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The influence of selected parameters on the photocatalytic degradation of azo-dyes in the presence of TiO_2 aqueous suspension

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ABSTRACT

The aim of this study was to determine the influence of various parameters such as the initial concentration of dye and catalyst, the volume of irradiated solution and its absorbance on the kinetics of photocatalytic degradation of azo-dyes.

The studies were carried out in aqueous solutions containing the individual azo-dyes (Acid Black 1, Acid Orange 7, Basic Orange 66) and in their mixtures, in the presence of two types of TiO_2 as photocatalyst and under UV light irradiation. It was found that under given experimental conditions, the photocatalytic degradation of investigated dyes exhibited pseudo first-order kinetics according to the Langmuir-Hinshelwood's heterogeneous catalysis model but only in the limited range of initial dyes concentrations. Moreover, the optimum TiO_2 concentration, the pH value of zero charge point, the adsorption efficiency of dyes on catalysts and the optimum volume of irradiated solution were found. It was stated that in mixtures, dyes underwent photodegradation slower than in the one-component solutions. This phenomenon has been connected with the absorbance of irradiated solutions.

1. Introduction

One of the most effective methods for elimination of many hazardous, toxic, organic pollutants from the environment and particularly from wastewater is their photocatalytic degradation in the presence of catalyst particles. Among various semiconducting materials (sulfides, oxides, etc.) most attention has been given to TiO_2 due to its high photocatalytic activity, low cost, non-toxicity and high stability in aqueous solution [1,2]. The principles of heterogeneous photocatalysis are based on free-radical reactions initiated by UV light onto a semiconductor surface. These reactions can lead to contaminant degradation of substrate to simpler intermediates, harmless compounds or even to their complete mineralization [1,3–5].

The majority of researchers assume that the photocatalytic degradation of most organic compounds is described by pseudo first-order model [1,2,6,7]:

$$r_i = -\frac{dC_i}{dt} = k_{obs}C_i \tag{1}$$

where r_i is the reaction rate, t is the irradiation time, C_i is the molar concentration of substrate, k_{obs} is the observed (experimental) pseudo first-order reaction rate constant. The integration of Eq. (1) results to the expression:

$$\ln\frac{C}{C_0} = -k_{obs}t \tag{2}$$

where C_0 is the initial concentration of substrate. From Eq. (2) follows a straight-line relationship between $\ln(C/C_0)$ and irradiation time (t). The value of k_{obs} may be determined as a slope this line. Moreover, the k_{obs} is dependent on the initial concentration (C_0) of substrate [7–11].

The step that limits the photocatalytic reactions in the presence of TiO_2 is probably the adsorption of a substrate onto the catalyst surface [6,8,12–14]. The Langmuir-Hinshelwood's expression has been used to describe the reaction kinetics for heterogeneous catalysis with respect to reactions occurring at a solid–liquid surface. This model presents the relationship between the degradation rate and the substrate concentration:

$$r_i = k_{ri}\frac{K_iC_i}{1+\sum_i K_iC_i} \tag{3}$$

where, k_{ri} is the reaction rate constant and K_i is the equilibrium constant for the adsorption of substrate on TiO_2.

In the one-substrate system, for the initial reaction stage we obtained from Eq. (1) and (3) the linear form relationship as follows:

$$\frac{1}{k_{obs}} = \frac{C_0}{k_r} + \frac{1}{k_rK} \tag{4}$$

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Nomenclature

abs	absorbance
C	molar concentration (mmol L^{-1}, mM)
C_0	initial molar concentration (mmol L^{-1}, mM)
I_A	radiation intensity absorbed by catalyst (Einstein s^{-1} m^{-3}, Einstein min^{-1} L^{-1})
I_o	radiation intensity that reaches directly to exposed sample (Einstein s^{-1} m^{-3}, Einstein min^{-1} L^{-1})
I_{oS}	surface intensity of radiation (Einstein s^{-1} m^{-2})
k_{obs}	experimental (observed) rate constant (min^{-1})
k_r	reaction rate constant (min^{-1})
K	adsorption coefficient, constant in Eq. (3)
pH_{pzc}	pH value of zero charge point
r	reactions rate (mol L^{-1} min^{-1}, mM min^{-1})
r_0	initial reactions rate (mol L^{-1} min^{-1}, mM min^{-1})
t	reactions time, irradiation time (min)

Greek letters

ε	molar extinction coefficient ($mmol^{-1}$ L cm^{-1}, mM^{-1} cm^{-1})
λ	wavelength (nm)
φ	quantum yield in Eq. (5)

where r_0 is the initial reaction rate of photodegradation. From Eq. (4) follows that according to L-H theory the inverse of k_{obs} is proportional to C_0.

