Use of Halloysite-TiO$_2$ Nanocomposites for the Decomposition of Tebuconazole Fungicide in Water

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Abstract

In this study we present halloysite clay mineral combined with TiO$_2$, as promising new class of nanomaterials that can be used as an effective, cost efficient and environmental friendly methodology for the decomposition of Tebuconazole, C$_{16}$H$_{22}$ClN$_3$O, [(RS)-1-p-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)-pentan-3-ol], TEB-fungicide, in water. For this purpose halloysite-TiO$_2$ nanoparticles were fabricated using the sol-gel methodology combined with hydrothermal treatment of the samples in mild conditions. The halloysite-TiO$_2$ nanocomposites are characterized by X-Ray diffraction (XRD), scanning electron microscopy (SEM), and N$_2$ sorption-desorption isotherms analysis by BET for determine specific surface area (SSA). The total pore volume of the halloysite 40% - TiO$_2$ 60% prepared nanocomposite and its specific surface area is 0.35 cm^3/g and 188 m^2/g respectively. This nanocomposite showed a photocatalytic efficiency of 39.5% to TEB decomposition after 240 minutes of UV irradiation. The best photo-degradation efficiency, 47.4% of TEB was achieved with the halloysite 10% - TiO$_2$ 90% nanomaterial, instead of 33.2% decomposition efficiency using commercial TiO$_2$ (Degussa P25). In this case, the halloysite 10% - TiO$_2$ 90% nanocomposite showed the highest specific surface area of 222 m^2/g. The degradation of TEB in all the samples studied did not change after 150 minutes of UV exposure.

Keywords: Fungicide, Photocatalysis, Tebuconazole, Halloysite, TiO$_2$ nanocomposites

1. Introduction

The remarkable and rapid socio-economic development over the past few decades has further stressed the hydrogeological system. In many areas, locally and worldwide, population affected by diseases related with the consumption of unsuitable water, containing mainly bacteriological, organic and inorganic pollutants (FAO, 1991; WHO, 1993). Fresh and ground water contamination by pesticides is a subject of a great importance affecting a big number of people living mainly in areas with intense agricultural activities (RIVM, 1992; Reichenberger et.al., 2007). The effects of past and present land-use practices become apparent in fresh and ground water contamination and there is an increasing need for the development of water purification technologies. Among them, Advanced Oxidation Processes have been used as effective methods for the photocatalytic degradation of pesticides in the natural environment (Konstantinou and Albanis, 2003). One of the common fungicides used in agricultural applications all over Europe is Tebuconazole (TEB). It belongs to the triazoles group of toxic-organic substances, in concentrations up to 18.72 μg/L in natural waters (Stamatis et.al., 2015). TEB is a bio-refractory contaminant which cannot be degraded using conventional techniques and limited studies are available for the photocatalytic treatment of this fungicide (Stamatis et.al., 2015; Calza et.al., 2002; De Hermann et.al., 2010). The most common photocatalyst used for the degradation of TEB in water suspensions is TiO$_2$ (Stamatis et.al., 2015; Calza et.al., 2002; De Hermann et.al., 2010). However, new studies shows that new materials as, clay minerals combined with TiO$_2$ can be used as efficient photocatalyst for water purification purposes (Papoulis et.al., 2014; Papoulis et.al., 2013 a; Papoulis et.al., 2013 b; Papoulis et.al., 2013 c).

To this perspective we synthesized clay mineral based nanocomposites, Halloysite-TiO$_2$ and used them for the degradation of TEB fungicide in solution. The characterization and photocatalytic efficiency of the new class of material is presented.

2. Methodology

2.1. Materials Synthesis and Methodology

2.1.1. Materials and Chemical Reagents

A halloysite sample from Utah USA was used for the synthesis of the Hal-TiO$_2$ nanocomposites. Titanium tetraisopropoxide, Ti(OC$_3$H$_7$)$_4$, HCl acid, nanopure water (3D) and absolute ethanol were used for the preparation of the TiO$_2$ sol dispersion. Tebuconazole, C$_{16}$H$_{22}$ClN$_3$O, [(RS)-1-p-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)-pentan-3-ol], was used for the fungicide samples preparation. Commercial TiO$_2$ (Degussa-P25) used as standard photocatalyst has an anatase to rutile ratio 80:20, particle size 20 nm and particle specific area 50 m^2/g. All reagents were of analytical grade commercially available from Merck and Sigma−Aldrich.

A stock TiO$_2$ sol dispersion was prepared by mixing titanium tetraisopropoxide, Ti(OC$_3$H$_7$)$_4$, with hydrochloric acid, nanopure water (3D) and absolute ethanol. The TiO$_2$ stock dispersion was diluted in absolute ethanol, stirred for 2 h and then a halloysite-water dispersion was added. The slurry was stirred for 24 h and the resulting dispersion was washed with 3D water and centrifuged. The halloysite−TiO$_2$ composites were treated in mild hydrothermal conditions in an autoclave for 5 h at 180 °C. The detail methodology used for the preparation of the halloysite−TiO$_2$ nanocomposites described by Papoulis et.al., (2013 a). In order to study the photocatalytic performance of the halloysite−TiO$_2$ materials, we examined four samples. The information for each sample is given in table 1. In addition, we have chosen the TEB concentration as 1mg/L. The mass/volume ratio was 0.1375g of catalyst / 250ml of TEB sol, in order to give 550 mg/L of catalyst concentration in the solution (Stamatis et.al., 2015).

