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Photobleaching and photomineralization of azobenzene and substituted azobenzenes in aqueous solution by photocatalytic membranes immobilizing titanium dioxide [1]

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Abstract

The kinetics of photobleaching (by spectrophotometric analysis) and integral photomineralization (by total organic carbon (TOC) analysis) of azobenzene (**I**) and substituted azobenzenes in aqueous solution were followed in laboratory-scale runs on photocatalytic membranes immobilizing 30 ± 3 wt.% of semiconductor TiO_2. Experiments were carried out by the technique described in preceding papers of this series, employing stoichiometric hydrogen peroxide as the oxygen donor. The following azobenzenes were examined: (4-diethylamino)-phenylazobenzene (**II**), 4'-(((4-diethylamino)phenyl)azo) benzoic acid (**III**), 4'-(((2-amino-5-diethylamino)phenyl)azo) benzoic acid (**IV**), 4'-(((2-acetamido-4-diethylamino)phenyl)azo) benzoic acid (**V**), 4'-(((4-dimethylamino)phenyl)azo) benzenesulphonic acid, sodium salt (**VI**) and 4'-(((2-acetamido-4-diethylamino)phenyl)azo) benzenesulphonic acid, sodium salt (**VII**). From the Langmuir–Hinshelwood treatment of the initial rate data as a function of the initial concentration ($((0.10–1.0)\times10^{-3}$ M), the kinetic parameter k and the pseudo-thermodynamic parameter K for photobleaching were obtained.

With regard to photobleaching, **I** and **II** were certainly the most reactive, followed by **IV**. The remaining molecules showed a photo-oxidation rate of one-third to one-quarter of that of **I** chosen as reference structure. Consequently, the presence of an amino group in the 4-position (**II**) does not stabilize the azobenzene structure against photo-oxidation leading to bleaching, whereas the same group in the 2-position (**IV**) decreases the photobleaching rate by about 40% when a carboxylic group is also present in the 1'-position. Acetylation of this amino group, such as in **V**, decreases the photobleaching rate more markedly.

With regard to photomineralization, it was observed that, when photobleaching was virtually complete, a certain amount of TOC was already mineralized. The maximum amount of TOC remaining at the end of photobleaching ranged from about 90% to about 30%, varying with the dye structure and initial concentration as well as with the power and type of irradiation source.

By examining the TOC concentration profiles as a function of the substituted azobenzene structure, the following hypotheses were proposed:

1. during the photobleaching period, the ring containing the diethylamino group breaks down (more markedly if further amino or acetamido groups are present in the structure), and photomineralization of the other ring occurs more slowly;
2. both rings break down, within certain limits, during photobleaching; however, the aliphatic fragments containing carboxyl or sulphonic groups are mineralized more slowly.

The fact that a small initial plateau in the TOC profile is followed by another more evident plateau at the end of the photobleaching period, for both **VI** and **VII**, suggests that hypothesis (1) is more probable in these cases. When the second plateau is reduced to a sigmoidal curve or an inflection point, hypothesis (2) also needs to be considered.

Keywords: Azo dyes; Photobleaching; Photocatalytic membranes; Photomineralization; Titanium dioxide

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1. Introduction

The widespread interest in azo dyes is due to many factors. Firstly, they represent the largest class of dyes used in industry, being valuable for polyesters in view of their ready availability, cheapness and good stability towards both light and oxidation [1,2]. Furthermore, they have found extensive application in analytical chemistry as acid–base, redox and metallochromic indicators. They are of interest from a theoretical aspect in view of the sensitivity of their physical and chemical properties to changes in the substituents and medium, as well as other perturbing agents [1,3]. From the

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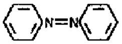
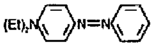
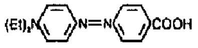
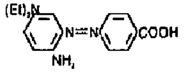
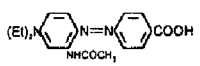
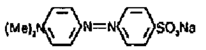
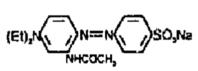
environmental viewpoint, it is estimated that 10%–15% of the dye is lost during the dyeing process and is released as effluent, being resistant to aerobic degradation [4]. The hazard represented by the potential for azo dyes to be reduced under anaerobic conditions, as well as in mammals, to carcinogenic aromatic amines has been highlighted [5].