The experimental data confirmed that in the presence of TiO_2 a photocatalytic reaction rate depends on, among others, the intensity of radiation [15]. In these cases, a radiation intensity that reaches directly to a sample (I_o) is absorbed almost completely by the catalyst due to its high value of absorbance. However, a part of the radiation is also absorbed by the solution (dispersion medium). Therefore the intensity of radiation absorbed by the particles of catalyst (I_A) is lower then I_o.

It is possible that the decrease in the I_A value (due to absorption of part of the radiation in solution) causes decrease in the photodegradation rate. Thereby, the kinetics of photocatalytic reaction in the presence of TiO_2 might also depend on the intensity of radiation absorbed by the illuminated solution.

The kinetics of a photochemical reaction is described by Eq. (5):

$$r = \varphi I_A \tag{5}$$

where φ is the quantum yield of photochemical reactions.

Based on Eq. (5) and the Lambert-Beer law:

$$\text{abs} = \log \frac{I_o}{I_A} \tag{6}$$

it is possible to determine a relationship between r and absorbance (abs) of the used radiation (measured at λ) in irradiated solutions that do not contain the catalyst (after the separation of the catalyst suspension). This relationship can be expressed as follows:

$$\log r = \log I_o\varphi - \text{abs} \tag{7}$$

If the expression ($\log I_o\varphi$) does not depend on the absorbance of irradiated solutions (and the initial concentration of degraded substances), it means that ($-\log r$) is proportional to abs. A similar correlation was shown in the case of many dyes with different chemical structure [16].

Table 2
The comparison of adsorption efficiency and photocatalytic degradation of dyes (0.1 mM) in the presence of TiO_2 (2.5 g L^{-1}, Riedel-de Haën and Degussa)

Dye	Catalysts	pH	Adsorption efficiency (%)	k_{obs} (min^{-1})	$R^{2\,a}$
AB1	TiO_2 (R-H)	5.0	≈0	0.013	0.9996
	TiO_2 (P-25)	4.6	90	0.093[b]	0.9250[b]
AO7	TiO_2 (R-H)	6.9	≈0	0.028	0.9964
	TiO_2 (P-25)	5.2	38	0.035	0.9836
BO66	TiO_2 (R-H)	6.5	13	0.039	0.9964
	TiO_2 (P-25)	5.1	1.5	0.030	0.9985

[a] For linear function $\ln(C/C_0)=f(t)$ and for irradiation time 0–60 min.
[b] For irradiation time 0–20 min.

The aim of our research was to study the influence of catalyst and dye concentration, adsorption on the catalyst surface, volume and absorbance of irradiated solution on the photocatalytic degradation of azo-dyes in the presence of aqueous TiO_2 suspension. The correlation between the photodegradation rate of the investigated compounds, their initial concentrations and absorption of the used radiation by the irradiated solutions was also determined.

2. Experimental

2.1. Reagents

The studies were conducted with use of azo-dyes as model compounds. The dyes were of laboratory reagent grade. Their characteristics are presented in Table 1. None of the investigated dyes underwent photolysis under the experimental conditions. The titanium dioxide powders used as the photocatalyst were purchased from Riedel-de Haën (TiO_2 R-H, anatase, the surface area was 9–11 m^2 g^{-1}, residues on filter >40 μm after dispension in water was <0.02%) and from Degussa (TiO_2 P-25, anatase 80%–rutile 20%, 42.7 m^2 g^{-1}, 10–1000 nm). Doubly distilled water was used throughout this experiment.

Before the irradiation of aqueous dyes solutions containing TiO_2, the samples were only stirred magnetically 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.

No buffer was added into the reaction mixture to avoid the addition anions that may interfere with the processes occurring onto the catalytic surface [17]. For this reason, all experiments were carried out at natural pH of the investigated dyes solutions. It was found that the pH values of samples were within the 6.0–7.5 range, only in the AB1 solution (0.1 mM) pH was 5.0. Detailed data concerning pH selected samples was presented in Table 2. Experimentally, it was stated that in the used pH range, the changes in photodegradation

Table 1
The characteristics of investigated dyes

Dye	Colour index	Chemical formula	Classification	Manufacturer	λ_{max}[a] (nm)	ε[a] (M^{-1} cm^{-1})	Solubility[b] in water (g L^{-1})	Abbreviation in text
Acid Orange 7	C.I. 15510	$C_{16}H_{11}N_2NaO_4S$	Anionic	Fluka	480	18300	116	AO7
Acid Black 1	C.I. 20470	$C_{22}H_{14}N_6Na_2O_9S_2$	Anionic	POCH, Poland	618	15700	10	AB1
Basic Orange 66	–	$C_{20}H_{23}N_3O_5S$	Cationic	Boruta, Poland	480	11400	No data	BO66

[a] Experimentally determined.
[b] On the base of manufacturer data (at 25 °C).