Table 1. Structural characteristics of photocatalysts used.

Sample	Sample Identification	Basal Spacing d (001)	Total Pore volume (cm^3/g)	SBET (m^2/g)
Degussa	P25	-	0.25	50
Halloysite	Hall 1	7.40	0.29	47
Halloysite 40% - TiO$_2$ 60%	Hall 2	7.29	0.35	188
Halloysite 10% - TiO$_2$ 90%	Hall 3	7.29	0.35	222

2.1.2. Instrumentation

X-ray diffraction (XRD) applied using a Bruker D8 advance diffractometer, with Ni-filtered CuKα radiation, for the determination of the phase compositions of TiO$_2$ treated halloysite samples. The XRD patterns are given in Figure 1.
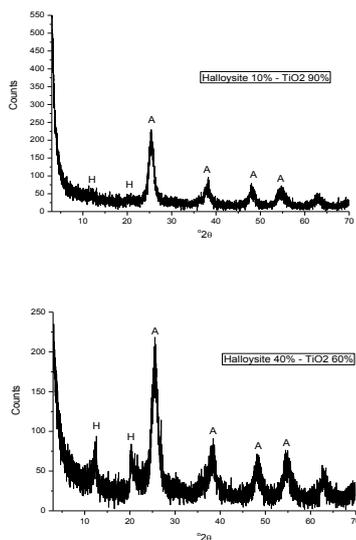

Figure 1. XRD patterns of Halloysite-TiO$_2$ nanocomposites.

Halloysite-TiO$_2$ morphology was examined by Scanning Electron Microscopy with Field Emission, FE−SEM, FEI Inspect TM F50. The SEM images are given in Figure 2.
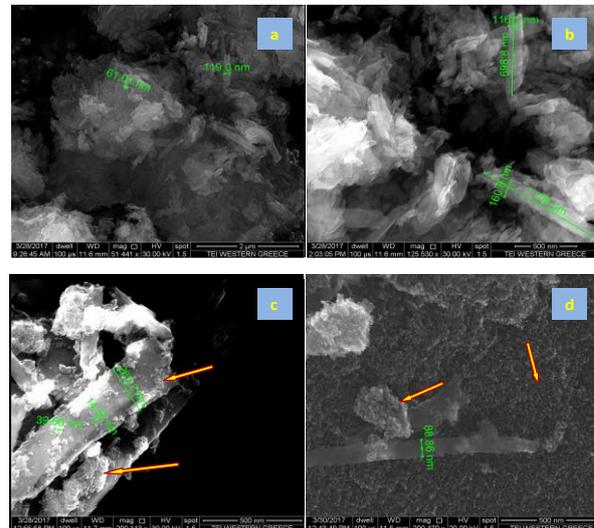

Figure 2. (a), (b) Halloysite nanotubes morphology in different magnification; (c) Halloysite 40% - TiO$_2$ 60% sample. The arrows indicate the TiO$_2$ nanoparticles on the halloysite nanotubes; (d) The Halloysite 10% - TiO$_2$ 90% sample. The arrows indicate the TiO$_2$ nanoparticles.

Nitrogen sorption-desorption isotherms for each sample degassed at 100 ^{o}C for 3 hours were obtained with a Micromeritics Tristar 3000 and the surface area, porosity,

and pore size distribution were derived by differentiating them according to Brunauner-Emmet-Teller (BET) method (Table 1).

For the photocatalytic tests, a cylindrical reactor was used in all experiments (Fig. 3). Four black light fluorescent tubes of 4 W each nominal power, were placed around the reactor. The whole construction was covered with a cylindrical aluminum reflector. Before the UV illumination, we applied continuous stirring to the samples, for 15 minutes in the dark in order to achieve the zero point of adsorption prior to the photocatalytic tests.

Cooling was achieved by air flow from below the reactor using a ventilator. Continuously stirring of the samples in the reactor was achieved with a magnetic stirrer.
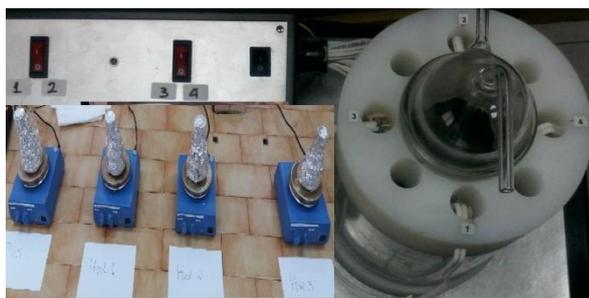
Figure 3. Photographs showing the photocatalytic reactor used.

