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ASSESSMENT OF RADIANT FLUX ABSORPTION BY IRRADIATED PHASE ON THE KINETICS OF PHOTOCATALYTIC REACTIONS

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In this study, the kinetics equation describing heterogeneous photocatalytic process in relation with the absorption of radiation by inactive photochemically reagents was presented. The proposed expression was verified based on the results of degradation process of selected azo-dyes. The experiments were carried out in one- and two component solutions in the presence of TiO_2 (anatase) during UV-a irradiation.

keywords: photocatalysis, kinetics, radiant flux, Langmuir-Hinshelwood, absorption

1. INTRODUCTION

In the last decade, there have been high hopes for the use of a photocatalytic process as an effective method for the degradation of toxic and biologically persistent substances. Usually, this process is carried out under heterogeneous conditions in the presence of TiO_2 [1-5]. Its photocatalytic properties have been known since the end of the 1930s [5]. This substance may be used in the form of particles suspended in an

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aqueous solution/ medium or may be applied on the surfaces of different materials. Moreover, a modification of TiO_2 surface by doping with various metals having positive reduction potential (e.g., Ag, Au, Pt, Cu), lanthanides dopants, Fe(III) and nonmetal such as boron, carbon and nitrogen have been studied [3,6-8].

Among the factors having the significant effect on the efficiency of the photocatalytic process are [1,3-5,9,10]:

- crystal structure of TiO_2
- way of the preparation and application of the photocatalyst surface
- photocatalyst concentration
- useful spectrum of UV-VIS light absorbed by photocatalyst
- sorption properties of photocatalyst
- concentration of degraded compounds
- ability of degraded substances to the adsorption onto TiO_2 surface
- presence of other substances such as strong oxidants or reducing agents in the irradiated samples
- ability of degraded compounds to photolysis
- oxygen saturation of the irradiated samples.

Moreover, important parameters of the photocatalytic process are:

- intensity and wavelength of the used radiation
- thickness of the layer of the irradiated samples
- temperature and pH of medium.

The limiting step of photocatalytic processes carried out in the presence of TiO_2 may be the adsorption of substrates onto the photocatalyst surface and the absorption of radiation having energy sufficient for generation of electron-hole pairs (h^+,e^-) [3-5,9,10]:

$$TiO_2 + h\nu \rightarrow TiO_2(h^+,e^-) \quad (1)$$

These pairs can react with water and dissolved oxygen molecules:

$$h^+ + H_2O \rightarrow HO^\bullet + H^+ \quad (2)$$

$$e^- + O_2 \rightarrow O_2^{-\bullet} \quad (3)$$

Moreover, the photogenerated pairs can participate directly in the redox reactions with photochemically inactive substances:

$$h^+ + RH \rightarrow R^\bullet + H^+ \quad (4)$$

$$ne + Me^{m+} \rightarrow Me^{(m-n)+} \quad (5)$$

The kinetics of photochemical process is usually described by the Langmuir-Hinshelwood's theory [1-5]:

$$r_i = -\frac{dC_i}{dt} = k_i \Theta_i = k_i \frac{K_i C_i}{1 + \sum_i K_i C_i} \quad (6)$$

where: r_i is the reaction rate (i-th substrate), C_i is the molar concentration of substrate, t is the irradiation time, k_i is the reaction rate constant, Θ is the degree of coverage of photocatalyst surface, and K_i is the adsorption coefficient for the adsorption of substrate on TiO_2.

In very diluted solutions, Eq.6 can be simplified to the following form:

$$r_i = -\frac{dC_i}{dt} = k_i K_i C_i \tag{7}$$

Experimental data show that in the wide range of the radiation intensity, the reaction rate is directly proportional to its value [1,3,4,11]. Therefore the following equation is correct:

$$r_i = -\frac{dC_i}{dt} = \Phi_i I_A \tag{8}$$

where: φ is the quantum yield and I_A is the intensity of radiation absorbed by photocatalyst.

