Swimming Upstream- Photocatalytic Depolymerization of Lignosulfonate in Seawater

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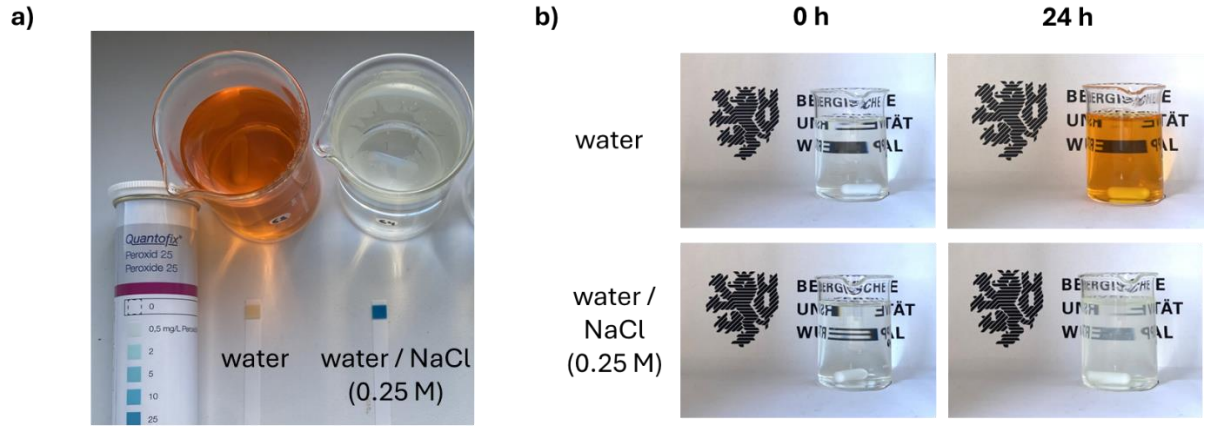

***Figure S1**: (a) Photographs of Quantofix hydrogen peroxide test stripes placed in beakers containing AQ2S in water (left) and AQ2S in 0.25 M aqueous NaCl solution (right) after 4 days of UV LED irradiation. (b) Photographs of beakers containing AQ2S in water (top row) and AQ2S in 0.25 M aqueous NaCl solution (bottom row), shown before irradiation (left column) and after 24 h UV LED irradiation (right column).*

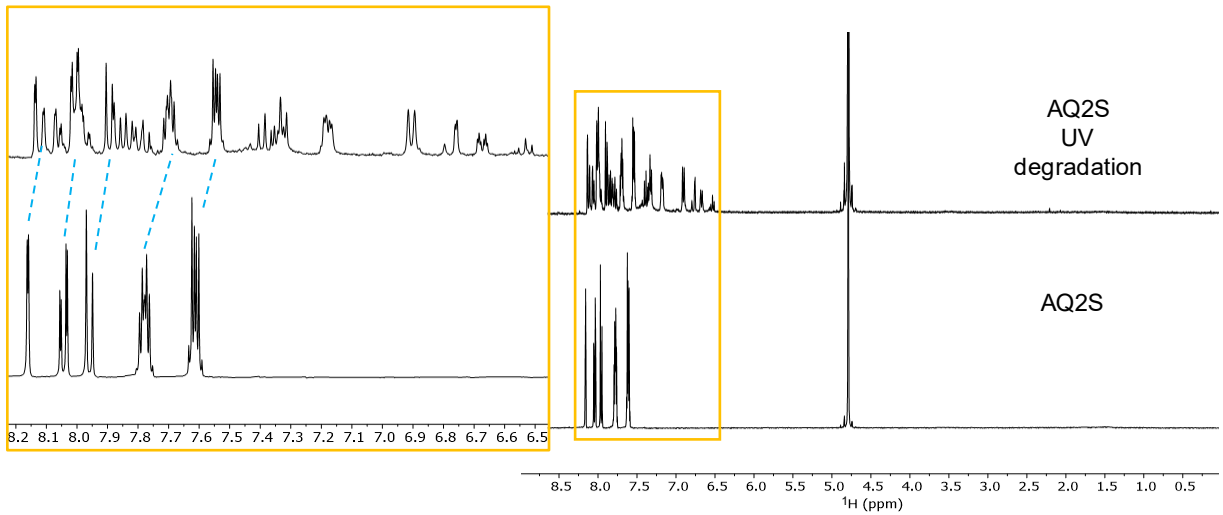

***Figure S2**: ^{1}H NMR spectra (D_2O, 400 MHz) recorded for pure AQ2S (bottom spectrum) and AQ2S in water after UV LED irradiation for 3 days (top spectrum).*