With regard to the treatment methods for dye elimination from wastewater, it has been reported [5] that flocculation with lime or activated carbon adsorption require costly disposal technologies, and biotreatment, due to the resistance of the dyes to aerobic biodegradation, is unlikely to be effective. A detailed study has been carried out recently [5] to examine the suitability of the Fenton process for the advanced oxidation of some model azo dyes. A probable mechanism for the generation of aromatic byproducts in this process, where the degradation of azo dyes with a phenylazo substituent is performed, has been suggested [5].

Advanced oxidation processes generally include the addition of oxidizing agents, such as hydrogen peroxide, ozone or oxygen, in the presence of a catalyst or UV radiation or both. From earlier technologies based on the use of Fenton's reagent, these have led to photocatalytic oxidation, mostly with a freely suspended semiconductor photocatalyst, such as TiO_2, or with the photocatalyst immobilized in thin films [6]. Photocatalytic methods, based on the use of suspended TiO_2, have been extensively applied mainly to the photobleaching step of azo dyes, without following their mineralization [7–14]. A marked and decisive advancement was achieved [15–22] by immobilization of the TiO_2 semiconductor in microporous membranes, prepared by photografting onto suitable supports. This approach has allowed the transformation of a photocatalytic process into a reliable technology.

In this paper, a laboratory-scale study of photobleaching is described. Also considered is the successive integral photomineralization of azobenzene and substituted azobenzenes, the structures of which are reported in Table 1. The approach involves the examination of the respective kinetics in order to determine the classical Langmuir–Hinshelwood parameters and to provide information on the rates of breakdown relative to that of azobenzene considered as the reference structure.

Table 1
Structural formulae and IUPAC names of azobenzene and substituted azobenzenes employed in the photobleaching and photomineralization experiments (concentration range, (0.10–1.0) × 10^{-3} M)

Dye	Structural formula	IUPAC name
I		azobenzene
II		(4-diethylamino) phenyl-azobenzene
III		4'(((4-diethylamino) phenyl)azo)benzoic acid
IV		4'(((2-amino, 5-diethylamino) phenyl)azo)benzoic acid
V		4'(((2-acetamido, 4-diethylamino) phenyl)azo)benzoic acid
VI		4'(((4-dimethylamino) phenyl)azo)benzene sulphonic acid,sodium salt
VII		4'(((2-acetamido, 4-diethylamino) phenyl)azo)benzene sulphonic acid,sodium salt

2. Experimental details

2.1. Materials

Azobenzene (I) and 4'-(((4-dimethylamino)phenyl)-azo) benzenesulphonic acid, sodium salt (VI) were obtained from Fluka (Switzerland) (purity, greater than 99.5%). These were used as received. The other substituted azobenzenes (II–V and VII) (see Table 1) were supplied by ACNA S.p.A. (Milan, Italy). They were purified by repeated crystallization from 1-butanol [23,24]. Due to the differences in structure and solubility, solutions in bidistilled water were prepared by adding 0.001 M Na_2HPO_4 and 0.001 M NaH_2PO_4 buffer, or 1 N HCl, to obtain clear solutions. For I and III–VII, the pH was 8.0±0.1 in the kinetic runs; for I, further addition of 2 M KCl and 2 h sonication at 60 °C were necessary to reach the optimal conditions of solubility in the range of concentrations examined. For II, the pH was 2.0±0.1. No satisfactory solubility could be obtained for the latter at higher pH values. The concentrations tested in the kinetic runs were kept constant for all of the dyes in the range (0.10–1.0) × 10^{-3} M.

2.2. Photocatalytic membranes

The photocatalytic membranes supplied by Chimia Prodotti e Processi, Milan, I were standard membranes immobilizing 30±3 wt.% TiO_2 without any photocatalytic promoter (used and described in previous studies [16]).

2.3. Apparatus and procedures

The laboratory-scale reactor was the same as that described in Ref. [16]. It could be equipped with either a 500 W medium-pressure mercury arc lamp, for which the polychromatic spectrum below 400 nm corresponded to an emitted energy of 145±5 W (obtained actinometrically) or a 20 W low-pressure mercury arc lamp, which emitted, monochromatically, 8±1 W at 254 nm, in the absorption range of the semiconductor. Given the overall energy output of the medium-pressure lamp and the refrigerating water flow in the reactor jacket, the temperature of the photoreactor could be well regulated at 313±2 K when employing this radiation source. When using the low-pressure lamp, no cooling was necessary, and the temperature was 296±2 K. In all of the kinetic runs, the volume of solution treated was kept constant (4.00 l).