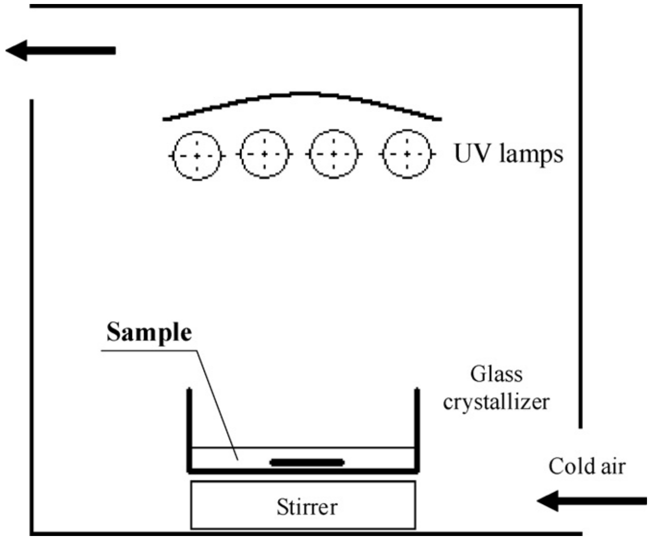

Fig. 1. The scheme of test stand.

rate of dyes caused by differences in the pH values of irradiated samples were <10%.

2.2. Irradiation

The scheme of test stand is showed in Fig. 1.

In all cases during the experiments, the samples containing the appropriate concentration of 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 wavelength at 366 nm. The surface intensity of the radiation (I_{oS}) determined by Parker's actinometer [18] was 8.76×10^{-5} Einstein s^{-1} m^{-2}. The exposed samples surface was 102 cm^2. The reaction temperature was kept at 21 ± 2 °C. During irradiation the solutions had a free contact with atmospheric air but, additionally, were not aerated.

2.3. Analytical methodology

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% (except of experiment that was described in Section 3.3). In order to separate the photocatalyst from the suspension, samples were centrifuged for 30 min at 4000 rpm.

In samples containing only one dye, its concentration (before and after irradiation) was determined according to abs measurement at λ_{max} (Table 1) using UV-VIS spectrophotometer Secomam S 750. During the preliminary studies it was found that the dyes solutions follow the Lambert-Beer law in the used concentration range (Table 2). In these ranges, the correlation coefficients of the calibration curves (R^2) obtained for AO7, AB1 and BO66 were 0.9952, 0.9989 and 0.9982, respectively. The values of the molar extinction coefficient (ε) determined based on calibration curves are presented in Table 1. In this case, the following relationship has been assumed:

$$\frac{\text{abs}}{\text{abs}_0} = \frac{C}{C_0} \qquad (8)$$

The dyes concentrations in samples containing mixtures of AO7 and AB1 were determined using HPLC methods (HPLC Merck Hitachi, detector UV L 7400, λ 254 nm; column SEPARON SGX 7 μm, C-18, 250 mm × 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 366 nm.

A thickness of layer of the irradiated dye solution which absorbed 90% of the radiation at λ 366 nm is established as the effective thickness of the layer. This value was set by extrapolation based on the absorbance measurement of samples containing TiO_2 suspension as well as TiO_2 suspension and dye solution before and after the UV irradiation for 60 min at λ 366 nm. The measurements were made in samples diluted by water in ratio 1:2 in quartz cuvettes with 2 mm optical path length using UV-VIS spectrophotometer Secomam S 750.

In all cases, the pH values were determined by pH meter HD22569.2 (Delta OHM).

2.4. Adsorption

In order to estimate the adsorption efficiency of dyes on the catalysts surface (Riedel-de Haën and Degussa) the absorbance of dyes solutions without TiO_2 and after addition of TiO_2 (2.5 g L^{-1}) and after stirring in darkness for 30 min was measured in the whole range of applied concentrations (at λ_{max} – Table 1). Moreover, in order to separate the photocatalyst from the suspension, samples were centrifuged for 30 min at 4000 rpm. The color of TiO_2 sediment obtained after centrifugation of the samples was also observed. Additionally, in the case of AO7 (C_0 = 0.1 mM) the change in the dye concentration in solution after addition of TiO_2 (Riedel de Haën) was examined after 8 h.

2.5. Point of zero charge

The pH value of the point of zero charge (pH_{pzc}) was determined based on the measurement of flocculation of the TiO_2 suspensions (Riedel-de Haën and Degussa) containing 100 mg L^{-1} TiO_2 in distilled water, in the pH range of 1.3–9.0. The effect of flocculation of suspensions after 60 min of sedimentation were estimated in the way described in the paper of Baran et al. [19].

3. Results and discussion

3.1. Effect of TiO_2 concentration

It is known that TiO_2 concentration in irradiated suspensions has a significant role in the studies concerning the photocatalytic degradation rate [1,6,7]. In order to determinate the optimum TiO_2 (R-H) concentration under conditions used in our studies, the degradation rate of AO7 (0.1 mM) was determined at different TiO_2 (R-H) concentration, from 0 to 3.5 g L^{-1}. The volume of irradiated samples was 100 mL.

