

# Photocatalytic Activity of Immobilized Nano-TiO<sub>2</sub> in Complex Wastewaters: Case Study of Multiple Dye Composition

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## ABSTRACT

Titanium dioxide (TiO<sub>2</sub>) is widely investigated for its photocatalytic properties and for the possibility of obtaining nanotubular oxide films with high specific surface area directly immobilized on a substrate.

In the present work, nanotubular TiO<sub>2</sub> was obtained through anodization of titanium in ethylene glycol-based electrolyte. Photodegradation tests were performed with four different organic dyes, i.e. Rhodamine B, Methylene Blue, Direct Red 80 and Acid Orange 7. Single dye solutions and binary solutions were tested under a UV lamp for six hours. The results show that, after 6 hours irradiation, most dyes are degraded by almost 90%, confirming that nanotubular TiO<sub>2</sub> can be well-exploited as a photocatalyst both for single dye and for binary solutions.

Furthermore, dyes can degrade with different kinetics depending on the type of solution in which they are mixed, and absorbance spectra of different mixed dyes can overlap, showing the necessity of more advanced analyses.

**Keywords:** Titanium dioxide, anatase, photocatalysis, dyes, nanotubes.

natural water bodies. Particularly, dyes are considered a harmful waste product due to their interference with the photosynthetic activity and their chelation with metal ions which can produce micro-toxicity to flora and fauna [3].

At the moment, few studies have been performed on the photocatalytic properties of titanium dioxide for the degradation of dye mixtures that can approach the chemical complexity of textile wastewaters.

Here we present an analysis of the photocatalytic properties of nanotubular titanium dioxide arrays for the degradation of solutions containing different organic dyes.

Acid Orange 7, Direct Red 80, Methylene Blue and Rhodamine B were chosen as reference dyes since they represent a class of pollutants largely used by textile industries. Moreover, their photodegradation process can be easily monitored through spectrophotometric analyses, allowing a simple control of the variation of dye concentration inside the solution, which is a valid estimation of the photocatalysis efficiency [1,4].

Single dye solutions and binary solutions were tested in order to analyze the behavior of different dyes in different environments, allowing to understand how their mixing can affect the photocatalytic process.

## 1 INTRODUCTION

Titanium dioxide has attracted an increasing scientific attention for wastewater treatments through photocatalytic processes, that is the capability of TiO<sub>2</sub> to generate radical species able to degrade both organic and inorganic pollutants by means of light-produced charge carriers [1,2].

Anodization of titanium in a fluoride-containing organic electrolyte leads to the formation of nanotubular oxide films, allowing to obtain photocatalytic nanostructures with high specific surface area directly immobilized on a substrate, hence avoiding the drawbacks of suspended titanium dioxide powders, such as possible agglomeration and the necessary step of water filtration after photocatalysis [1,2].

Photocatalytic properties of titanium dioxide can be highly exploited for purification of textile waste effluents, since these are mixtures of pigments, dyes, organic compounds (such as cleaning solvents) and heavy metals that significantly contribute to the environmental pollution of

## 2 EXPERIMENTAL

Experimental tests were performed on 3x3 cm<sup>2</sup> titanium grade 2 sheets polished with P600 SiC abrasive paper. After an ultrasonic cleaning treatment in EtOH for 5 minutes, each sample was anodized in an ethylene glycol-based electrolyte (0.2 M of NH<sub>4</sub>F and 2 M of H<sub>2</sub>O) at 45 V for 30 minutes in potentiostatic conditions, as reported in previous work [4]. Subsequently, annealing process was performed at 500 °C for two hours, in order to induce the crystallization of the nanotubular array to the photoactive anatase structure. SEM was performed with a Cambridge Instruments Stereoscan 360. X-ray diffraction was performed with a Panalytical Empyrean diffractometer using CuK<sub>α</sub> and CuK<sub>β</sub> radiations.

