, as erroneously denoted by the authors. Nevertheless, when applying Chick's law to the given kinetic data (p. 5) it results in k = -ln(0.000001) / 60 min = 0.23 min^{-1} which is a factor of 3.4 larger than the k-value derived by the authors (0.068 min^{-1}). Similar discrepancies arise for all presented kinetic data (e.g. k = 0.082 min^{-1} (on p. 13) from $\log(C/C_0) = -6$ in 45 min, Fig. 5F).

k-values were determined as "slope of the best-fitting line for the plot of $\ln(C/C_0)$ vs. t" (p. 14). It is obvious from Fig. 2 (and also from Fig. S5 and others) that $C(t)$ does not follow first-order kinetics, which should yield a straight line in semi-logarithmic coordinates $\ln(C/C_0)$ vs. t. To make evident what such a discrepancy in numbers means: calculating the extent of bacteria deactivation from k = 0.068 min^{-1} and applying a first-order kinetics results in $\log(C/C_0) = 0.068\ min^{-1} \cdot 60\ min / \ln(10) = 1.77$. In words: the estimated decrease of bacteria concentration would be less than two orders of magnitude, rather than six orders as claimed (and determined experimentally) by the authors.

To feel sufficiently informed about the content of the study, the reader is recommended to read the SI part, which comprises 39 pages and 34 figures. For

instance, Figure S11A shows the temperature course in a water sample during a typical photocatalytic disinfection experiment. The temperature increases steadily from 19 to 33°C during 60 min of irradiation. This raises questions about the meaning of rate coefficients *k* under non-isothermal conditions.

The authors designed a series of quenching experiments aiming at the identification of photo-catalytically generated ROS (reactive oxygen species) which are responsible for the bacteria deactivation. The authors detected four types of ROS ($\bullet O_2^-$, $^1O_2$, H_2O_2, and •OH). They conclude "The related scavenger-quenching experiments indicated that H_2O_2 plays the most important role in bacterial inactivation among all the ROS." (p. 6). This statement raises a number of questions. H_2O_2 is produced and accumulates steadily during irradiation up to 4 µM after 60 min (Figure S15D). It is hard to explain first-order disinfection kinetics (with respect to bacteria concentrations) when concurrently the concentration of the most active reagent (H_2O_2) is linearly rising with irradiation time. In order to prove the key role of H_2O_2 as disinfectant, it might be helpful to check it as a reactant in the absence of a photo-catalyst; however, such an experiment is missing in the study. Adding micromolar concentrations of H_2O_2 (4 µM correspond to 0.14 g H_2O_2 per m^3 water) from an external source to the water to be disinfected would then be a robust alternative to the photo-catalytic technique.

The reader might be interested in the experimental conditions applied in the various quenching experiments, in order to be able to assess the conclusions. Unfortunately, full information is neither presented in the article nor in the SI part: only incomplete information such as "The rate constant for the generation of $^1O_2$ and FFA (furfuryl alcohol) is 1.8×10^8 M^{-1} s^{-1}." is provided (p. S3).

The identification of the dominant ROS may have consequences for the applicability of the proposed disinfection method: the efficiency of a H_2O_2-based disinfection is adversely affected by the availability of catalase in a microbial consortium. *Escherichia coli* (as well as *Salmonella D6 and Enterococcus faecalis*, Fig. S6) may not be representative of bacteria with a high catalase activity, which is, however, typical for many aerobic bacteria. If H_2O_2 is actually the key disinfectant, the presence of catalase activity could significantly decrease the disinfection performance of the presented photo-catalytic method.

Frank-Dieter Kopinke and Hauke Harms

Helmholtz Centre for Environmental Research - UFZ, Leipzig D-04318, Germany

Departments of Environmental Engineering and Environmental Microbiology

E-mail: frank-dieter.kopinke@ufz.de, hauke.harms@ufz.de

REFERENCES

1. Teng, Z., Yang, N., Lv, H., Wang, S., Hu, M., Wang, C., Wang, D., Wang, G. (2019). Edge-functionalized g-C3N4 nanosheets as a highly efficient metal-free photocatalyst for safe drinking water. *Chem 5*, 1-16.