It was found that the increase in amount of TiO_2 enhances the initial degradation rate of dye achieving the maximum rate at the TiO_2 concentration equal 2.5 g L^{-1}. Further increase in its concentration did not cause any significant influence in the reaction rate. The plateau, which was observed after addition of a certain amount of TiO_2 may be due to the decrease of light penetration into the solutions (screening effect) [6,20]. Based on these results, the optimum catalyst concentration was estimated as 2.5 g L^{-1}. This concentration was used in further experiments in this study.

3.2. Effect of the thickness of irradiated layer

Bizani et al. [6] and Velegraki et al. [20] described the screening effect accompanying the photocatalytic reactions carried out in the presence of TiO_2 suspension. For this reason, it seems that the thickness of the irradiated layer of dye solution may be also an important factor from the viewpoint of the photodegradation kinetics.

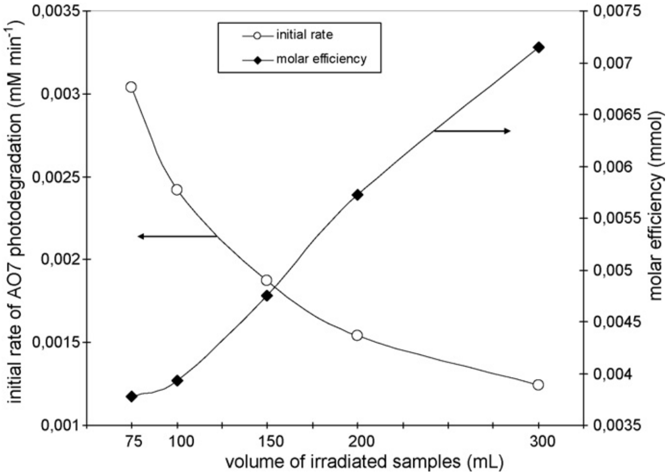

Fig. 2. The relationship between the volume of irradiated solution and the initial rate or the molar efficiency of photocatalytic degradation of AO7 (0.1 mM) in the presence of TiO_2 (2.5 g L^{-1}).

Our experiments were carried out using variable volumes (75–300 mL) of irradiated AO7 solution (0.1 mM) with 2.5 g L^{-1} of TiO_2 (R-H) but maintaining the constant surface of irradiated samples.

As shown in Fig. 2, the increase in the volume of irradiated solution causes the decrease in observed the photocatalytic degradation rate. Moreover, it is a straight-line dependence ($R^2 = 0.9994$) between the inverse of the thickness of irradiated solution layer (in the range 7.6–30.5 mm) versus the photocatalytic degradation rate of dye. This effect may be a consequence of the fact that the reaction proceeds only in a thin, surface layer of solution and may be a testimony to the effect of reciprocal screening of catalyst particles. The effective thickness of layer of the irradiated TiO_2 (R-H) suspension was 0.41 ± 0.02 mm. The dye presented in sample and products its photocatalytic degradation had not a significant influence on the thickness of this layer under investigated conditions. Based on extrapolation of the relationship between the inverse of the thickness of irradiated solution layer versus the photocatalytic degradation rate we estimated that the initial photodegradation rate of AO7 in this layer was about 0.05 mM min^{-1}. However, during irradiation of the solution, the fast decrease in the AO7 concentration causes decrease in the dye degradation and, in consequence, low energy efficiency. The more effective use of the radiant flux may be warranted by continuous influx of the new amounts of dye. This effect can reach using the flow reactors or batch reactors witch intense stirring. In the second case, the optimum reactor volume depends on the fixed irradiation time.

Fig. 2 presents example results showing the influence of the irradiated solution volume in the batch reactor (Fig. 1) on the photocatalytic degradation rate of AO7 and absolute amount of moles of decomposited AO7 (molar efficiency) after 20 min irradiation. From Fig. 2 it is clear that the increase in the volume of irradiated sample causes the decrease in the initial degradation rate of dye and, on the contrary, the increase in the molar efficiency in this process. Therefore, from the viewpoint of efficiency of photocatalytic process (i.e., its rate and yield) there is an optimum volume of irradiated samples. This information should take into account during design the apparatus to photocatalytic process.

In order to eliminate the differences caused by the thickness of irradiated layer of dyes solutions, in all further experiments the volumes of irradiated samples were constant and equal 100 mL.

