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The effect of UV radiation absorption of cationic and anionic dye solutions on their photocatalytic degradation in the presence TiO_2

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Abstract

The aim of the study was to examine the correlation between the absorbance of various cationic and anionic dye solutions exposed to UV radiation and their photocatalytic degradation in solution. The dye solutions were illuminated with UV radiation in the presence of a TiO_2 aqueous suspension. Photodegradation rate constant and adsorption efficiency of dyes were determined using spectrophotometric methods.

Only cationic dyes can be adsorbed on the surface of the photocatalyst; simultaneously, their photocatalytic degradation is faster than the degradation of anionic dyes.

The change of the nature of the dye particle from inert to cationic causes intensification of its adsorption and acceleration of photodegradation. There is a linear correlation between the absorbance of the illuminated dye solution and the photodegradation rate constant.

Keywords: Dyes; Photocatalysis; UV/TiO_2; Absorbance; Photodegradation

1. Introduction

Photocatalytic degradation in the presence of TiO_2 is used, for example, in removing dyes from water solutions [1–3] and as a way of determining the resistance of a dye to light [4–6]. Dyes are often used as standard compounds during the examination of modified photocatalyst activity [7–14].

The mechanism of the photocatalytic reaction in the presence of TiO_2 consists of a free radical reaction initiated by UV light. The mechanism may depend on the ability of the degraded compound to be adsorbed on the surface of the catalyst. The extent of such adsorption depends on many factors, such as the charge of the degraded compound. It was found that in photocatalytic degradation, the adsorption level on unmodified TiO_2 is higher for dyes with a positive charge (cationic) than for those with a negative charge (anionic) [12]. As the charge depends on the pH of a given solution, it follows that both pH and the nature of a particular dye influence the photocatalyst activity [2,8,9,15–17]. In spite of the adsorption, the chemical resistance of a dye (which is closely correlated to its structure) significantly influences the susceptibility of a dye to photocatalytic degradation.

The potential effect of degraded dyes on free radical generation is often omitted from the examination of a photocatalytic process. A photochemical reaction rate (r) is proportional to the intensity of light absorbed by a photocatalyst (I_A). The light absorbed by the catalyst is determined by the difference between the light reaching a whole sample (I_o) and the light absorbed by a dye (Fig. 1).

Dyes that intensively absorb UV light may negatively influence the generation of hydroxyl radicals and thus, influence their degradation process. This phenomenon was confirmed by the observed relationship between the absorbance of aqueous solutions of mixtures of C.I. Acid Orange 7 and C.I. Acid Black 1 and degradation rate [18]; this clearly showed that the phenomenon could be a key factor in determining photocatalyst activity, in terms of the quantum yield of photocatalytic reactions and structure/activity relationship.

The aim of this work was to examine the correlation between the absorbance of various cationic and anionic dyes in

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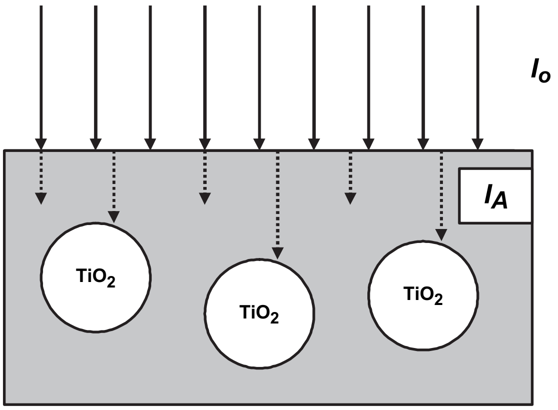

Fig. 1. The absorption of UV radiation in dye solution.

solution when exposed to UV radiation and their photocatalytic degradation.

2. Experimental

2.1. Reagents

The solutions of the dyes shown in Table 1 were prepared by dissolution of 10 mg of dye in 1 dm^3 distilled water (except for Bromocresol Purple and Quinizarine for which solutions of natural pH were used). To the solutions, solid TiO_2 p.a. (2.5 g dm^{-3}, Riedel-de Haën) was added. Before illumination, the solutions were homogenised for 10 min by means of magnetic stirrers.

2.2. Illumination

Samples of dye solutions (100 cm^3) were illuminated by means of 4 UV lamps (Philips TL-40 W/05) of wavelength 366 nm. The intensity of the radiation (I_o), determined by Parker's actinometer, was 8.76×10^{-9} E s^{-1} cm^{-2}. The exposed surface of the samples was 102 cm^2. The solutions were magnetically stirred and had free contact with air. The temperature of the solutions was 21 ± 2 °C.