Degradation tests of different dyes were performed over 6 hours by using a batch reactor built during the experimental stage, made of a sample immersed in a beaker containing 40 ml of the tested solution, a UV LED (Nichia NCSU033B with emission peak at 365 nm) having a distance of 3.5 cm

from the sample, and a stirring system to obtain a homogeneous concentration of the dye in the solution.

The photocatalytic efficiency was evaluated through the measurement of the dye absorbance in correspondence of the maximum peak in the visible light range with a spectrophotometer ThermoScientific® SPECTRONIC 200; the decrease of the dye absorbance  $A$  can be associated to a decrease in its concentration  $C$ , as set out by Beer Lambert law:

$$A = \varepsilon l C \quad (1)$$

where  $\varepsilon$  is the molar attenuation coefficient of the evaluated dye and  $l$  is the optical path. Data were then used to calculate the reaction rate constant  $k$ , considering a first order Langmuir-Hinshelwood kinetic model:

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (2)$$

where  $C_0$  is the initial dye concentration and  $t$  the reaction time.

Photodegradation tests were performed by using four different organic dyes: Acid Orange 7 (AO7,  $C_{16}H_{11}N_2NaO_4S$ ), Direct Red 80 (DR80,  $C_{45}H_{26}N_{10}Na_6O_{21}S_6$ ), Methylene Blue (MB,  $C_{16}H_{18}ClN_3S$ ) and Rhodamine B (RhB,  $C_{28}H_{31}ClN_2O_3$ ), diluted in distilled water (pH 6). Four single dye solutions, characterized by same initial absorbance, were tested to verify the degradation of the single molecules in presence of nanotubular  $TiO_2$ ; their absorbance spectra in the range of visible light, together with the peak position, are shown in Figure 1. Six binary solutions were also tested, obtained by mixing the same single dye solutions at 50/50 percentage in volume, so that the concentration of each dye in the binary solution is halved with respect to the single dye solution one; the wavelengths exploited for the analysis of the single dye photocatalytic degradation (Figure 1) were used for binary solutions too. Each test has been performed three times to ensure good reliability of the results.

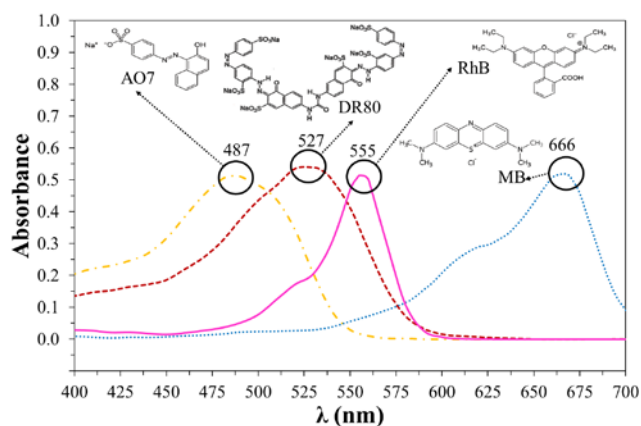


Figure 1: Absorbance spectra of the single dye solutions.

### 3 RESULTS

Firstly, characterization of the samples through SEM and XRD analyses was performed in order to evaluate the oxide morphology and the crystal structure, confirming the formation of a nanotubular oxide layer via anodization. XRD analyses allowed to identify the anatase phase which is fundamental for an efficient photocatalytic process.

Since several specimens anodized with same parameters were used during the experimental part, analyses were carried out to evaluate sample reproducibility by measuring the nominal surface area of each sample with ImageJ software. The results showed a maximum discrepancy of 4% with respect to the theoretical surface area ( $9 \text{ cm}^2$ ) and a standard deviation of  $0.17 \text{ cm}^2$ . Furthermore, photodegradation tests repeated on both the same sample and on different samples anodized in identical conditions showed only slight variation in the measured photoactivity, not depending on the tested specimen but rather on the experimental setup, proving that small differences in nominal surface area or oxide morphology among the tested samples can be considered negligible.