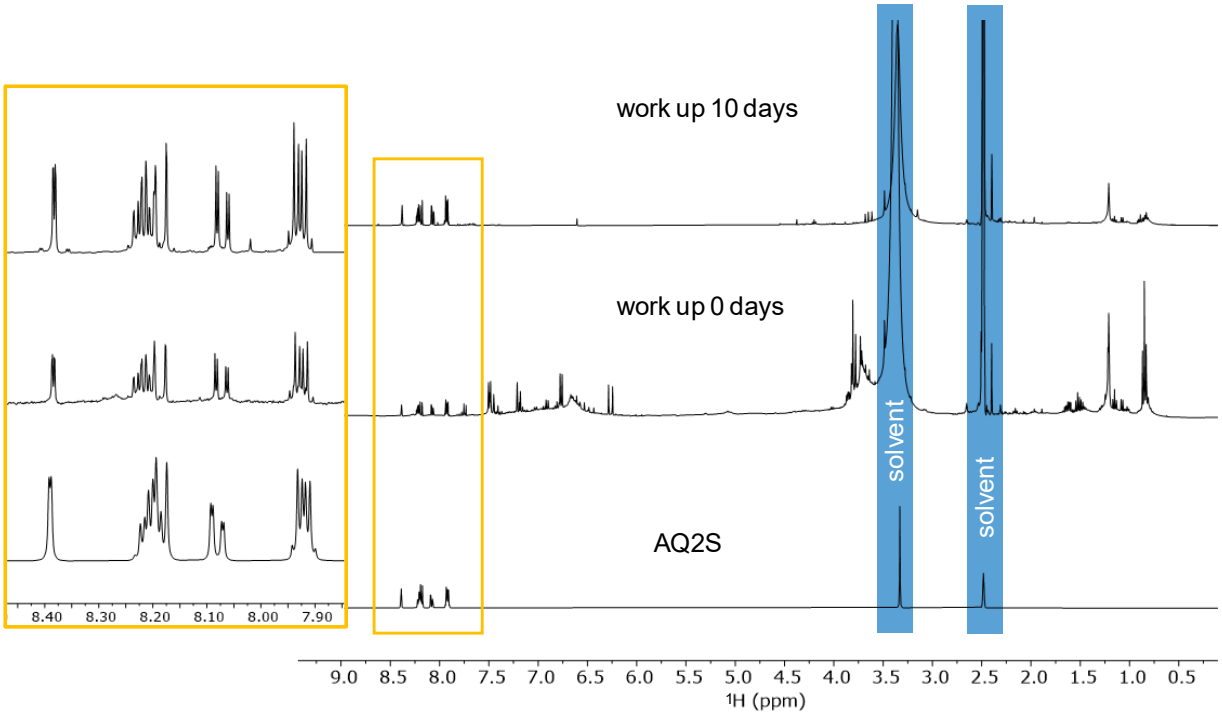

***Figure S3**: ¹H NMR spectra (DMSO-d_6, 400 MHz) recorded for: pure AQ2S (bottom spectrum); solids obtained after workup of a reaction mixture containing LS, AQ2S in NaCl solution without prior UV LED irradiation (middle spectrum); and solids obtained after workup of a reaction mixture containing LS, AQ2S in NaCl solution after UV irradiation for 10 days (top spectrum). The workup procedure involved acidifying the reaction mixture to pH of 4-5, adding 10 g of NaCl, and performing a liquid-liquid extraction with 3 x 50 mL ethyl acetate. The solids were recovered from the organic phase after drying over sodium sulfate and removing the solvent under reduced pressure.*