The zero-order initial rate of photobleaching (r_0) was evaluated from curves of the concentration of the dye vs. time, determined spectrophotometrically, in the initial linear range. Experiments were repeated for each set of conditions, essentially for each value of the initial concentration C_0 of the dye, so that the mean initial rate and its standard deviation could be estimated. The usual Langmuir–Hinshelwood kinetic rate law, combining the apparent adsorption equilibrium constant (K) and the apparent zero-order surface reaction constant (k) in the initial stage of photodegradation (Eq. (1)), was used

$$1/r_0 = (1/k) + (1/kKC_0) \qquad (1)$$

Eq. (1) was used to obtain the values of k and K for the photobleaching step.

The total organic carbon (TOC) disappearance was followed by TOC analysis, carried out by a Shimadzu TOC 5000 instrument, from which the contribution of inorganic carbon was evaluated (TOC was obtained from the difference between the total carbon and inorganic carbon determinations). Information on the rate was obtained by comparing the TOC values remaining at the end of photobleaching for the various substrates, as well as the half-times $t_{1/2}$ corresponding to 50% mineralization of TOC.

3. Results and discussion

The initial rate of photobleaching of azobenzenes **I**–**VII** in aqueous solution (structural formulae in Table 1) was studied as a function of the initial concentration of the substrate using the linearized form of the Langmuir–Hinshelwood equation (Eq. (1)) during both monochromatic and polychromatic irradiation. The k and K parameters of Eq. (1), obtained by regression analysis of the experimental data, are reported in Table 2.

For **I**, the K parameter is not dependent on the radiation intensity or wavelength. This behaviour was also observed in the study on trichloroethene [16]. For all the other substrates, however, the larger (**IV**, **V** and **VII**) or smaller (**III** and **VI**) K values obtained are influenced by the radiation wavelength and/or intensity. The latter type of behaviour seems to be the most general [20–22]. This, together with the experimental evidence of a critical K dependence on the flow rate [20], suggests the abandonment of the concept of the truly physical meaning of the adsorption constant for the K parameter. A kinetic significance, as proposed [25] on the basis of kinetic models, is justified. Strictly speaking, the dependence of K on the wavelength and/or radiation intensity may be explained, alternatively, in terms of the photoadsorption of substrates, intermediates, products and/or radical species.

Table 2
Parameters k and K of the Langmuir–Hinshelwood equation (Eq. (1)) for the photobleaching of **I**–**VII** by monochromatic irradiation (254 nm) at 296±2 K and by polychromatic irradiation at 313±2 K. Uncertainties, expressed as probable errors, were obtained by the theory of error transmission

Dye (see Table 1)	$k \times 10^5$ (mol min^{-1})	$K \times 10^{-4}$ (l mol^{-1})
Monochromatic irradiation		
I	4.2±0.2	0.63±0.03
II	4.2±0.2	0.85±0.04
III	1.4±0.3	0.42±0.02
IV	2.4±0.7	3.7±0.3
V	1.1±0.1	15±2
VI	1.1±0.1	0.53±0.03
VII	1.2±0.4	16±2
Polychromatic irradiation		
I	18±1	0.64±0.04
II	–	–
III	5.9±0.4	0.65±0.05
IV	10±1	0.65±0.07
V	4.0±0.2	1.1±0.1
VI	5.2±0.3	0.92±0.07
VII	6.1±0.4	0.63±0.06

This is because the dependence of K on the concentration of hydrogen peroxide (oxygen donor) [16,20] may be interpreted in terms of competitive adsorption. However, it is hard to rationalize the dependence of a purely thermodynamic parameter on the flow rate.

In order to compare the experimental results, reactivity ratios R were calculated. These were defined as the ratios of the initial rates of photobleaching of **II**–**VII**, expressed by the respective k values, to that of **I**, considered as the most easily photodegradable reference structure. This corresponds to the calculation and evaluation of the reactivity ratios at "infinite" concentration of substrate, i.e. concentrations of the order of 10^{-2} M or higher. The R values are given in Table 3.