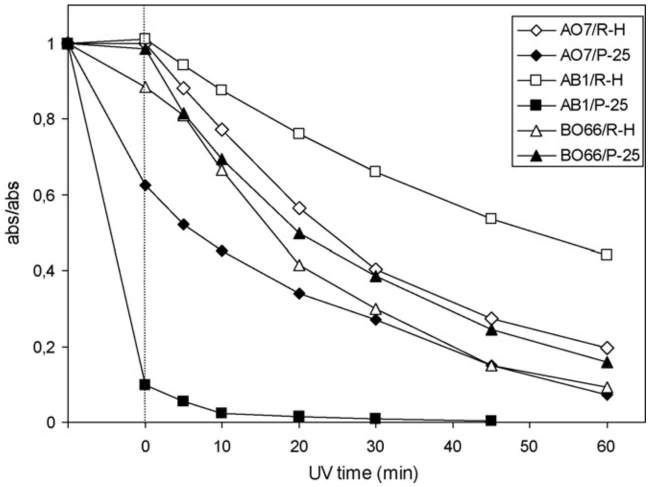

Fig. 3. The change of absorbance (measured at λ_{max}) of dyes solutions ($C_0 = 0.1$ mM) after addition of TiO_2 (2.5 g L^{-1}, Riedel-de Haën and Degussa) and during irradiation in the presence of TiO_2.

3.3. *Comparison of catalysts*

The exemplary changes of the absorbance in dyes solutions measured at their λ_{max} (Table 1) after addition of photocatalysts (before irradiation) and during their irradiation are presented in Fig. 3. The initial concentrations of dyes were 0.1 mM. It was stated that no changes were found in concentrations of two anionic dyes namely AO7 and AB1 after addition of TiO_2 (R-H) but before the irradiation of samples. Moreover, after centrifugation of the non-irradiated samples with dyes the color of TiO_2 (R-H) sediment remained white, same as the color of the TiO_2 (R-H) powder. This implied that an adsorption efficiency of examined anionic dyes onto the used photocatalyst was very low (Table 2). The similar results were observed for the anionic azo-dyes in the whole range of investigated concentrations (Table 3). Only the cationic azo-dye BO66 was adsorbed well onto the TiO_2 (R-H) surface (Table 2). In the range of BO66 concentrations, which were used in further experiments (from 0.012 to 0.128 mM), the adsorption efficiency of dye was changed from 37 to 11%, respectively.

In the case of TiO_2 (R-H), it was found that pH_{pzc} was 3.00 ± 0.05. In turn pH in the dyes samples were always higher than pH_{pzc} for this catalyst (Table 2). Therefore its surface should be negatively polarized:

$$\mathrm{Ti{-}OH_2}^{+} \overset{\mathrm{pH<pH_{pzc}}}{\longleftrightarrow} \mathrm{Ti{-}OH} \overset{\mathrm{pH>pH_{pzc}}}{\longleftrightarrow} \mathrm{TiO^{-}} \tag{9}$$

Probably for this reason the anionic dyes (AO7 and AB1) undergo adsorption onto TiO_2 (R-H) surface with a very low efficiency.

In the case of TiO_2 (P-25) pH_{pzc}, determined in the same way, was 6.26 ± 0.05. In each case in samples containing dyes and this catalyst, pH was lower than pH_{pzc} and in result, the TiO_2 (P-25) surface was positively polarized (Eq. (9)). This fact explains the considerably higher adsorption of anionic dyes and lower adsorption of cationic dye in the presence of TiO_2 (P-25) (Table 2).

It was found that all investigated dyes underwent the photocatalytic degradation (Fig. 3). The decrease in abs of dyes solutions containing TiO_2 during irradiation testifies to this process. In accordance with our assumptions, the photocatalytic degradation rate depended on their adsorption efficiency onto TiO_2. The increase in adsorption efficiency of dyes caused the increase in their photodegradation rate. This fact is in agreement with the heterogeneous catalysis theory (L-H model).

Table 3
The kinetics data of photocatalytic degradation of azo-dyes in the presence of TiO_2 (2.5 g L^{-1}, Riedel-de Haën)

Dye	Range of initial concentration (mM)		Function[a]	R^2	Figures
	Used in study	Applied to L-H theory			
AB1	0.0065–0.10	0.0065–0.0406	$k_{obs}^{-1} = 543.96C_o + 4.1588$	0.9465	4A
AO7	0.015–0.50	0.015–0.30	$k_{obs}^{-1} = 251.55C_o + 8.0454$	0.9922	4B
BO66	0.0060–0.16	0.0060–0.128	$k_{obs}^{-1} = 256.62C_o - 0.4997$	0.9907	4A

[a] For the range of concentration applied to L-H theory.

3.4. Kinetics of photodegradation

Based on the Eqs. (2) and (8), and changes in abs of solutions during their irradiation (Fig. 3), the relationship (10) can be expressed:

$$\ln\left(\frac{\text{abs}}{\text{abs}_o}\right) = -k_{obs}t \tag{10}$$

The straight-line functions with high values of (R^2) were obtained (Table 2). The results confirm that a decrease in the dye concentration in irradiated solutions was followed by the pseudo first-order kinetics. Therefore, the discussed k_{obs} (Table 2) was determined as a slope of linear relationship (Eq. (10)). This method for determination of k_{obs} was used in further steps of the experimental studies. In all cases, the r_0 values were calculated according to Eq. (1).