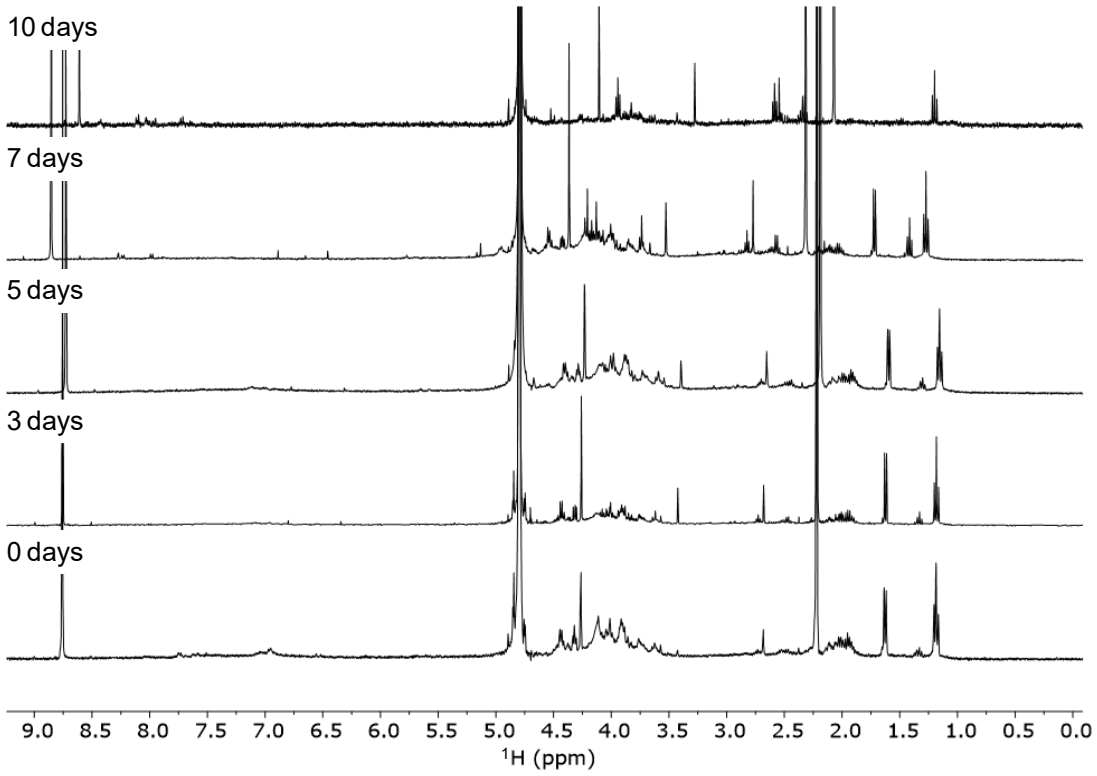

***Figure S4**: ¹H NMR spectra (D_2O, 400 MHz) of reaction mixtures containing LS and AQ2S irradiated with UV LED light in 0.5 M aqueous NaCl for 0, 3, 5, 7, and 10 days. Spectra were recorded after removal of the solvent under reduced pressure. Variations in peak positions across the spectra are likely due to differing amounts of NaCl dissolving in D_2O during sample preparation.*

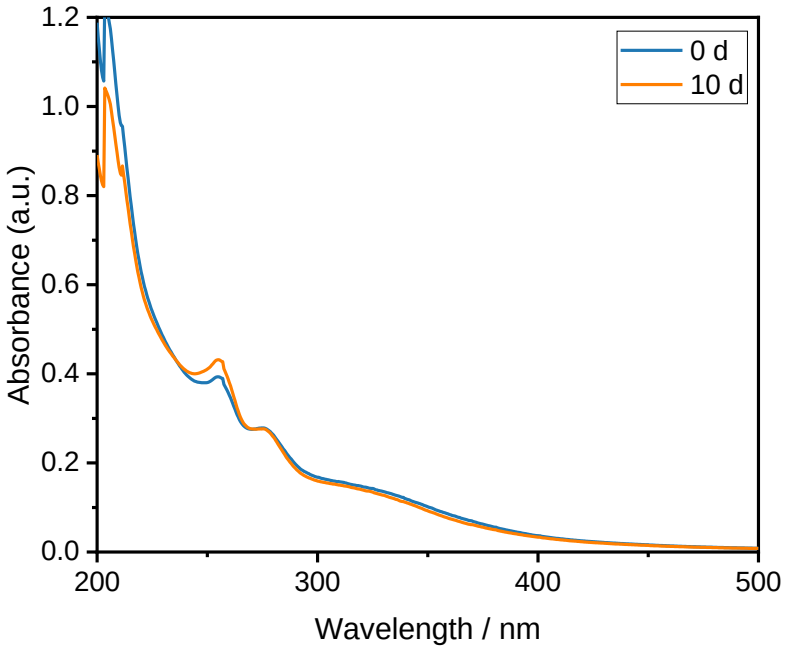

***Figure S5**: UV–vis absorption spectra of a mixture containing LS (100 mg) and AQ2S (5 mg) in 50 mL of 0.5 M aqueous NaCl, recorded immediately after preparation (blue, labeled "0 d") and after 10 days of storage in the dark (orange, labeled "10 d"; sample covered with aluminum foil). This control experiment demonstrates that no depolymerization occurs in the absence of light.*