It can be readily observed that, within experimental uncertainty, there is practically no difference in behaviour between monochromatic and polychromatic irradiation. Furthermore, the following conclusions may be drawn concerning photobleaching.

Table 3
Reactivity ratios R between the k values related to the photobleaching of **II**–**VII** and of **I** for the two irradiation conditions (monochromatic, within the range of semiconductor absorption, and polychromatic)

Dye (see Table 1)	Monochromatic irradiation R	Polychromatic irradiation R
II	0.96	–
III	0.33	0.33
IV	0.57	0.56
V	0.26	0.22
VI	0.26	0.29
VII	0.29	0.34

1. Substrate **II** has substantially the same photobleaching rate as that of azobenzene. This assertion must be treated with caution, however, as **II** was the only molecule examined at a pH different from that of all the other azo compounds. The influence of pH on the rate has not been ascertained for any of the investigated substrates.
2. Substrate **IV**, with a rate about 40% less than that of **I**, is the most reactive compound after **I**.
3. A carboxyl group in the 1′-position (**III**), a sulphonic group in the 1′-position (**VI**), a further acetamido group in the 2-position in addition to the sulphonic group in the 1′-position (**VII**) and a further acetamido group in the 2-position in addition to the carboxyl group in the 1′-position (**V**) affect the photobleaching rate, decreasing it by about the same amount (from one-quarter to one-third) with respect to **I** (if, as described above, the dialkylamino group in the 4-position (**II**) has the same photobleaching activity as **I**). This results in an indirect confirmation of (1) above. The presence of a further acetamido group in the 2-position does not seem to exert any clearly appreciable stabilizing or destabilizing influence on the dye structure, with respect to photobleaching, outside a small experimental uncertainty (cf. **III** with **V** or **VI** with **VII** in Table 3). Consequently, the strongest influence on the stabilization of the dye structure against bleaching through photo-oxidation is exercised by the carboxyl group or the sulphonic group in the 1′-position.
4. The presence of an amino group in the 2-position (**IV**), compared with its acetyl derivative, appears to destabilize the dye structure, as it leads to a decrease in the photobleaching rate (see (2) above) with respect to **I** less than that induced in **V** (if the effect of the diethylamino group in the 5-position is comparable with that of the same substituent in the 4-position). Acetylation of the 2-amino group (**V**) leads to a sensible decrease in the photobleaching rate. Thus stabilization of the dye structure occurs.

From the environmental viewpoint, the overall photomineralization is much more important than bleaching. It was found that, at the end of the bleaching period, a certain amount of TOC was already mineralized, as shown by the data in Table 4 in which the half-times $t_{1/2}$ of photomineralization are reported.

Typical profiles of TOC vs. time, such as that illustrated in Fig. 1 for **VI**, show that the concentration of TOC remains practically constant for a small interval of time, at the beginning of the photodegradation experiments, during which photobleaching occurs. TOC then decreases with progressive bleaching. At the end of bleaching, the TOC values, shown in Table 4, are less than those present initially, with a maximum amount of residual TOC ranging from about 90% to about 30% for **VI** on polychromatic irradiation. A further TOC plateau is then observed (see Fig. 1), which finally gives rise to a decrease until mineralization is complete. This second plateau is not always evident as shown in Fig. 1. Depending on the dye structure and concentration, the plot sometimes appears to be sigmoidal with an inflection point.

Table 4
Total organic carbon (TOC (%)) remaining in kinetic runs at the end of photobleaching of **I–VII**, expressed as a percentage of that initially present (at initial concentration C_0 of substrate). Half-times $t_{1/2}$ (min) corresponding to 50% mineralization of TOC as a function of the initial concentrations C_0 of the substrates

