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Letter to the editor

Dear Sir,

We would like to comment on the paper by Shu and Chang [1] published recently in Dyes and Pigments concerning the kinetic analysis of C.I. Acid Black 1 (AB1) decolorization in the UV/H_2O_2 process. Under the conditions described there, the OH radicals produced from the peroxide destroy the dye. By using spectrophotometry the authors measured the dye concentration as a function of UV irradiation time in a tank reactor. They described the time dependence of decolorization by applying pseudo-first-order kinetics. (Pseudo-first-order treatment was used to describe the decolorization also in other papers reporting on similar reactions [2–7].) Based on these pseudo-first-order rate constants they developed important semi-empirical equations for the description of decolorization dependence on the peroxide concentration, dye concentration, pH, irradiation intensity, etc. These equations can be used in practical decolorization processes. We mention that in several other Advanced Oxidation Processes like treatment with ionizing radiation (radiolysis), sonolysis, photocatalytic reactions, the OH radical plays important role in the destruction of organic molecules.

Here we suggest a reconsideration of the theoretical interpretation of the kinetic results of Shu and Chang [1].

Assuming that the hydroxyl radicals produced in UV decomposition of peroxide react only with the intact dye molecules: they describe the time dependence of the decolorization by the differential equation:

$$-\frac{dC_d}{dt} = kC_dC_{OH} \tag{1}$$

In the equation C_d represents the AB1 concentration, C_{OH} is the hydroxyl radical concentration, and k is the second-order rate constant. They assume constant hydroxyl radical concentration and integrate the obtained pseudo-first-order rate equation ($k_{obs} = kC_{OH}$):

$$-\frac{dC_d}{dt} = k_{obs}C_d \tag{2}$$

$$\ln\frac{C_d}{C_{d,0}} = -k_{obs}t \tag{3}$$

They calculate the pseudo-first-order rate constant, k_{obs} from the $\ln(C_d/C_{d,0})$ vs. t plot ($C_{d,0}$ is the initial dye concentration). From chemical kinetic point of view the pseudo-first-order treatment they applied is incorrect.

During the UV/H_2O_2 process and during several other Advanced Oxidation Processes used for decolorization (e.g. radiolysis) the OH radicals form with a constant rate (r_{OH}) and they decay with the same rate:

$$\frac{dC_{OH}}{dt} = r_{OH} - kC_dC_{OH} \approx 0 \tag{4}$$

At the beginning of the process, when the dye concentration is high, the OH radicals live for shorter time since they quickly react with the solute molecules, and therefore the OH radical concentration is low. Towards the end of the process C_d is lower and C_{OH} is higher. Substituting $C_{OH} \approx r_{OH}/kC_d$ into Eq. (1), after integration we obtain linear time dependence (linear dose dependence):

$$C_d = C_{d,0} - r_{OH}t \tag{5}$$

Such linear dependence was observed during the initial part of decolorization several times, e.g. in the case of ionizing radiation treatment of the monoazo dye Apollofix Red [8,9] when the hydrated electrons (e^-_{aq}) or the hydrogen atoms (H) produced during the radiolysis of water reacted with the dye molecules. e^-_{aq} and H were found to react with the azo group causing destruction of the intensive conjugation in the molecule through the azo bond. The other parts of the molecule, or the products formed have smaller reactivity with e^-_{aq} and H than the $-N{=}N-$ double bond in the starting compound.

The reaction of the OH radicals with the dye molecules is different from the reactions of e^-_{aq} and H. They react with practically diffusion limited rate constants ($k \approx 10^{10}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$) with the aromatic rings and probably also with the $-N{=}N-$ double bonds. The dye molecules have several places for the attack, for instance AB1 has 4 aromatic rings and two $-N{=}N-$ double bonds. The reaction of any of them may lead to the destruction of the extensive conjugation in the molecule, so may decolorize the molecule. However, the remaining part of the reacted molecule has also high reactivity towards the OH radicals. That is probably true for the product formed from the product, i.e. for the secondary product, tertiary product, etc. For that reason the rate equations should be written in the following form:

$$-\frac{dC_d}{dt} = kC_dC_{OH} \tag{6}$$

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$$\frac{dC_{OH}}{dt} = r_{OH} - kC_d C_{OH} - kC_{Product} C_{OH} \approx 0 \tag{7}$$

Since – as it was mentioned before – the reaction of OH with both the dye and the products is practically diffusion limited, we use for both reactions the same rate coefficient k. Applying the simplification $C_{Product} \approx C_{d,0} - C_d$, and also $C_{OH} \approx r_{OH}/kC_{d,0}$ expressed from Eq. (7), the differential equation has the form:

$$-\frac{dC_d}{dt} = \frac{C_d r_{OH}}{C_{d,0}} \tag{8}$$

After integration, we obtain exponential time dependence (Eq. (3)) with rate parameter of $k_{obs} = r_{OH}/C_{d,0}$. This model, which involves a constant hydroxyl radical concentration, is now in agreement with the experimental observations.

The conclusions of this letter to the editor may be summarized as follows:

During decolorization of aqueous dye solutions in a tank reactor if the reactive intermediate radicals react with high rate constant with the dye molecules and the rate constant of the reaction with the products is much smaller, the time dependence (or dose dependence) is linear (at least in the initial period of the reaction). However, when the rate constants are high with both the dye molecules and the products, the time dependence is exponential.

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