If we assume that the quantum yield of photochemical reaction is the product of k_i and Θ, the relationship can be expressed as follows:

$$r_i = -\frac{dC_i}{dt} = k_i \Theta_i I_A \tag{9}$$

Therefore, the I_A value may depend on the absorption of radiation by solution containing suspended TiO_2 particles.

We supposed that the important factor that limited the photocatalytic process rate can be the absorption of part of the radiation by solution containing degraded substrates. This effect causes the decrease in the radiation intensity reaching the photocatalyst surface. In previous studies we have found the correlation between the absorbance of dyes solutions and their photocatalytic degradation rate [12]. According to the Lambert-Beer law the intensity of radiation absorbed by photocatalyst should by exponentially proportional to the sum of the product of the molar extinction coefficients for the used radiation *(ε),* concentrations of all components in solution (C) and the thickness of the layer of irradiated samples absorbing radiation *(l):*

$$I_A = I_o^{-l\sum_i \varepsilon_i C_i} \tag{10}$$

where: I_o is the radiation intensity that reaches directly the surface of exposed sample.

Based on Eqs.6, 9 and 10, we propose the following equation to describe the kinetics of photocatalytic process:

$$r_i = -\frac{dC_i}{dt} = k_i \frac{K_i C_i}{1 + \sum_i K_i C_i} I_o e^{-l \sum_i \varepsilon_i C_i} \tag{11}$$

The mathematical model concerning the use of electromagnetic radiation energy in photocatalytic processes was presented by Brandi et al. [13,14]. It can be useful for the determination of the effective radiation flux reaching the reactor mixture in the closed flow reactor with an external source of radiation; however, the authors did not analyze the effect of distribution of radiant flux between the various components within the reaction mixture. Thus, they omitted the fact of absorption of radiation by photochemically inactive components of this mixture.

The aim of the work was to verify experimentally the kinetics equation, taking into account that the radiation absorption by irradiated solution effects on the photocatalytic reaction rate.

2. EXPERIMENTAL

2.1. Reagents

The experiments were carried out with the use of two azo-dyes as model compounds. Acid Orange 7 obtained from Fluka and Acid Black 1 purchased from POCH were of analytical grade. None of the investigated dyes underwent photolysis under the experimental conditions. The titanium dioxide powder (TiO_2, anatase, pH of isoelectric point was 3, the surface area was 9-11 m^2g^{-1}, residues on filter >40μm after dispersion in water was <0,02%) used as the photocatalyst was purchased from Riedel-de Haën. In all experiments amount of photocatalyst was 2.5 g l^{-1}. Doubly distilled water was used throughout experiments.

2.2. Irradiation

Before irradiation of aqueous dyes solutions with TiO_2, the samples were magnetically stirred in the dark for 30 min in order to reach the adsorption/desorption equilibrium among the dyes, photocatalyst and the dissolved oxygen. The stirring was continued throughout the whole process. Since the pH values in the irradiated samples were in the range of 5.8 - 6.8, the influence of changes of pH on the obtained results was eliminated (the adsorption of azo-dyes onto TiO_2 surface was very low at this pH value). In all cases during the experiments, the samples at volume 100 ml containing TiO_2 and dyes were irradiated in glass crystallizer (500 ml) by means of four UV lamps (Philips TL-40 W/05) emitting radiation with a maximum energy at λ 366 nm. The surface intensity of the radiation determined by Parker's actinometer [15] was $8.76 \cdot 10^{-5}$

Einstein $s^{-1}m^{-2}$. The exposed samples surface was 102 cm^2. The reaction temperature was kept at 21 ± 2ºC. During irradiation the solutions had a free contact with atmospheric air but, additionally, were not aerated.

2.3. Analysis

The samples of the investigated suspensions (2 ml) were taken at the appropriate irradiation time, when the degree of degradation of each dye was <80%. In order to separate the photocatalyst from the suspension, samples were centrifuged for 30 min at 4000 rpm.