Dye (see Table 1)	C_0 (mol l^{-1}) $\times 10^4$	TOC (%)	$t_{1/2}$ (min)
Monochromatic irradiation			
I	1.0	83 ± 4	210 ± 15
	3.0	87 ± 4	275 ± 26
II	1.0	69 ± 5	135 ± 9
III	3.0	68 ± 5	500 ± 45
	10	40 ± 4	1100 ± 100
IV	3.0	55 ± 5	214 ± 16
	10	48 ± 7	456 ± 58
V	1.0	48 ± 7	170 ± 20
	3.0	41 ± 8	230 ± 25
VI	1.0	71 ± 6	–
	3.0	66 ± 5	–
VII	1.0	91 ± 15	186 ± 69
	3.0	72 ± 12	422 ± 65
Polychromatic irradiation			
I	1.0	81 ± 9	82 ± 8
	3.0	88 ± 9	109 ± 12
II	–	–	–
III	1.0	56 ± 5	44 ± 5
	3.0	51 ± 4	66 ± 9
	10	31 ± 4	102 ± 14
IV	1.0	68 ± 5	35 ± 6
	3.0	48 ± 4	48 ± 8
	10	37 ± 3	92 ± 9
V	1.0	45 ± 4	32 ± 4
	3.0	42 ± 3	41 ± 5
	10	42 ± 4	79 ± 8
VI	1.0	89 ± 7	35 ± 6
	3.0	43 ± 4	53 ± 7
	10	29 ± 3	108 ± 15
VII	1.0	84 ± 7	59 ± 8
	3.0	73 ± 6	75 ± 9
	10	62 ± 5	148 ± 24

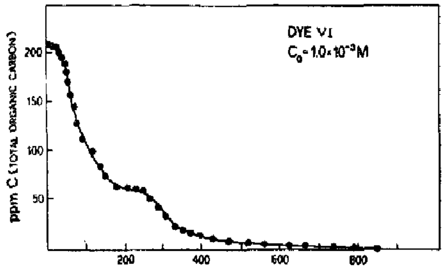


Fig. 1. Profile of total organic carbon (TOC, ppm) vs. time (min) during photobleaching and photomineralization of a 1.0×10^{-3} M aqueous solution of 4′-(((4-dimethylamino)phenyl)azo) benzenesulphonic acid, sodium salt (**VI**, see Table 1 for structural formula) on a photocatalytic membrane immobilizing 30 wt.% of titanium dioxide semiconductor, irradiated polychromatically, in the presence of stoichiometric hydrogen peroxide as oxygen donor.

The TOC plateau or inflection point, corresponding to a decrease in rate, indicates that hydroxylation (reaction with hydroxyl radicals) of a chemical group, such as an aromatic ring, is taking place. This event does not result in a decrease in the organic carbon content of the resulting intermediates, or an increase in the production of carbon dioxide. The experimental observations can be interpreted as follows.

1. During the photobleaching period, the aromatic ring containing the dialkylamino group, and predominantly this ring only, breaks down into fragments. If a hydrogen atom of this ring is substituted by an amino or acetamido group, the rate of TOC decrease during this period is even more marked. This is shown by the residual TOC values in Table 4 for **IV**, **V** and **VII**. Photomineralization of the other ring occurs more slowly.
2. Both of the aromatic rings of the azobenzene structure begin to break down during the photobleaching period. However, certain aliphatic intermediates (probably those containing carboxyl or sulphonic groups) are photomineralized more slowly.

Interpretation (1) is probably closer to the truth for substrates showing a second TOC plateau, relatively persistent with time, such as **VI** (see Fig. 1) or **VII** and, less markedly, **IV** and **V**. When the second TOC plateau of the mineralization profile, such as that in Fig. 1, is reduced to an inflection point, mechanism (2) should also be taken into account. The general dependences of the TOC values remaining at the end of bleaching and the $t_{1/2}$ values on the initial concentration of the dye and type of irradiation (see Table 4) indicate the necessity of considering the role of both mechanisms as a function of the dye substituent and experimental conditions.

The risk that benzene may result from hydroxyl radical attack of azo dyes containing phenylazo substituents in advanced oxidation processes [5] does not appear to be a real problem for the process investigated in this paper, in which the residual organic carbon may be reduced to as low a value as desired, even if the starting substrate is aromatic [15,19,20]. This has been shown not only for benzene, toluene and phenols, but also for molecules much more toxic than benzene itself, such as pentachlorophenol, which has been smoothly and fully mineralized to carbon dioxide, chloride ions and water without any inconvenience [26] with quantum yields of up to 31% of the maximum allowable. In the present work, no evidence of incomplete mineralization was observed for any of the dyes tested.

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