3.5. Effect of the initial dye concentrations on the experimental rate constant

In order to investigate the influence of initial dyes concentration on the degradation rate, in further experiments the various initial concentrations of solutions were used and the correlation between inverse of k_{obs} and C_0 was also being studied. The C_0 values are showed in Table 3. In all cases, 100 mL dyes solutions containing 2.5 g L^{-1} of TiO_2 (R-H) were irradiated.

The experimental data were plotted as the inverse of experimental rate constant (k_{obs}^{-1}) versus C_0. The results are presented in Fig. 4A (for AB1 and BO66) and in Fig. 4B (for AO7). The linearity of the function:

$$k_{obs}^{-1} = f(C_0) \tag{11}$$

with high values of R^2 was observed for all investigated dyes but only in the limited range of their C_0 (Fig. 4 – dashed line, Table 3). This may be confirmation that kinetics of the examined photocatalytic degradation follows according to the L-H equation (Eq. (4)) but only at low, initial concentrations of dye. At present, this opinion is generally accepted [6–8,12–14]. We have found that when the C_0 of dyes was high, their k_{obs} was significantly lower than that calculated with the L-H equation (Fig. 4 – solid line). These effects were observed in the cases: AB1 at $C_0 \geq 0.0795$ mM, BO66 at $C_0 = 0.160$ mM (Fig. 4A) and AO7 at $C_0 \geq 0.40$ mM (Fig. 4B). It means that after exceeding of a defined, limited concentration of substrate the kinetics of photocatalytic degradation does not fit the L-H model. It is possible that the effect described above is caused by the decrease in the radiation intensity reaching the surface of TiO_2 particles in result the absorption of part of the radiation by dye solution.

3.6. Degradation of dyes in multicomponent solutions

The process of photocatalytic degradation of anionic azo-dyes (AO7 and AB1) was examined in solutions containing the mixtures of these dyes. The range of C_0 used in the investigated mixtures is shown in Table 4. The samples (100 mL) containing 2.5 g L^{-1} of TiO_2 (R-H) and dyes were irradiated in all the experimental runs. In mixtures, the pH values were within the 6.2–6.9 range. In order to eliminate the influence of dyes adsorption onto catalyst surface, the TiO_2 (R-H) and anionic dyes were used in the experiment. In the case of these compounds, the adsorption level was ≈0.

It was found that in the case of mixtures the photocatalytic degradation of dyes follows also the pseudo first-order kinetics. For this reason, for each dye in mixtures the values k_{obs} and r_0 were calculated similarly as in the earlier experiments (Section 3.4). The obtained data showed that the degradation rate of individual dyes in mixture was always lower than in the case of one-substrate mixture (Fig. 5). Fig. 5A shows the effect of the increase in AO7 concentration on the AB1 degradation rate (C_0 AB1 was constant). Fig. 5B shows the effect of the increase in AB1 concentration on the

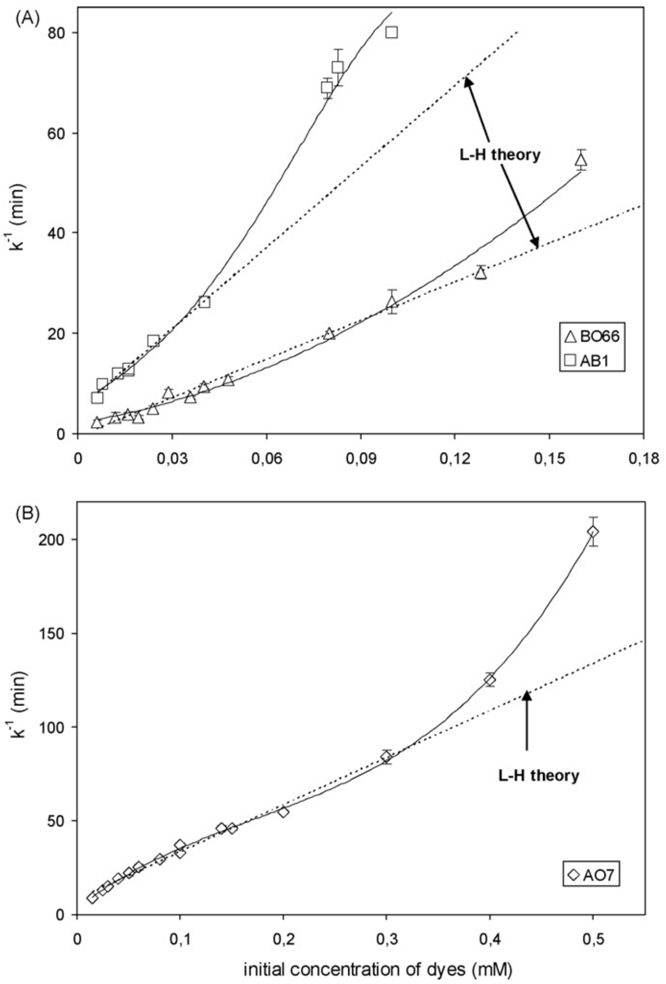

Fig. 4. The influence of initial dyes concentrations on the inverse of photocatalytic degradation rate constants (dashed line is according to L-H model), catalyst: TiO_2 (2.5 g L^{-1}, Riedel-de Haën), pH: 6.0–7.5 only in the AB1 solution (0.1 mM) pH was 5.0.