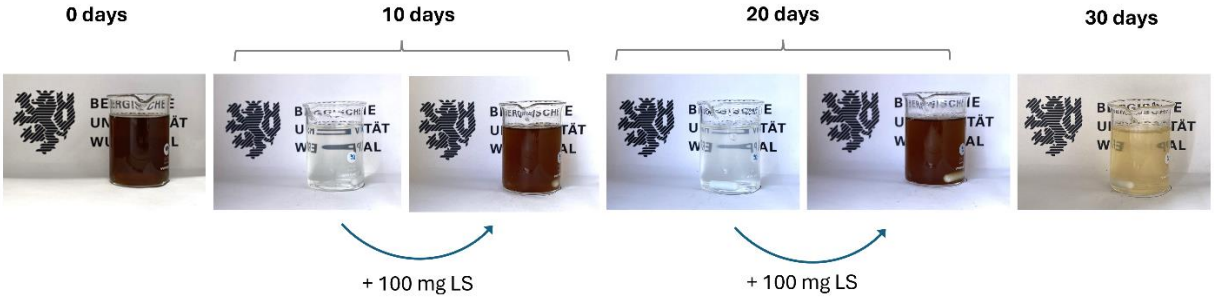

***Figure S6**: Photographs of a solution containing 100 mg of LS and AQ2S in 50 mL of 0.5 M aqueous NaCl, subjected to UV LED irradiation for 10 days. After the solution became clear and colorless, an additional 100 mg of LS was added, followed by another 10 days of irradiation, again resulting in a clear and colorless solution. A third addition of 100 mg LS and 10 more days of irradiation produced a solution that was no longer fully colorless but appeared lighter and yellow in color.*

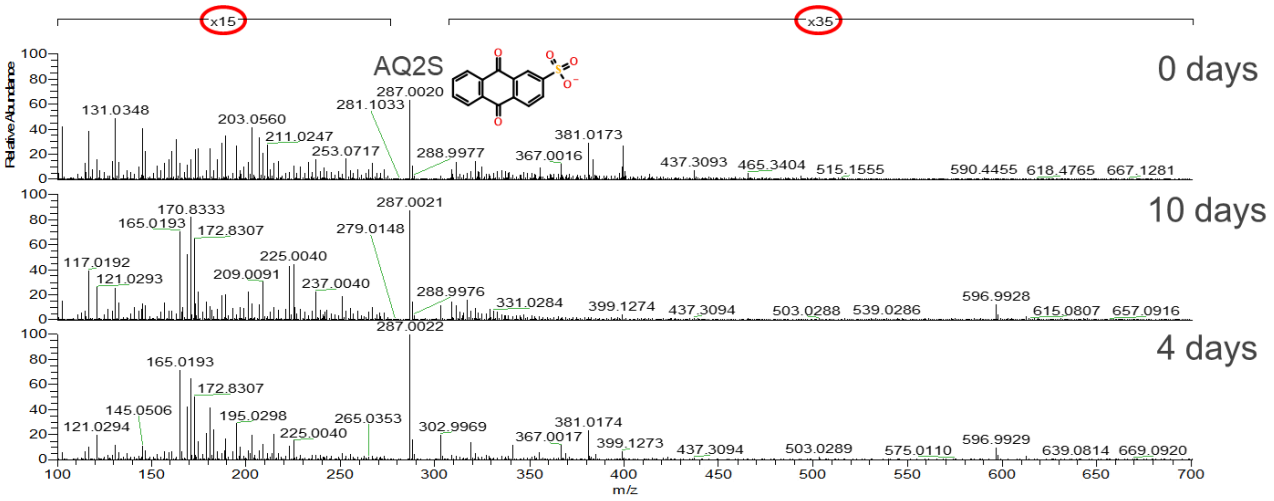

***Figure S7**: ESI-MS spectra recorded in negative ion mode [ESI(−)] for samples extracted from reaction mixtures of AQ2S and LS in 0.5 M aqueous NaCl after 0, 4, and 10 days of UV LED irradiation. Only a fraction of each reaction mixture was analyzed, obtained through liquid–liquid extraction using ethyl acetate as the solvent.*