2.3. Analytical methodology

After a specific time, aliquots of the examined solutions were centrifuged for 30 min at the rate 4000 rpm. The absorbance of the dye solutions before (abs_o) and after (abs) illumination were measured using a Secomam S 750 spectrophotometer; measurements were made in quartz cells at λ_{max} and $\lambda = 366$ nm. The efficiency of photocatalytic degradation was determined from the degradation rate constant which was taken as the slope of

Table 1
Characteristics of investigated dyes

Dye	C.I.	Chemical formula	Classification	Manufacturer
Acid Black 1	20470	$C_{22}H_{14}N_6Na_2O_9S_2$	Azoic-anionic	POCh, Poland
Acid Orange 7	15510	$C_{16}H_{11}N_2NaO_4S$	Azoic-anionic	Fluka
Acid Orange 20	14600	$C_{16}H_{11}N_2NaO_4S$	Azoic-anionic	Boruta, Poland
Acid Red 88	15620	$C_{20}H_{11}N_2Na_3O_{10}S_3$	Azoic-anionic	Zachem, Poland
Acid Yellow 23	19140	$C_{16}H_9N_4Na_3O_9S_2$	Azoic-anionic	Fluka
Direct Yellow 9	19540	$C_{28}H_{19}N_5Na_2O_6S_4$	Azoic-anionic	Fluka
Acid Red 27	16185	$C_{20}H_{11}N_2Na_3O_{10}S_3$	Azoic-anionic	Boruta, Poland
Food Black 1	28440	$C_{28}H_{17}N_5Na_4O_{14}S_4$	Diazoic-anionic	Aldrich
Acid Red 14	14720	$C_{20}H_{12}N_2Na_2O_7S_2$	Azoic-anionic	Aldrich
Acid Red 18	16255	$C_{20}H_{11}N_2Na_3O_{10}S_3$	Azoic-anionic	Aldrich
Food Yellow 3	15985	$C_{16}H_{10}N_2Na_2O_7S_2$	Azoic-anionic	Aldrich
Direct Blue 53	23860	$C_{34}H_{24}N_6Na_4O_{14}S_4$	Diazoic-anionic	Fluka
Direct Red 28	22120	$C_{32}H_{22}N_6Na_2O_6S_2$	Diazoic-anionic	Aldrich
Eriochrome Black T	14645	$C_{20}H_{12}N_3NaO_7S$	Azoic-anionic	POCh, Poland
Reactive Red 45	18206	$C_{27}H_{19}ClN_7Na_3O_{10}S_3$	Azoic-anionic	Boruta, Poland
Mordant Yellow 1	14025	$C_{13}H_8N_3NaO_5$	Azoic-anionic	Fluka
Quinizarine	58050	$C_{14}H_8O_4$	Anthraquinone[a]	Lobachemie
Natural Red 4	75470	$(C_{22}H_{20}O_{13})_2Al$	Anthraquinone-lake	Fluka
Reactive Blue 5	61205	$C_{29}H_{20}ClN_7O_{11}S_3$	Anthraquinone-anionic	Boruta, Poland
Basic Violet 3	42555	$C_{25}H_{30}ClN_3$	Triphenylmethane-cationic	BDH, England
Solvent Red 49	45170	$C_{28}H_{31}ClN_2O_3$	Anthraquinone-cationic	Suchardt
Basic Green 1	42040	$C_{27}H_{30}N_2O_4S$	Triphenylmethane-cationic	Ubichem
Methyl Green	42590	$C_{27}H_{35}Cl_2N_3 \cdot ZnCl_2$	Triphenylmethane-cationic	Gurr
Brilliant Cresyl Blue	51010	$C_{17}H_{20}ClN_3O_{16}Cl \cdot 0.5ZnCl_2$	Cationic	Lobachemie
Basic Orange 2	11270	$C_{12}H_{13}ClN_4$	Azoic-cationic	Fluka
Basic Red 22	11055	$C_{14}H_{21}ClN_6$	Azoic-cationic	Boruta, Poland
Basic Blue 41	11105	$C_{19}H_{23}ClN_4O_2S \cdot 0.5ZnCl_2$	Azoic-cationic	Boruta, Poland
Basic Orange 66	–	$C_{20}H_{23}N_3O_5S$	Azoic-cationic	Boruta, Poland
Basic Yellow 12	–	–	Azoic-cationic	Boruta, Poland
Bromocresol Purple	–	$C_{21}H_{16}Br_2O_5S$	Triphenylmethane[b]	POCh, Poland

[a] Anionic under applied conditions.
[b] Chemical nature dependent on the pH.

a linear function ln abs/abs$_o$ = $f(t)$. The adsorption efficiency of the dyes onto the TiO_2 surface was examined in solution after homogenization but before they were exposed to UV.