For all the evaluated single dye solutions the linearity between absorbance and dye concentration, hypothesized by applying Beer Lambert law, was experimentally confirmed by the calibration curves (Figure 2) which were fitted with a linear trend line, showing  $R^2$  values always higher than 0.998 (AO7:  $y = 0.0196x + 0.0162$ ; DR80:  $y = 0.0878x + 0.0156$ ; MB:  $y = 0.0617x + 0.0227$ ; RhB:  $y = 0.1012x + 0.0146$ ).

Finally, six-hours degradation tests in dark room were performed in order to evaluate the possible occurrence of dye adsorption on the  $TiO_2$  surface. Results showed that dye adsorbance can be considered negligible, being generally lower than 5%. Considering that the  $TiO_2$  point of zero charge lies in the pH range of 4.5-7.0 [1] and that tests were carried out at pH 6, these tests confirm that interactions between dyes and photocatalyst are minimal due to negligible electrostatic force.

The reaction rate constants of single dye solutions subjected to photocatalysis and to photolysis are shown in Figure 3. Photolysis tests were carried out in order to evaluate the decrease in dye concentration in the absence of the photocatalyst; the resulting reaction rate values showed negligible values with respect to the overall photodegradation process, so that photolysis effects could be considered negligible in single dye solutions. Tests were repeated in binary dye solutions, giving analogous results.

In all the evaluated conditions, nanotubular  $TiO_2$  provided good photocatalytic activity, leading to an overall dye photodegradation higher than 97% (100% for RhB and MB).

It is possible to appreciate the difference in the photocatalytic activity among dyes by comparing the reaction rates; this behavior can be related to the dye structure. Particularly, Muthukumar *et al.* [5] reported that an increase in the number of azo groups significantly affects the photocatalytic degradation, so that their increase involves

longer discoloration time. Moreover, the authors have noticed that the higher the number of sulphonic acid groups, the lower is the degradation time, due to an increase in dye solubility which favors its interaction with photogenerated radicals. This can explain the lower degradation rate of AO7 with respect to DR80, since this has a ratio of sulphonic acid groups over the azo groups (6:4) higher than AO7 (1:1).

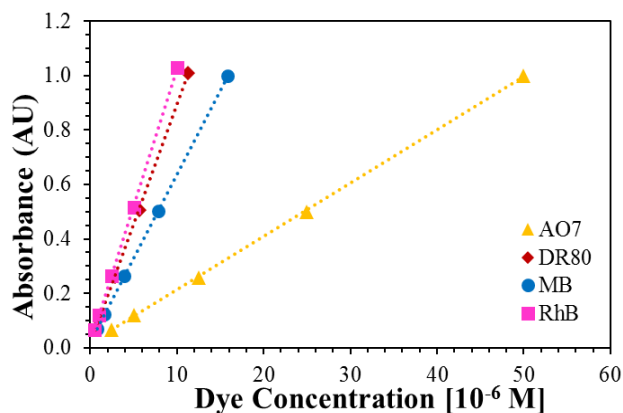


Figure 2: Calibration curves for dyes in single dye solutions.

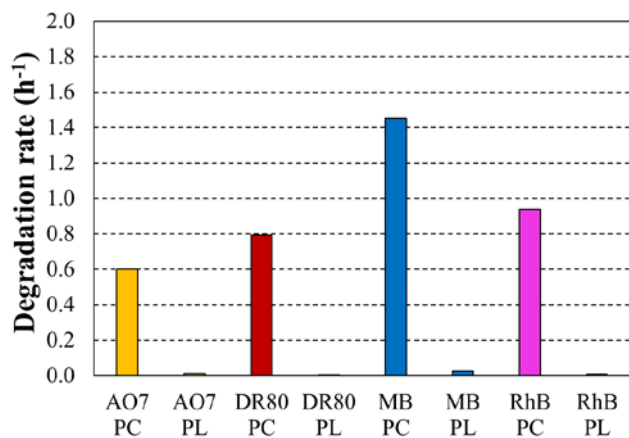


Figure 3: Degradation rate of single dye solutions subjected to photocatalysis (PC) and photolysis (PL).

