

New approaches to determination of the quantum yield of hydroxyl radical generation and its reactivity with persistent contaminants

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Fe (III) carboxylate complexes are photoactive natural compounds that are intensively studied and are considered to be one of the promising systems for the degradation of pollutants in the so-called advanced oxidation processes (AOPs). They demonstrate high quantum yields of photolysis and efficient generation of $\cdot\text{OH}$ radicals under the action of UV radiation. However, there is very little information on the quantum yields of $\cdot\text{OH}$ radicals (ϕ_{OH}) upon excitation of such systems. At the same time, the ϕ_{OH} values and the reactivity of $\cdot\text{OH}$ with respect to the target compounds are the most important parameters for the application of any photosystem in AOPs. This work presents valid approaches to determining the ϕ_{OH} values during UV photolysis of natural Fe(III) carboxylate complexes and determining the rate constants of hydroxyl radical reactions (k_{OH}) with priority environmental pollutants.

The first approach is based on the use of the FeOH^{2+} hydroxocomplex as a reference system with the well-known ϕ_{OH} value and benzene as a selective trap for $\cdot\text{OH}$ radicals. For the first time, ϕ_{OH} was determined for the most popular Fe(III)-oxalate photosystem in a wide range of initial parameters (pH, excitation wavelength, concentration of oxalate and Fe(III) ions). Also, the oxidative potential of the oxalate photosystem was tested on a set of resistant organic herbicides, and the quantum yields of photodegradation of these herbicides were compared with the ϕ_{OH} value.

The second approach is based on the application of the method of laser flash photolysis using the FeOH^{2+} complex as a standard source of hydroxyl radicals at pH 3, and methylviologen dication (MV^{2+}) as a selective probe for the $\cdot\text{OH}$ radical. The use of MV^{2+} makes it possible to determine the k_{OH} values even for those compounds that do not themselves form optically detectable adducts in the reaction with hydroxyl radicals. The applicability of this approach has been tested on a wide range of resistant organic herbicides, and its main advantages and disadvantages are discussed compared to existing stationary and time-resolved methods.

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