

# Photocatalytic Degradation of Tebuconazole Fungicide using Palygorskite-TiO<sub>2</sub> Nanocomposites.

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## Abstract

In our study a combination of Palygorskite clay mineral with TiO<sub>2</sub> nanoparticles used for the decomposition of the common tebuconazole (TEB), C<sub>16</sub>H<sub>22</sub>ClN<sub>3</sub>O, [(RS)-1-p-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)-pentan-3-ol], fungicide in water. For this purpose, Palygorskite-TiO<sub>2</sub> nanocomposites fabricated using the sol-gel process combined with hydrothermal treatment of the samples under mild conditions. The Palygorskite-TiO<sub>2</sub> nanocomposites were characterized by X-Ray diffraction (XRD), scanning electron microscopy (SEM), and N<sub>2</sub> specific surface area (SSA) analysis by BET. The total pore volume and SBET was 0.49 cm<sup>3</sup>/g and 258 m<sup>2</sup>/g for the Palygorskite 40% - TiO<sub>2</sub> 60% sample. The Palygorskite 10% - TiO<sub>2</sub> 90% sample has 0.33 cm<sup>3</sup>/g and 220 m<sup>2</sup>/g pore volume and SBET respectively. The highest degradation efficiency 88.4% was achieved for Palygorskite 40% - TiO<sub>2</sub> 60% sample while commercial TiO<sub>2</sub> nanopowder Degussa P25 sample exhibited 33.0% degradation efficiency which is much lower.

The Palygorskite-TiO<sub>2</sub> nanocomposites show that they are effective and promising new class of materials for the photocatalytic degradation of TEB fungicide in water.

**Keywords:** Fungicides, Photocatalysis, Palygorskite, TiO<sub>2</sub>, Nanocomposites

## 1. Introduction

Photocatalysis is a well-known methodology used for the degradation of pesticides and has been applied for the decomposition of these persistent pollutants. In much research, TiO<sub>2</sub> nanomaterials have been used as effective photocatalyst to degrade organic pollutants using solar light irradiation (Konstantinou and Albanis 2003). Tebuconazole (TEB), C<sub>16</sub>H<sub>22</sub>ClN<sub>3</sub>O, [(RS)-1-p-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)-pentan-3-ol], is a bio-refractory organic contaminant with toxic levels up to 18.72 µg/L in natural waters (Stamatis et.al., 2015). TEB decomposition was not effective using conventional techniques, however advanced oxidation technologies can be applied for the destruction of this fungicide.

Degradation of TEB has been achieved with success during the past using TiO<sub>2</sub> as the photocatalyst (Stamatis et.al., 2015), however new class of materials combined clay minerals with TiO<sub>2</sub> showed much promising results (Panagiotaras et.al., 2018).

**Table 1.** Structural characteristics of photocatalysts used.

Sample	Abbreviation	Total Pore volume (cm <sup>3</sup> /g)	SBET (m <sup>2</sup> /g)
Degussa	P25	0.24	49
Palygorskite	Pal	0.87	293
Palygorskite 40% - TiO <sub>2</sub> 60%	Pal 1	0.49	258
Palygorskite 10% - TiO <sub>2</sub> 90%	Pal 2	0.33	220

In this sense, we fabricated clay mineral Palygorskite/TiO<sub>2</sub> nanocomposites in order to use them for the photocatalytic destruction of TEB in water.

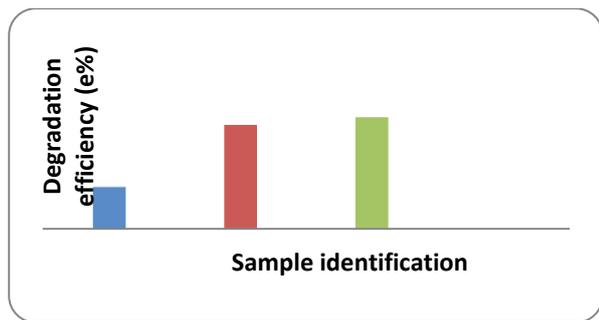
## 2. Methodology, Results and Discussion