Furthermore, RhB and MB structures do not show any azo groups, which explain their higher degradation rate.

It can also be noted that MB has a significantly higher reaction rate compared to the RhB one. This can be related to the presence of the MB functional groups  $-C=S$  and  $-C=N$  that can favor the bond cleavage [6].

Subsequently, binary solutions were tested for the evaluation of the titanium dioxide photocatalytic properties in presence of two dyes (Figure 4). Degradation percentages, and corresponding reaction rates, were obtained by measuring the absorbance variation at the same wavelengths used for single dye ones.

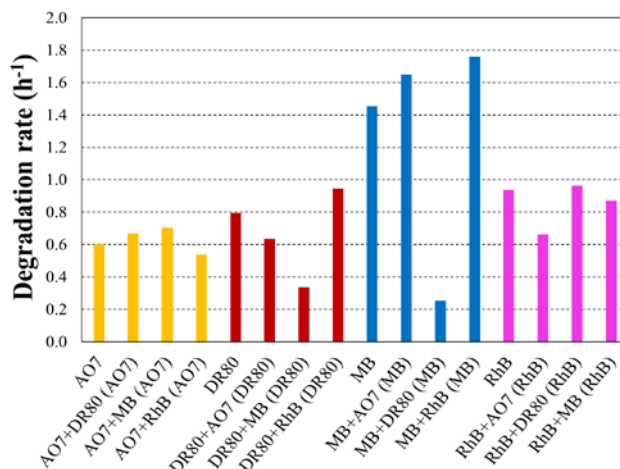


Figure 4: Photocatalytic degradation rate of binary solutions.

It was noticed that, in most cases, the presence of two dyes at the same time did not affect significantly the degradation rate of each dye: in almost all the binary solutions, nanotubular  $TiO_2$  provided photocatalytic activity analogous to that shown in single dye solutions, with MB which confirms to be the most reactive dye in both single and binary solutions, with the single exception of the MB+DR80 solution that will be discussed in the following.

On the other hand, AO7 seems to be the dye that less changes its activity when mixed with the other ones. Considering its behavior in single dyes and binary solutions, its photodegradation rate is not strongly affected by the presence of other dyes, even if it is possible to see a slight increase in presence of MB (16% faster) and a slight decrease if mixed with RhB (10% slower). The same behavior can be noticed if MB degradation in MB + AO7 solution or the RhB one in RhB + AO7 solution are considered (MB is 14% faster and RhB is 29% slower in AO7 containing solutions). This can be related to interactions and adsorbance competition among different dyes on the photocatalyst surface; however, it must be pointed out that these variations do not drastically affect the photodegradation efficiency, since in most cases it is higher than 97%.

The only significant exception to this behavior is given by DR80 + MB binary solutions, in which a drastic decrease in degradation rate for both MB and DR80 was observed (82% and 58% decrease, respectively), leading to lower photodegradation efficiencies.

Different considerations must be done for the explanation of this unexpected behavior. Although dye concentration may affect the solution pH, in the range of work this effect should be discarded, as also confirmed by other binary dye mixtures with same DR80 or MB concentration where no drop in photocatalytic activity was noticed. On the other hand, the formation of a complex between the two dyes, very resistant to photodegradation, could lead to such a large suppression of degradation rate; this hypothesis needs experimental verification.