Table 4
The kinetics data of photocatalytic degradation of mixtures azo-dyes in the presence of TiO_2 (2.5 g L^{-1}, Riedel-de Haën)

Mixture	Initial dye concentration (mM)		Function[a]	R^2	Figures
	AB1	AO7			
Mix I	0.00325	0–0.0429	$\log r = -7.4995\text{abs} - 3.1911$	0.9798	5A, 6A
Mix II	0.00812	0–0.0857	$\log r = -2.9398\text{abs} - 3.0739$	0.9388	5A, 6A
Mix III	0.0162	0–0.0571	$\log r = -2.7034\text{abs} - 2.7463$	0.9709	5A
Mix IV	0–0.024	0.0057	$\log r = -8.8653\text{abs} - 2.6973$	0.9969	5B, 6B
Mix V	0–0.0487	0.0143	$\log r = -3.7955\text{abs} - 2.5755$	0.9903	5B, 6B

[a] abs was measured at 366 nm under the initial experimental conditions.

AO7 degradation rate (C_0 AO7 was constant). According to the L-H theory, the observed effect is connected with the competition both of dyes in mixtures to access to the active centers of catalyst (TiO_2).

Moreover, an alternative interpretation of the obtained experimental data was carried out. We supposed that the important factor that limited the photocatalytic process rate is the absorption of part of the radiation by solution containing degradated substrates. This fact causes the decrease in the radiation intensity reaching to the photocatalyst surface. According to the Lambert-Beer law (Eq. (6)) the intensity of radiation absorbed by catalyst should by exponentially proportional to the absorbance of solution that the radiation passes through. In order to determine the effect of absorbance of irradiated solutions on the photocatalytic reaction kinetics, the degradation dynamics in solutions containing two anionic azo-dyes namely AB1 and AO7 was investigated. In studies, C_0 of first dye was constant while the abs value was modified through the change of second dye concentration (Table 4). The results are presented as a function (12) in Fig. 6 and in Table 4.

$$\log r_0 = f(\text{abs}) \qquad (12)$$

It was found a linear correlation between the $\log r_0$ values of photodegradation individual dyes in the two-component mixtures and the reciprocal values of abs in irradiated solutions (measured at λ 366 nm) (Table 4, Fig. 6). This means that a change of abs in

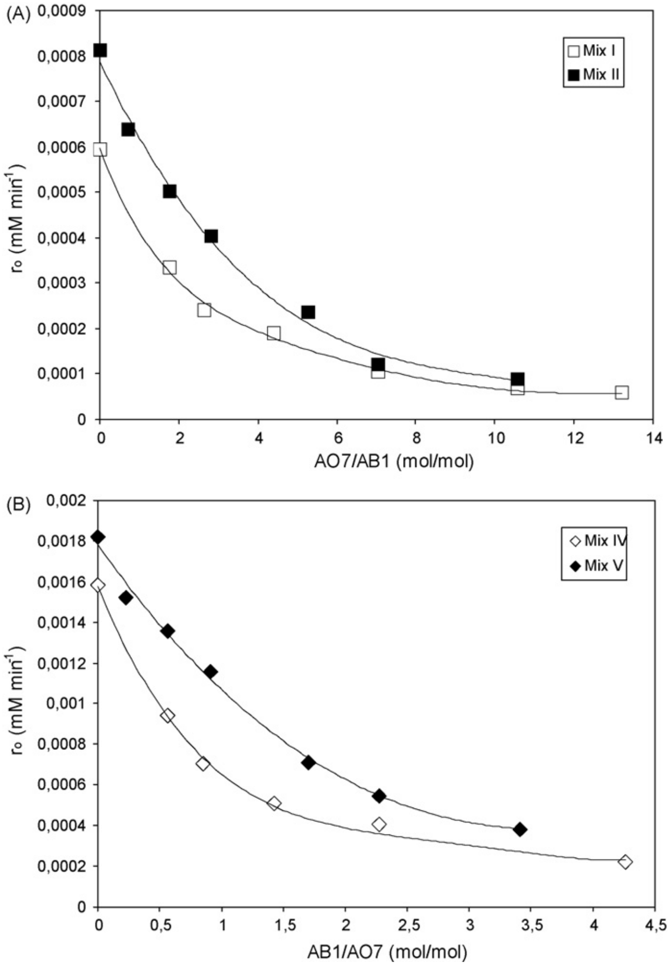

Fig. 5. The influence of AO7 addition on the initial rate of AB1 photocatalytic degradation (A) and AB1 addition on the initial rate of AO7 photocatalytic degradation (B). The dyes concentrations in Mix I–V are presented in Table 4, catalyst: TiO_2 (2.5 g L^{-1}, Riedel-de Haën), pH: 6.2–6.9.