### 2.1. Materials Synthesis and Methodology

Palygorskite rich samples were collected from Venzia continental basin, in western Macedonia, Greece. The Palygorskite-TiO<sub>2</sub> nanocomposites fabricated following the methodology reported by Papoulis, et.al., 2013. The Palygorskite-TiO<sub>2</sub> nanocomposites characterized by X-Ray diffraction (XRD), scanning electron microscopy (SEM), and N<sub>2</sub> specific surface area (SSA) analysis by BET and the results are presented in Table 1. For the photocatalytic tests, the methodology and operational parameters used were the same by those reported from Panagiotaras et.al., 2018.

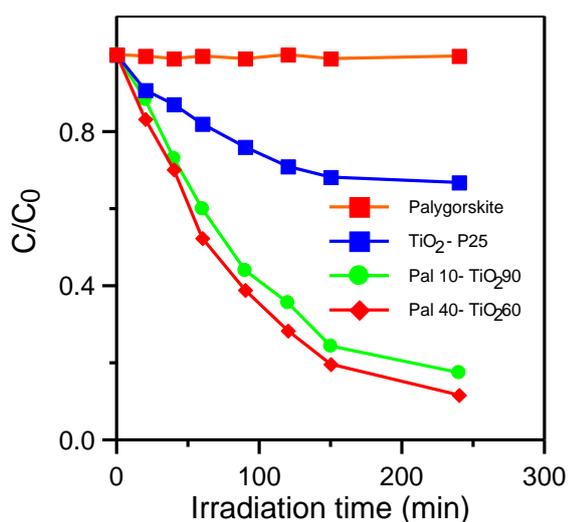
## 2.2. Results and Discussion

The results show that anatase was well fabricated on the palygorskite nanofibers.



**Figure 1.** Degradation efficiency (e%) of all samples were used.

The total pore volume of both palygorskite-TiO<sub>2</sub> samples is higher than Degussa P25. Furthermore, the specific surface area (SSA) of both palygorskite-TiO<sub>2</sub> nanocomposites is also higher than Degussa P25 (Table 1).



**Figure 2.** TEB decomposition with time of irradiation in the presence of various photocatalysts.

In order to estimate the photo-decomposition rate ( $r$ ) of TEB fungicide we employed the following equation:

$$r = (C_0 - C) / C_0$$

Where  $C_0$  is the initial concentration of the pollutant measured in solution and  $C$  is the final concentration after irradiation with UV light. Then we can calculate the decomposition efficiency (e%) as:

$$e\% = [(C_0 - C) / C_0] \times 100\%$$

As we expected, the pristine palygorskite sample did not perform any photocatalytic effect to the TEB fungicide. In addition, the palygorskite 10%-TiO<sub>2</sub> 90% sample shows better decomposition efficiency than Degussa P25 but not very good dispersion of the TiO<sub>2</sub> photocatalyst on the palygorskite nanofibers (Fig. 1).

The Degussa P25 decomposition efficiency reaches a maximum of 33.0% after 240 minutes of irradiation, while the palygorskite 10% - TiO<sub>2</sub> 90% nanocomposite shows 82.5% degradation efficiency at the same period of time. After 150 minutes of illumination no change was observed for the photo-degradation of TEB in all samples studied (Fig. 2).

## 3. Conclusions

In this study we have examined the photocatalytic performance of new Palygorskite-TiO<sub>2</sub> nanocomposites. We synthesized Palygorskite 10%-TiO<sub>2</sub> 90% and Palygorskite 40%-TiO<sub>2</sub> 60% nanocomposites. The decomposition efficiency of Degussa P25, Palygorskite 40%-TiO<sub>2</sub> 60% and Palygorskite 10%-TiO<sub>2</sub> 90% was 33.0%, 88.4% and 82.5% respectively. In addition, the maximum 88.4% of Tebuconazole content has been decomposed within the first 150 minutes under UV irradiation while no further photocatalytic activity was observed after that point.

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