Liquid–liquid extraction was performed on reaction mixtures containing AQ2S and LS, irradiated in 0.5 M aqueous NaCl for 4 and 10 days, as well as on a non-irradiated control, using ethyl acetate as the solvent. Although the extraction was originally intended to isolate AQ2S post-irradiation, it also revealed the presence of various low-molecular-weight compounds in all three samples. While the extracted quantities were small and not necessarily representative of the overall reaction mixture, the consistent detection of these low-molecular fragments across all conditions suggests that the monomers remain stable under the given experimental conditions. Representative structures identified by MS analysis are shown in **Figure S8**.

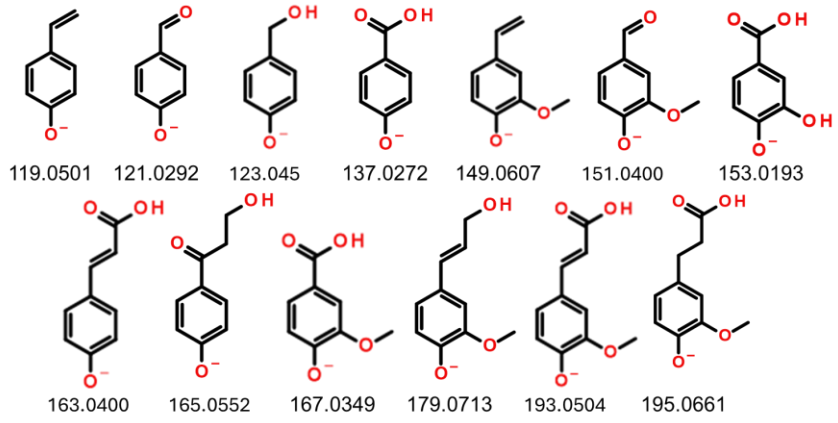

***Figure S8**: Representative examples of compounds detected by ESI-MS analysis in negative ion mode [ESI(−)] from samples extracted from reaction mixtures of AQ2S and LS irradiated in 0.5 M aqueous NaCl for 0, 4, and 10 days. Only a fraction of each reaction mixture was analyzed, obtained via liquid–liquid extraction using ethyl acetate as the solvent. The compounds shown were identified in all three samples.*

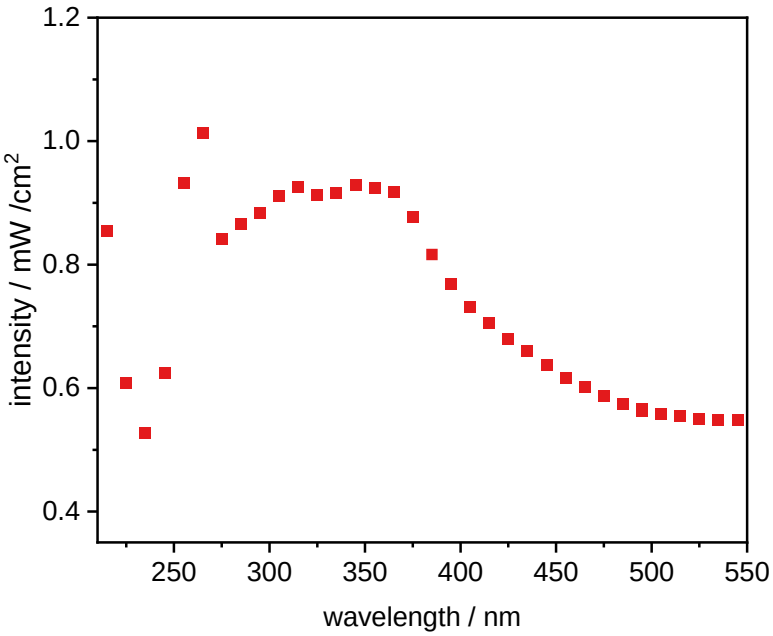

***Figure S9**: intensities of irradiation measured for the UV LED tube used in the experiments of this study for wavelengths between 200 and 550 nm. Intensities reported in mW/cm² were measured in a distance equal to the distance between solution and LEDs (approximately 3 cm) with a Newport Power Meter Model 843-R, set to the respective wavelength.*