In samples before and after irradiation the concentration of azo-dyes were determined according to *abs* measurement at 480 and 618 nm for Acid Orange 7 and Acid Black 1, respectively, using UV-VIS spectrophotometer Secomam S 750. During the preliminary studies it was found that the dyes solutions follow the Lambert –Beer's law in the used concentration range. In these ranges, the determination coefficients (R^2) of the calibration curves obtained for Acid Orange 7 and Acid Black 1 were 0.9952 and 0.9989, respectively. Moreover, results obtained in mixtures of dyes were also validated using HPLC methods (HPLC Merck Hitachi, detector UV L 7400, λ 254 nm; column SEPARON SGX 7 μm, C-18, 250×4 mm; mobile phase – $MeOH:H_2O$ in the ratio 3:7). Additionally, in all investigated mixtures before the irradiation the *abs* was measured at λ 366nm.

2.4. Calculations

According to Eq. 7, the photocatalytic process carried out in very diluted solutions is a pseudo-first order reaction. This fact is supported by experimental literature data [1-4]. Therefore, the values of observed reaction rate constant *(k)* were determined as a slope of linear relationship (Eq.12).

$$\ln\frac{C}{C_o} = -k\,t \tag{12}$$

In all cases, the initial reaction rate *(r_o)* was calculated as follows:

$$r_o = k\,C_o \tag{13}$$

3. RESULTS AND DISCUSSION

3.1. One-component samples

In the case of low adsorption efficiency and low concentration of substrates the following approximation is used:

$$1+\sum_i K_i C_i \cong 1 \tag{14}$$

Taking into account Eq. 14, the kinetics equation for photocatalytic process carried out in solution containing only one substrate (dye) and TiO_2 suspension can be simplified to the form:

$$r_i = k_i K_i C_i I_o e^{-l\varepsilon_i C_i} \tag{15}$$

According to Eqs.13 and 15 the k value can be expressed as follows:

$$k = k_i K_i I_o e^{-l\varepsilon_i C_i} \tag{16}$$

Since under the investigated conditions the k_i, K_i I_o, l and ε_i values are constant, the following relationship is obtained:

$$C_o \sim ln\,k \tag{17}$$

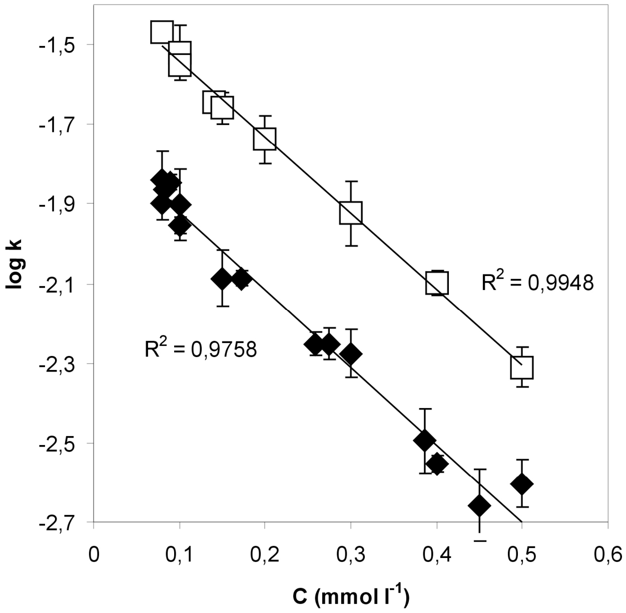

Fig. 1. The effect of initial dyes concentrations on the logarithm value of the photodegradation rate constant of Acid Orange 7 (□) and Acid Black 1 (◆)

Fig.1 presents the effect of initial dyes concentrations on the logarithm value of the photodegradation rate constant of Acid Orange7 or Acid Black1 in solutions with only one dye.

