Degradation kinetics of caffeine in water by UV/H$_2$O$_2$ and UV/TiO$_2$

Pedro M. Rendela,* Giora Rytwoa,b

Environmental Physical Chemistry Laboratory, MIGAL, Galilee Research Institute, Kiryat Shmona, Israel, Tel. +972 4 6953568; Fax: +972 4 6944980; emails: prendel@migal.org.il (P.M. Rendel), giorarytwo@gmail.com (G. Rytwo)

Department of Environmental Sciences, Tel Hai College, Upper Galilee, Israel

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ABSTRACT

Considered the world’s most widely consumed psychoactive drug, caffeine became a widespread environmental pollutant, contaminating both the hydrosphere as well as the pedosphere, by thus leading to an unclear effect on the surrounding biosphere. Unsuccessfully treated by regular waste-water-treatment plants, caffeine concentrations in discharged effluents and natural reservoirs are constantly rising. New water-treatment technologies are being developed to reduce the concentrations of such emerging contaminants. Photodegradation is recently drawing much attention due to its potential to oxidize such contaminating compounds and its large-scale deployment is still being evaluated. In order to optimize these processes, quantifying and developing new kinetics models are an essential step. In this work, the photodegradation kinetics of caffeine was evaluated under different UV-C doses (1.9–15.2 mJ cm$^{-2}$ s$^{-1}$ and $\lambda$ = 254 nm) and in the presence of two degradation agents, hydrogen peroxide (H$_2$O$_2$) and commercial titanium dioxide (TiO$_2$) nanopowder. For an initial concentration of 19,600 µg L$^{-1}$ caffeine, the removal rate was higher than 95% for both agents separately, yielding half-life times of 40–5 min for 16.3–163 µmol L$^{-1}$ H$_2$O$_2$ and 96–9 min for 1–100 µg L$^{-1}$ TiO$_2$ suspension, respectively. The degradation rates were governed by pseudo-zero-order reaction kinetics at high caffeine-to-agents ratios (>0.6 for H$_2$O$_2$ and >400 for TiO$_2$), whereas pseudo-first-order kinetics were seen at lower ratios in experiments with TiO$_2$. Empirical and theoretical rate laws describing the degradation kinetics and their possible mechanism are presented.

Keywords: Caffeine; Kinetics; Photodegradation; Hydrogen peroxide; Titanium dioxide; Wastewater