3. Results and discussion

The regression curves presented in Figs. 2 and 3 were generated omitting the results of the AQ dyes Quinizarine, C.I. Natural Red 4, C.I. Reactive Blue 5 and C.I. Solvent Red 49, because these dyes were characterized by a significantly higher resistance to photocatalytic process than the other dyes (Table 2).

It was found that TiO_2 adsorbed almost only cationic dyes, except for the anionic Quinizarine – adsorption efficiency of 21.8% and the cationic C.I. Basic Orange 2 which displayed no adsorption. This fact can be explained in relation to the surface structure of TiO_2. On the surface of unmodified crystal TiO_2, mainly oxygen atoms with a high electron density (negative centers) are present. Thus, the TiO_2 particles have a negative charge and should, therefore, more readily adsorb cationic molecules. The highest values of photocatalytic degradation rate constant were observed for cationic dyes (Table 2). These results confirm our expectations and the hypothesis that dye adsorption has a significant effect on its susceptibility to photocatalytic degradation. However, there was no correlation between adsorption efficiency and the values of the photodegradation rate constant (Fig. 2). It might be possible to find such correlation after collecting sufficient experimental data; Bromocresol Purple was one of the dyes chosen for this purpose. Its degradation was performed at pH 4.5 and 8.0; under acidic conditions, the molecule has a positive charge. As a result, after the solution was acidified from pH 8.0 to pH 4.5, a 6-fold increase in adsorption efficacy was observed. Such an increase in adsorption efficacy could not be explained only through changes of the TiO_2 surface (probably caused by a change of pH [19]). Hence, the observed increase was caused by a change in the charge of the Bromocresol Purple. The simultaneous, significant increase (4-fold) of dye degradation rate (Table 2) may indicate that pH change might also influence dye photodegradation. Unfortunately such an easy way to accelerate photocatalysis is impossible to achieve in the case of anionic dyes. The unavoidable increase in acidity will coagulate the photocatalyst and decrease its activity.

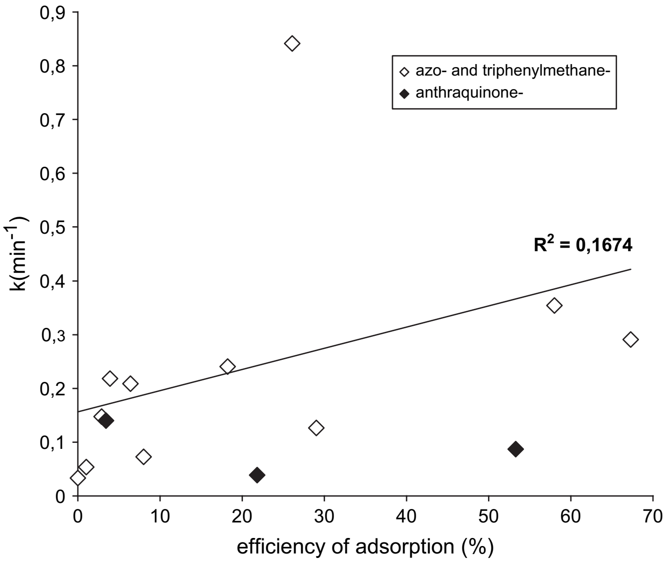

Fig. 2. The effect of adsorption efficiency of dyes on the photocatalytic degradation rate.

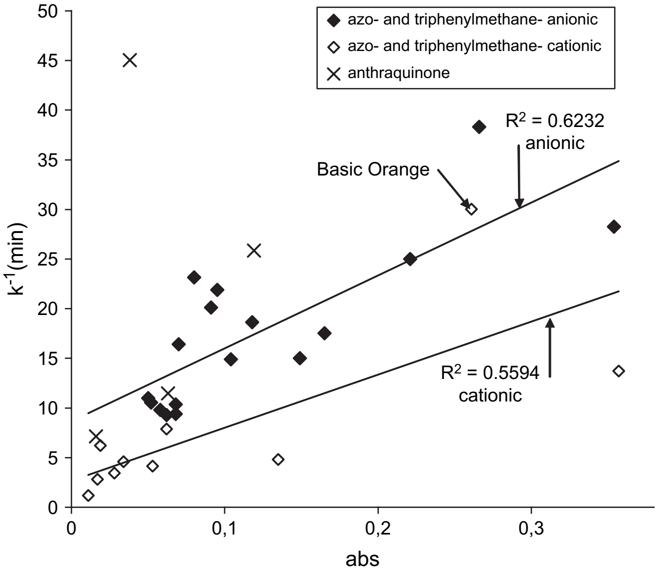

Fig. 3. Correlation between absorbance (λ 366 nm) of dye solutions and rate constant of their photocatalytic degradation.

