

Photocatalytic hydrogen peroxide synthesis from water and oxygen

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Motivation

Hydrogen peroxide (H₂O₂) is a versatile compound with a wide use in industrial applications. For example in medicine and water treatment it is used due to its disinfectant and sterilizing effect. It is also used as a reagent in many chemical reactions, as a ripening agent, for bleaching and even as a fuel.

The production of H₂O₂ by titanium dioxide or other heterogeneous photocatalysts (e.g. Fe₂O₃, ZnO) directly from oxygen and water under illumination with ultraviolet light is well known (cf. Fig. 1). The concentration achieved is characterized by a steady-state concentration, as the peroxide is also degraded at higher concentrations.^[1]

^[1] Kormann et al., Environ. Sci. Tech. 1988, 22, 798-806.

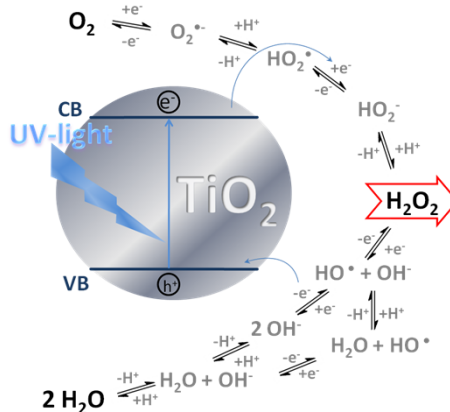


Figure 1: Possible reaction pathways of the photocatalytic generation of H₂O₂ from water and oxygen.

The aim of the project is to be able to precisely control the concentration of hydrogen peroxide for an integration of the *in situ* photocatalytic production into a H₂O₂-dependent process. Therefore understanding all influences on building and degradation processes is indispensable. For this purpose, the reaction kinetics will be studied under different conditions such as pH, temperature, and light intensity.

Advantages of this system are the homogeneous allocation of hydrogen peroxide within a set concentration regime and avoidance of detrimental concentration peaks. Also, no additional reagents are needed and separation of the catalyst by filtration is trivial. The only energy source needed is light, which is provided contactless and free of residue from outside the reactor.

H₂O₂-Analytics

I(fluorescence) ~ c(H₂O₂)

range: 0.02-10 μM

dependence: pH, temperature, inhibitors (e.g. Co²⁺), UV-absorbants (e.g. TiO₂)

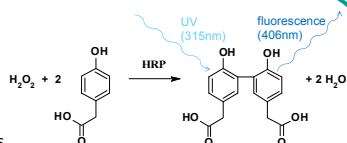


Figure 2: reaction scheme of H₂O₂ analytics.

To analyze H₂O₂ in the micro molar regime a literature described fluorescence method has been adapted.^[2] (cf. Fig. 2) The *horse radish peroxidase* (HRP) catalyzed dimerisation of *p*-hydroxyphenyl acetic acid (POHPAA) is dependent of different conditions. Therefore calibration was carried out for each of them. To estimate the H₂O₂ concentration a sample of the reaction solution was taken and TiO₂ was filtered off via a syringe filter. Afterwards HRP and POHPAA solutions were added and the fluorescence signal after 30 min was measured in a plate reader at 25°C.

^[2] Schick et al., Wat. Res., 1997, 31, 1371-1378.

pH / temperature

In a certain range the generation rate is independent of pH and temperature (T), while the degradation rate increases exponentially with higher pH and T.

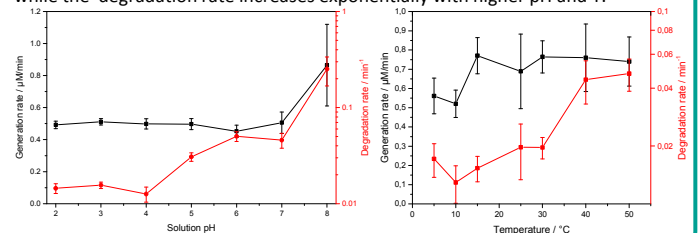


Figure 3: Kinetic parameters in dependence of pH (left) and temperature (right). (λ=365 nm, 5.11 mW/cm², O₂-bubbled, 0.05 g/l TiO₂, 25°C (left) / pH = 4.0 (right) 0.1 M phosphate)

Light intensity dependence

In contradiction to current literature^[1] the steady state concentration of H₂O₂ is dependent on the employed light intensity. The building rate can be linearly tuned by raising the light intensity.

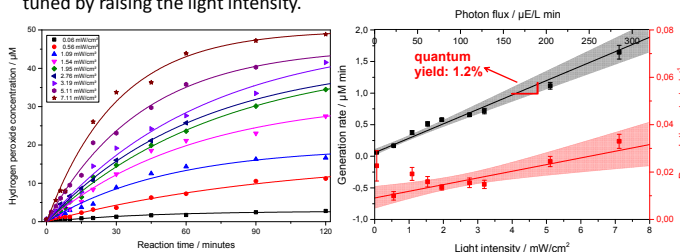


Figure 4: Light intensity dependence of H₂O₂ build up curves (left) and estimated generation and degradation rates (right). (λ=365 nm, O₂-bubbled, 0.1 g/l TiO₂, pH = 4.0, 0.1 M phosphate, 25°C. Photon flux was measured by ferrioxalate actinometry)

Long-term tests

After several hours, the steady state concentration drops, presumably due to a decrease in formation rate. Higher TiO₂ amounts and higher light intensities cause faster deactivation. Decrease in generation rate can be at least partially reversed by exchanging the solvent.

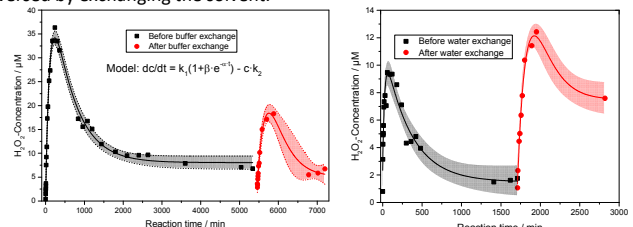


Figure 5: Long term study of photocatalytic H₂O₂ generation. (λ=365 nm, 5.11 mW/cm², O₂-bubbled, 0.05 g/l TiO₂, pH = 3.0, 0.1 M phosphate (left) / water (right), 25°C). In both reactions half of the buffer/water was exchanged without adding TiO₂.

Outlook

- Development of a continuous & enzyme independent H₂O₂ measurement system
- Understanding long term deactivation of the catalyst and finding a system without deactivation
- Influence of co-catalysts (Co/Ag/Au), salts (NaCl), different buffers (carbonate) and organic solvents (i-PrOH, t-BuOH)
- Integration of the *in situ* H₂O₂ production into a **photobiocatalytic** system

Set up

All experiments were performed in an O₂-saturated solution in a temperature-controlled, cylindrical 14 ml glass reactor with a 3.14 cm² illumination window. For the illumination a 365nm-LED with a collimation optic (up to 16.5 mW/cm²) was used.