A course of the function was comparable in dyes solutions at the concentration in the range of 0.08-0.5 mmol l^{-1}. In these ranges, the coefficient of determination (R^2) of the straight line function obtained for Acid Orange 7 and Acid Black 1 were 0.9948 and 0.9758, respectively. A very good fit to a linear regression (Fig.1) indicates that it can be treated as a confirmation of the hypothesis presented in Eq. 16. However, when concentrations of dyes in solutions were < 0.08 mmol l^{-1}, a linear dependence was not observed. In the experiments performed in the presence of TiO_2 (the *l* value is also very low) at very low concentration of dye, the approximation of expression $e^{-l\varepsilon C} \cong 1$ is correct. In this case, in one-component solutions ($C_o < 0.08$ mmol l^{-1}) the effect of absorption of radiation by dye molecules can be treated as a negligible.

3.2. Two - component samples

In mixtures containing constant concentration of one of the compounds (dye A), the degree absorption of radiation can be changed by other compounds, for example by other dye (B). For example, in the case of Acid Orange 7 (AO7, dye A) if the expression (14) is fulfilled, the kinetics equation can be described as follows:

$$r_{oAO7} = k_{AO7} K_{AO7} C_{AO7} I_o e^{-l(\varepsilon_{AO7} C_{AO7} + \varepsilon_{AB1} C_{AB1})} \tag{18}$$

In this case, the *ln* r_i value for dye A should be inversely proportional to the relationship:

$$\varepsilon_A C_A + \varepsilon_B C_B = \Sigma \varepsilon_i C_i \tag{19}$$

Table 1. The composition of the irradiated dyes mixtures and the fitting of linear function $\log r_o = f(\sum_i \varepsilon_i C_i)$

Mixture		Initial dye concentration (mmol l^{-1})		Function	R^2
		Acid Black1	Acid Orange7		
I	Fig. 2	0-0.0487	0.0143	$\log r_o = -4.6406x^a - 2.5711$	0.9955
II		0-0.024	0.0057	$\log r_o = -10.819x^a - 2.6973$	0.9969
III	Fig. 3	0.0162	0-0.0571	$\log r_o = -3.3474x^a - 2.7355$	0.9811
IV		0.00812	0-0.0857	$\log r_o = -3.717x^a - 3.0408$	0.9870
V		0.00325	0-0.0429	$\log r_o = -8.5405x^a - 3.2529$	0.9884

[a] $x = \sum_i \varepsilon_i C_i$; ε at 366 nm $\varepsilon_{\text{Acid Black1}} = 4031$ l mol^{-1} cm^{-1}; $\varepsilon_{\text{Acid Orange7}} = 3093$ l mol^{-1} cm^{-1}

