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A spectroscopic study of dyes decomposition by irradiated nanocrystalline TiO₂

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Abstract. The photocatalytic activity of the TiO₂ films prepared by wet-chemical techniques and deposited on the ITO glass was tested by examining the decomposition of violet gentian (VG), methylen blue (MB) and methyl green (MG) aqueous solutions under UV light illumination. The photodegradation processes of dyes have been studied using UV–VIS spectrophotometry and spectrofluorimetry. The comparative results of the present study demonstrate the capability of UV irradiation of the TiO₂/ITO photocatalytic system to degrade studied organic dyes from aqueous solutions.

1. Introduction
Paper, textile, cosmetics, ink, ceramic, leather, food processing produces a large volume of dyes in wastewater. These dyes create human health and environmental pollution problems by releasing toxic substances into the aqueous phase, with carcinogenic potential [1].

Heterogeneous photocatalysis processes are one of the most efficient methods for destroying organic pollutants in aqueous media [2,3]. Recently, titanium dioxide is considered an excellent inorganic photocatalyst used in the advanced oxidation process for degradation of a number of different dyes by TiO₂ under UV irradiation [4].

In the present study, it was evaluated the photocatalytic degradation of triphenylmethane dye (violet gentian), tetramethylthionine chloride (methylene blue) and pyronin (methyl green) by the TiO₂/ITO photocatalytic system under the UV light by measuring the degradation rate of dye aqueous solutions.

2. Experimental
2.1. Materials and procedures
Titania P-25 (ca. 80% anatase, 20% rutile) was kindly supplied by Degussa AG, Germany. The TiO₂ colloidal suspensions were prepared via wet-chemical techniques, using bi-distilled water, acetyl acetone (Merck, Germany), poly-propylene-glycol (Machery-Nagel, Germany) and Triton X-100 (Fluka, Switzerland) as additives [5]. Each sample (name samples NTC1, NTC2 and NTC3) was spread on a conductive indium tin oxide glass (ITO, 20 Ω/square) with Triton X-100 as the binder and then was dried in normal conditions and fired at 600°C in air for 90 min, with an increase rate of temperature of 5°C/min.
Violet gentian (Loba Chemie Fischamend, Austria), methylene blue (Fluka, Switzerland) and methyl green (May & Baker LTD, England) were used without any further purification. Solutions containing $3 \times 10^{-5}$ M of every studied dyes in bi-distilled water were prepared by dissolution.

2.2. Instruments
Optical characteristics of TiO$_2$ and the dyes solutions were examined with UV–VIS spectrophotometer and spectrofluorimeter. UV–VIS absorption spectra of the as-prepared photocatalysts were taken on a JASCO V-550 spectrometer. The fluorescence spectra were obtained using an ABL&Jasco V 6500 spectrofluorimeter with xenon lamp.

2.3. Irradiation experiments
The photocatalytic degradation of violet gentian (VG), methylene blue (MB) and methyl green (MG) aqueous solutions $3 \times 10^{-5}$ M have been studied in the presence of TiO$_2$/ITO photocatalytic system illuminated with a UV-Hg lamp (100 mW/cm$^2$) under continuous magnetic stirring. The reaction was performed in normal conditions. A 100 ml of dye solution was added in the photocatalytic system. Dye solutions samples were taken at different time intervals and were investigated by UV absorption spectroscopy. The irradiation time $t$ was: 0, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200 min.

The dyes degradation ratio was defined by the following formula (1):

$$\text{degradation\%} = \frac{\text{ABS}_0 - \text{ABS}_t}{\text{ABS}_0} \times 100$$

where: $[\text{ABS}_0]$ is the initial absorbance of dyes; $[\text{ABS}_t]$ is the absorbance of dyes on time $t$.

3. Results and discussion
3.1. UV–VIS spectra
Figure 1 shows UV–VIS absorption spectra of the TiO$_2$/ITO photocatalytic system and UV–VIS absorption spectra for dye solutions, before UV irradiation and after irradiation time $t = 200$ min.

![Absorption spectra](image)

**Figure 1.** Absorption spectra of TiO$_2$ films and dye aqueous solutions. a) before irradiation. b) after irradiation time $t = 200$ min.
From figure 1 it can be seen that one absorbance peak (about 310 nm) appears for all of three TiO$_2$ films. After irradiation it was observed any peak displacements in UV-VIS spectra.

VG dye shows absorption peaks at 248.0 nm and 303.1 nm in UV region and one absorption peak at 590 nm in visible region. MB dye shows absorption peaks at 248.0 nm and 293.5 nm in UV region and one absorption peak at 664.3 nm in visible region. Also MG dye has an absorption peaks at 248 nm and 291.7 nm in UV region and one absorption peak at 525.8 nm in visible region. After irradiation no significant changes has been observed in the UV-VIS spectra of the dye aqueous solutions.

Figure 2 shows absorption changes when the dye aqueous solutions were degraded by the TiO$_2$ photocatalytic films. However, it is clear that a total degradation needs a longer reaction time.

![Figure 2. Absorbance time dependence under UV light irradiation of dye aqueous solutions (3 x 10$^{-5}$M).](image)

### 3.2. Spectrofluorimetry spectra

The photodegradation processes of dyes have been studied using spectrofluorimetry as well.

Figure 3a shows the spectrofluorimetric spectra of TiO$_2$ films before UV irradiation. Fluorescence spectra of the TiO$_2$ films are similar (fluorescence maxima 349-354 nm, excitation 318-333 nm). Figure 3b shows the spectrofluorimetric spectra of TiO$_2$ films after the contact of the dyes aqueous solutions under UV light.

The fluorescence excitation wavelengths and the fluorescence emission maxima of the TiO$_2$ films after irradiation are presented in table 1.

| Probe | Excitation wavelength [nm] | Emission maxima [nm] |
|-------|----------------------------|----------------------|
| NTC 1 – VG | 309 | 328.6; 345.9; 424.2; 469.1 |
| NTC 2 – MB  | 316 | 343.5; 385.2; 414.9; 485.7 |
| NTC 3 – MG | 305 | 335.5; 392.9; 416.5; 463.5 |

### 3.3. Study degradation ratio of the dyes

Degradation efficiency of TiO$_2$/ITO photocatalytic system for the investigated dyes, evaluated with formula (1) is presented in figure 4. The catalytic activity after 200 min irradiation time followed the decreasing order 31.5%>28.8%>13.1%.
Figure 3. Spectrofluorimetric spectra of TiO$_2$ films. a) before irradiation; b) after irradiation time $t = 200$ min.

![Spectrofluorimetric spectra of TiO$_2$ films](image)

Figure 4. Degradation efficiency VG, MB and MG aqueous solutions with TiO$_2$ catalyst.

![Degradation efficiency](image)

4. Conclusions
Experimental results indicated that the degradation of VG, MB and MG dyes increased with increasing the irradiation time. Fluorescence of the active fluorescent dyes at excitation at the UV-VIS maxima absorption was put also into evidence.

The results of the present study demonstrate the capability of TiO$_2$/ITO photocatalytic system under UV irradiation to degrade the same organic dyes.

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