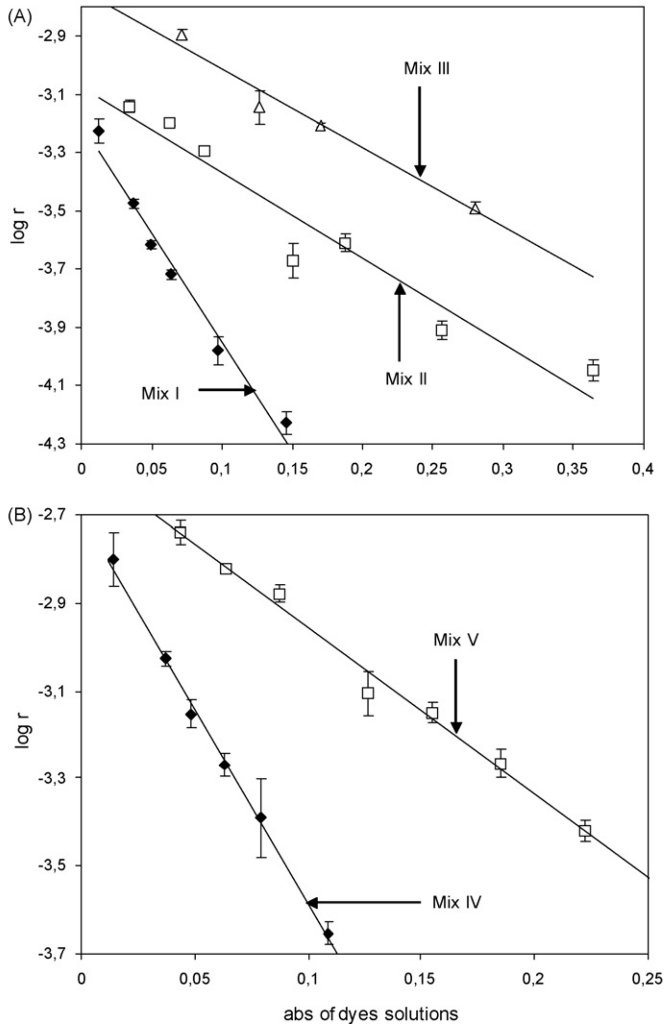

Fig. 6. The influence of absorbance of the irradiated, two-component dyes solutions (measured at λ 366 nm) on the common logarithm of initial rate of the photocatalytic degradation of AB1 (A) and AO7 (B). The dyes concentrations in Mix I–V are presented in Table 4, catalyst: TiO_2 (2.5 g L^{-1}, Riedel-de Haën), pH: 6.2–6.9.

the dyes solution is inversely proportional to observed change of $\log r_0$ value. This fact may confirm that the intensity of radiation reaches a catalyst (I_A) will be decreased if the abs of irradiated solution increases and obviously, the dyes concentration in solution increases. Thus, the photocatalytic degradation rate of dye is correlated with the absorption of radiation by its solution.

The fact, discussed above, is important from a practical viewpoint because it indicates that e.g. the absorbance of sewage should be considered during the designing of photocatalytic degradation process and its optimization.

4. Conclusions

In the photocatalytic processes carried out in the aqueous TiO_2 suspensions the screening effect of the catalyst particles occurs. For this reason, there is an optimum photocatalyst concentration that should be used in the studies concerning the dyes photodegradation. The photocatalytic process occurs only in a thin, surface layer of the irradiated solution. Therefore the increase in the volume irradiated solution causes the decrease in the photocatalytic process rate but simultaneously it leads to the increase of its energy efficiency.

In this study, the dyes photodegradation kinetics in the presence of TiO_2 suspension followed a pseudo first-order kinetics. The adsorption efficiency of dye onto TiO_2 surface has a significant effect on its photodegradation rate that is consistent with the L-H theory. However, this theory is confirmed only in the limited range of the initial concentrations of dyes. The rate of photocatalytic process in solutions containing a high concentration of degraded dyes is slower than come from L-H equation. Probably it is caused by high absorbance of irradiated solutions. There is a linear correlation between the logarithm of the photodegradation rate of dye and the absorbance value of its solution containing mixtures of dyes. Most probably, the results described in this work can generalize to others substances.

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