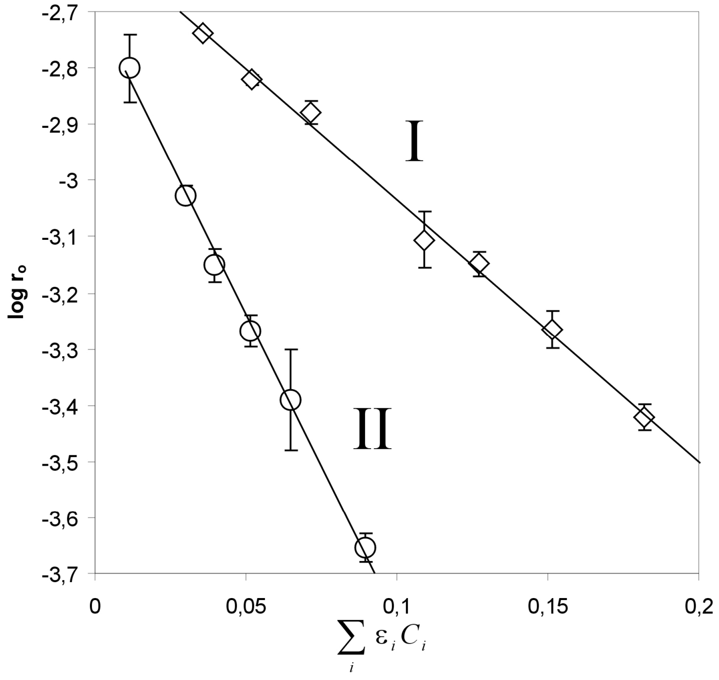

Fig. 2. The effect of $\sum_i \varepsilon_i C_i$ value in samples containing mixture of Acid Orange 7 and Acid Black 1 on the logarithm value of the initial photodegradation rate of Acid Orange 7, (◇) C_{AO7}=0.0143, C_{AB1}=0-0.0487 mmol l^{-1}; (○) C_{AO7}=0.0057, C_{AB1}=0-0.0244 mmol l^{-1}

The ε_A and ε_B values (for Acid Orange 7 and Acid Black 1, respectively) were determined experimentally at λ 366 nm. Table 1 presents the range of concentrations of both dyes and the fitting of the experimental data to the linear function. The values of ε are showed below Table 1. Figures 2 and 3 show the relationships between $ln\ r_i$ and $\varepsilon \Sigma_i C_i$.

A good fit to a linear regression in the range studied (Figs. 2 and 3) indicates that it can be treated as a confirmation of the hypothesis presented in Eq. 11.

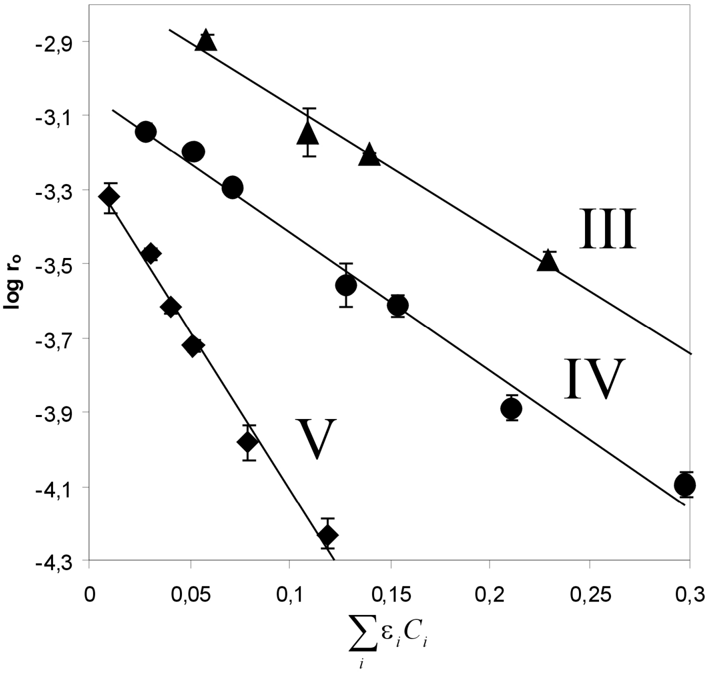

Fig. 3. The effect of $\sum_i \varepsilon_i C_i$ value in samples containing mixture of Acid Orange 7 and Acid Black 1 on the logarithm value of the initial photodegradation rate of Acid Black 1,
(▲) $C_{AB1} = 0.0162$, $C_{AO7} = 0\text{-}0.0571$ mmol l^{-1}; (●) $C_{AB1} = 0.00812$, $C_{AO7} = 0\text{-}0.0857$ mmol l^{-1};
(◆) $C_{AB1} = 0.00325$, $C_{AO7} = 0\text{-}0.0429$ mmol l^{-1}

4. CONCLUSION

The obtained results point out to the correctness of own hypothesis that the photocatalytic reaction rate depends on the radiant flux absorbed by the irradiated solution (i.e., depends on the thickness of solution layer over the photocatalyst surface) and on the sum of the products of concentrations and molar extinction coefficients. In the case of reaction carried out in clear water in the presence of TiO_2, this influence will be negligible. However, during the design engineering degradation processes of real wastewater having high level of radiation absorption and containing high concentration of substrates this effect can be significant. More particularly, in the cases of the use of photocatalyst applied onto the surface of other materials.

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