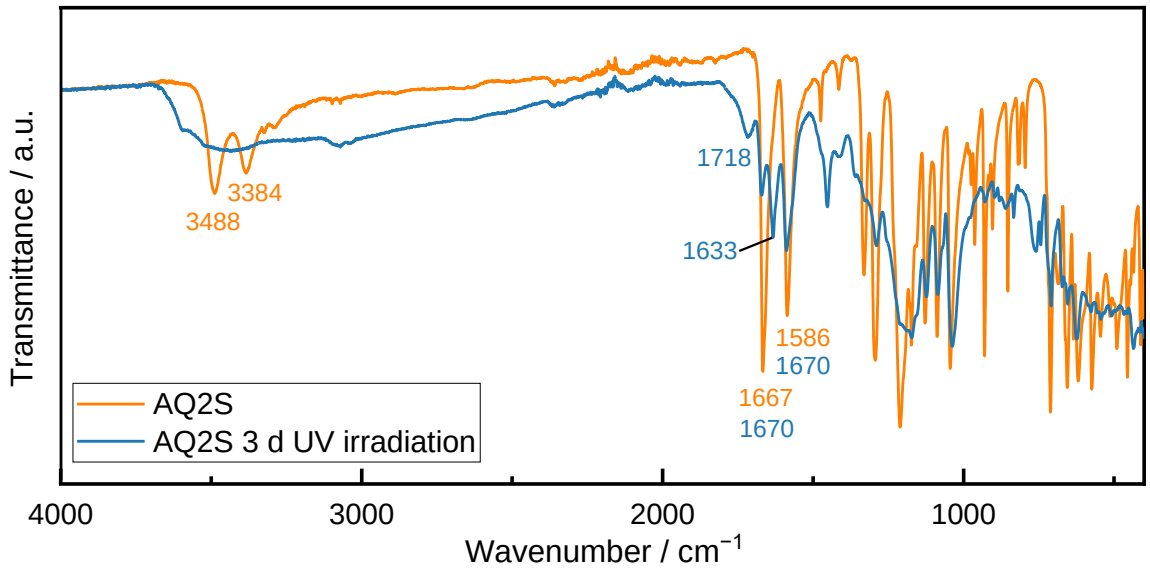

***Figure S10**: FTIR spectra of pure anthraquinone-2-sulfonate (orange) and anthraquinone-2-sulfonate dissolved in water and irradiated for 3 days (blue). The spectrum of the irradiated sample was recorded after solvent removal and drying of the recovered solid.*