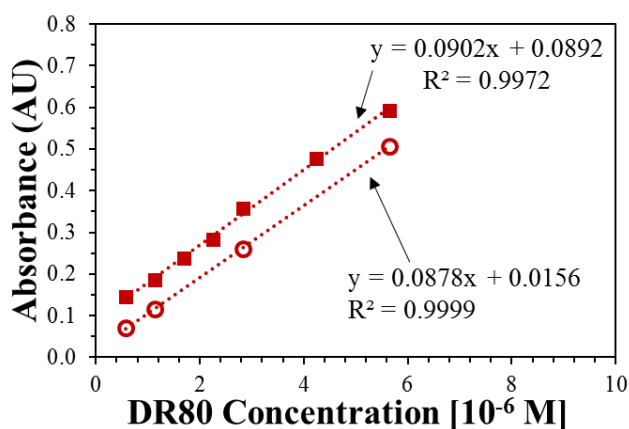


Figure 5: Calibration curves for DR80 in single dye (red, empty dot) and RhB-containing binary (full-colored red square) solution.

Lastly, it should be considered that mixing of dyes whose absorption spectra partially overlap may lead to issues in degradation evaluations. This is particularly evident for DR80 and RhB in their binary mixture. Figure 5 reports the calibration curves for DR80 both in a single dye solution and in the RhB-containing binary one. It is possible to see that, even if they show a comparable slope (0.0902 and 0.0878 respectively for binary and single dye solution) and a high  $R^2$  value, the binary solution trend line has intercept on the Y-axis different from zero, which does not comply with Beer Lambert law, where absorbance and concentration should show a direct linear proportionality without extra correction terms – i.e., in absence of dye ( $C = 0$ ) absorbance should also be nil ( $A = 0$ ).

Hence, due to spectra overlapping, the evaluation of the actual concentration of each dye in a binary mixture is not possible, since the measured absorbance value is given by the sum of the contributions of the two dyes, reducing the accuracy of the used method for the evaluation of the photodegradation rate. This can be noticed by evaluating the number of moles in the solutions before the photodegradation test and after 4 hours of UV exposure (Table 5).

Table 1: Mole variations inside DR80 and RhB single dye solutions and in DR80 + RhB binary solution.

Solution	Initial Moles [ $\cdot 10^{-6}$ mol]	Consumed moles after 4 hours [ $\cdot 10^{-6}$ mol]
Direct Red 80	0.23	0.23
Rhodamine B	0.2	0.19
DR80 + RhB	0.2 (0.11 of DR80 + 0.09 of RhB)	0.16 (not distinguishable)

While in single dye solutions we reach 100% and 95% photodegradation efficiency for DR80 and RhB, respectively, in the case of binary solution the number of consumed moles leads to a lower overall activity, since both dyes are measured on a same peak and therefore it is

impossible to distinguish between the single dye contribution to absorbance, and hence to degradation. Therefore, this method is not suitable for the evaluation of photocatalytic degradation of multiple dye solutions when the dyes involved have overlapping peaks.

## 4 CONCLUSIONS

Here we presented possible application of nanotubular titanium dioxide arrays for the photodegradation of solutions containing different organic dyes.

In general, the obtained results show that most dyes are degraded by almost 90% with good reaction rates, confirming that nanotubular  $\text{TiO}_2$  can be well – exploited as a photocatalyst both for single dye solutions and for binary solutions. In most cases, dyes degrade with similar kinetics in single or binary solutions, which enables the use of simpler single dye degradation tests to evaluate a dye suitability to photocatalytic degradation. Yet, in few cases – for instance, MB/DR mixtures – the co-presence of more than one dye inhibits overall efficiency. This means that the interaction between different dyes inside a solution can affect the overall kinetics of the photodegradation process, which needs to be taken into account in order to transfer this technology from laboratory experiments to field applications.

A limit of the evaluation method presented was found, i.e., the impossibility to distinguish single dyes degradation in mixtures containing dyes whose absorbance spectra overlap, such as RhB and DR80 ones: this can lead to inaccurate analyses of the degradation rate.

Further analyses are suggested in order both to investigate the nature of chemical interactions between dyes and to study the overlapped spectra through different mathematical approaches.

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