In our previous work [18], a linear correlation between the absorbance of illuminated solution and the inverse values of photodegradation rate constant of the dyes present in the solution was found. In this work it was possible to verify this hypothesis.

The linear correlation between the absorbance of dye solutions (both cationic and anionic) measured at 366 nm and inverse values of their photocatalytic degradation rate constant was found (Fig. 3). The obtained determination coefficient (R^2) values were 0.5594 for the cationic dyes and 0.6232 for the anionic ones. The regression equations are $k^{-1} = 53.439$ abs + 2.662 and $k^{-1} = 73.429$ abs + 8.6767, respectively. If only the results for the cationic dyes absorbed onto the TiO_2 surface are analysed (omitting the results of C.I. Basic Orange 2), the R^2 value would be 0.7493.

The obtained results confirm the theory presented inSection 1 that the radiation absorption by an illuminated dye solution (expressed as the absorbance of the solution) negatively influences the observed photocatalytic activity of TiO_2. This characteristic of a solution (other than catalyst) should be considered during the examination of photocatalyst activity and quantum yield calculations.

4. Conclusions

There is a linear correlation between absorbance of illuminated solution of dyes and reverse values of the dyes'

Table 2
Results of investigated dyes' adsorption and photodegradation

Dye	Initial concentration (mM)	abs$_o$ (λ 366 nm)	Efficiency of adsorption on TiO_2 (%)	k (min^{-1})	R^2
Acid Black 1	0.016	0.068	Not observed	0.0967	0.9735
Acid Orange 7	0.030	0.104	Not observed	0.0671	0.9130
Acid Orange 20	0.0286	0.068	Not observed	0.1063	0.9709
Acid Red 88	0.0166	0.058	Not observed	0.1022	0.9729
Acid Yellow 23	0.0187	0.221	Not observed	0.040	0.9894
Direct Yellow 9	0.0144	0.165	Not observed	0.0571	0.9495
Acid Red 27	0.0165	0.050	Not observed	0.0911	0.9004
Food Black 1	0.0115	0.080	Not observed	0.0432	0.9407
Acid Red 14	0.0199	0.062	Not observed	0.1076	0.9600
Acid Red 18	0.0165	0.052	Not observed	0.0948	0.9642
Food Yellow 3	0.0221	0.095	Not observed	0.0457	0.9845
Direct Blue 53	0.0104	0.091	Not observed	0.0497	0.9839
Direct Red 28	0.0144	0.266	Not observed	0.0261	0.9656
Eriochrome Black T	0.0217	0.149	Not observed	0.0666	0.9954
Reactive Red 45	0.0131	0.070	Not observed	0.0609	0.9342
Mordant Yellow 1	0.0323	0.354	Not observed	0.0354	0.9513
Quinizarine	0.0417	0.119	21.8	0.0387	0.9739
Natural Red 4	0.0099	0.063	53.3[a]	0.0873	0.8490
Reactive Blue 5	0.0129	0.038	Not observed	0.0222	0.9879
Basic Violet 3	0.0245	0.062	29	0.1267	0.9758
Solvent Red 49	0.0209	0.016	3.4	0.1399	0.9702
Basic Green 1	0.0207	0.034	3.9	0.2179	0.9980
Methyl Green	0.0164	0.017	58	0.354	0.9413
Brilliant Cresyl Blue	0.0259	0.028	67.3	0.2912	0.9580
Basic Orange 2	0.0402	0.261	Not observed	0.0333	0.9837
Basic Red 22	0.0266	0.019	2.9	0.1606	0.9957
Basic Blue 41	0.0211	0.011	26.1	0.8413	0.9779
Basic Orange 66	0.024	0.053	18.2	0.2408	0.9646
Basic Yellow 12	–	0.357	8	0.0728	0.9592
Bromocresol Purple, pH = 4.5	0.0185	0.135	6.4	0.2085	0.9869
Bromocresol Purple, pH = 8.0		0.118	~1	0.0536	0.9978

[a] Dye partly insoluble in water (suspension).

photodegradation rate constant. Only cationic dyes can be adsorbed on the surface of the photocatalyst. Simultaneously, their photocatalytic degradation is faster than that of anionic dyes.

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