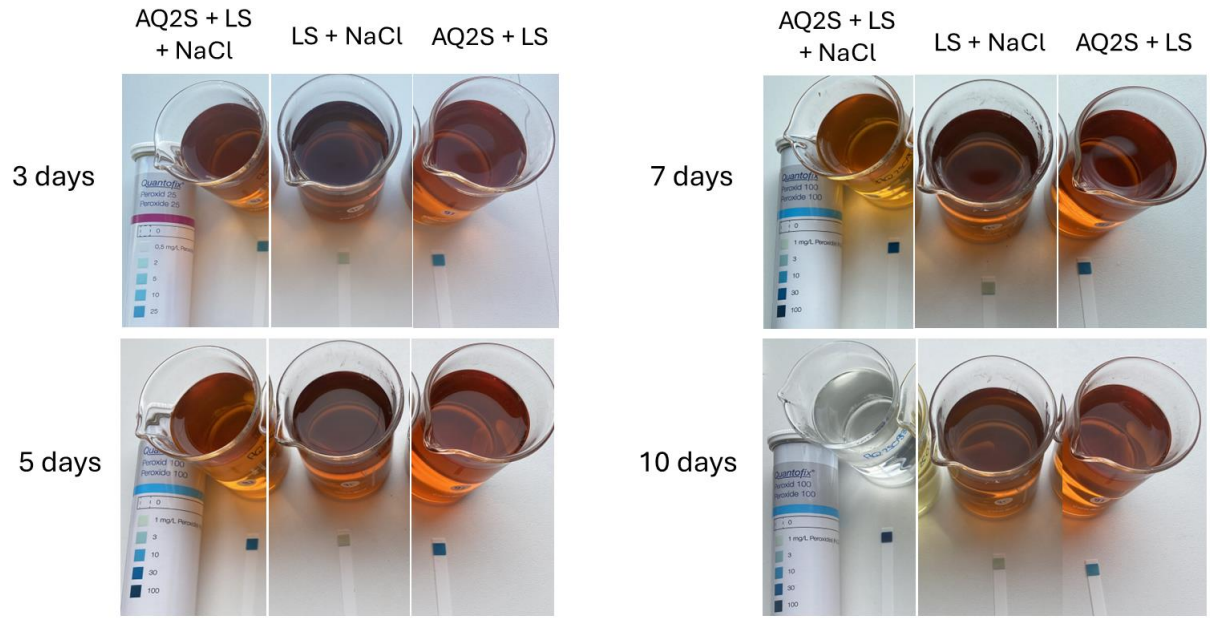

***Figure S11**: Semiquantitative tests for hydrogen peroxide using Quantofix peroxide test strips. Measurements were taken after 3, 5, 7, and 10 days of UV irradiation on solutions containing (i) AQ2S, LS, and NaCl; (ii) LS and NaCl; or (iii) LS and AQ2S in deionized water. Blue coloration of the test strips indicates detectable peroxide levels.*

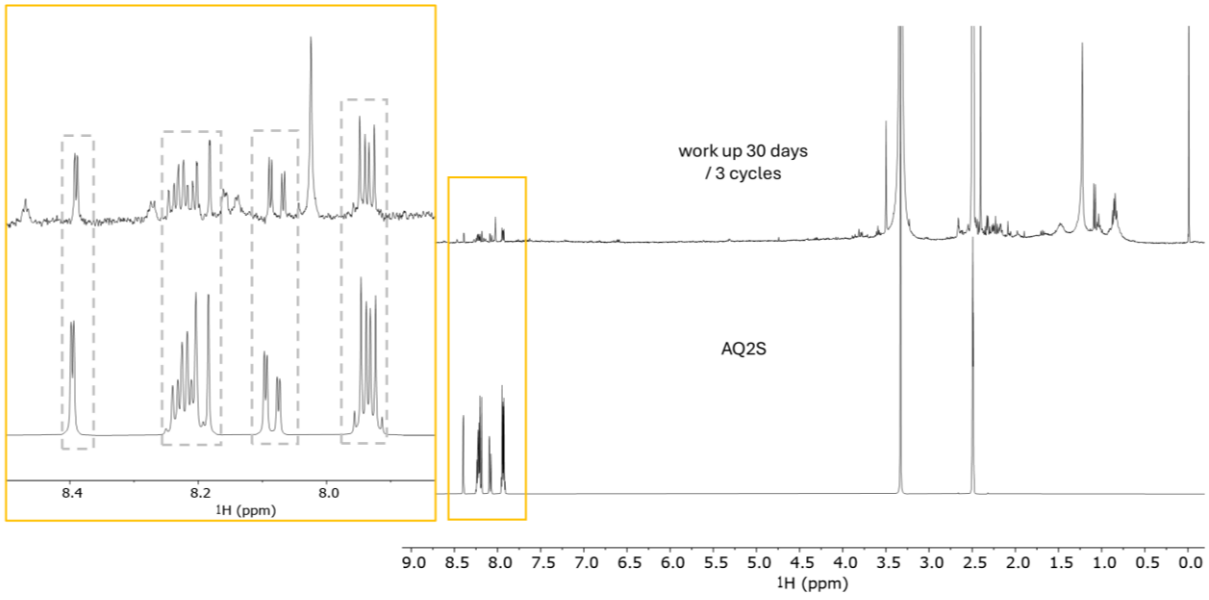

***Figure S12**: ^{1}H NMR spectra (DMSO-d_6, 400 MHz) of pure AQ2S (bottom) and AQ2S extracted after 30 days of irradiation with three cycles of LS additions (100 mg each). The workup involved acidifying the reaction mixture to pH of 4-5, adding 10 g of NaCl, and performing a liquid-liquid extraction with ethyl acetate (3 × 50 mL). The solids were obtained from the organic phase after drying over sodium sulfate and removing the solvent under reduced pressure.*

NMR spectra shown in **Fig. S12** clearly demonstrate the retention of the catalyst AQ2S after performing recycling experiments (**Fig. S6**), which involved 30 days of UV irradiation with a total of 300 mg of LS over three cycles. All signals attributed to AQ2S are still evident after extraction. The additional signals observed in the same region may originate from low-molecular-weight fragments of LS that were co-extracted with the catalyst.