The intensity of radiation was measured with a Solar Light PMA-2100 UV-Photometer and found equal with 0.9 mW/cm^2. The reactor was filled with 200 ml of the sample and the irradiation applied for a total of 300 minutes. TOC analysis was performed using the Combustion-Infrared method, Standard Method (SM) 5310B (Standard Methods for the Examination of Water and Waste Water, American Water Works Association) (Eaton, 2005; Bekiari and Avramidis, 2014). All analyses were carried out using a Shimadzu TOC analyzer (TOC-VCSH).

3. Results and Discussion

The results show that anatase was well fabricated on the halloysite nanotubes. Both patterns show the presence of halloysite 7Å and anatase, confirming the samples phase purity, while the intensities of basal reflections of halloysite 7Å are significantly smaller than those of anatase, especially in the nanocomposite with the lowest amount (10%) of halloysite (Fig. 1). The XRD patterns of both prepared nanocomposites showed all the characteristic reflections of anatase (γ-TiO$_2$), which are marked in Fig. 1. The XRD patterns also indicated that the relatively increased temperature (180 °C) of the hydrothermal treatment of both halloysite-TiO$_2$ nanocomposites did not modify the native halloysite 7Å structure (Fig. 2 a,b; Papoulis et.al., 2013 a). SEM images of the nanocomposites showed that many 10-30 nm uniform TiO$_2$ grains were deposited on the external surfaces of halloysite tubes (Fig. 2 c,d). The TiO$_2$ nanoparticles were found to be distributed not homogeneously but very well on halloysite external

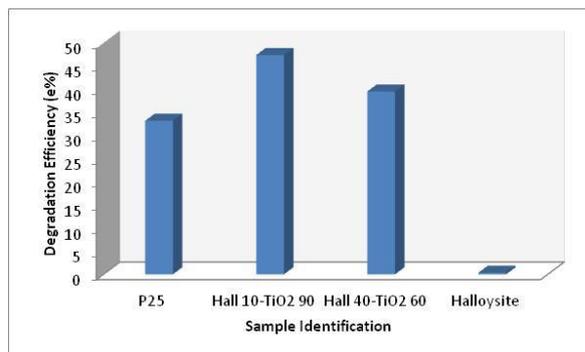surfaces (Fig. 2). TiO$_2$ nanoparticles seem to partially cover the lumen of most halloysite tubes (Fig. 2 c,d).

Figure 4. Degradation efficiency of the materials used.

The total pore volume of both halloysite-TiO$_2$ samples is higher than Degussa P25 and halloysite clay mineral. Furthermore, the specific surface area (SSA) of both halloysite-TiO$_2$ nanocomposites is also higher than Degussa P25 and halloysite clay mineral (Table 1). Pure halloysite has relative large pore volume and similar to that obtained for Degussa P25, while the high SSA of both nanocomposites indicates that there is a good distribution of TiO$_2$ on halloysite external surfaces.
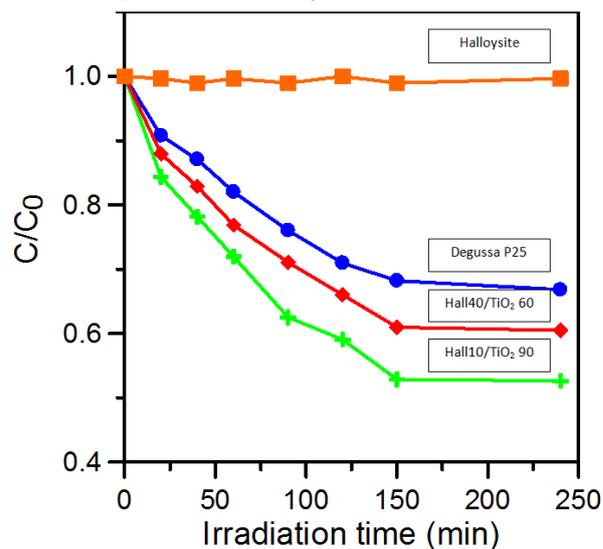
Figure 5. TEB decomposition with time of irradiation in the presence of various photocatalysts.

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

$r = (C_o-C)/C_o$

Where C_o 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:

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

As we expected, the pristine halloysite sample did not perform any photocatalytic effect to the TEB fungicide. In all samples examined halloysite is not the photocatalytic material. However, halloysite clay mineral acts as a

substrate in order to achieve better dispersion and avoid the agglomeration of the TiO_2 nanoparticles. This fact facilitates the photocatalytic performance of the halloysite-TiO_2 nanocomposites used. In addition, the photocatalytic efficiency of Degussa P25 is lower than the halloysite – TiO_2 nanocomposites. The highest photocatalytic efficiency, 47.4%, was achieved with the halloysite 10%-TiO_2 90% sample because of the high proportion and the high specific surface area, 222 m^2/g among all the materials used. In addition the halloysite 40%-TiO_2 60% sample shows better decomposition efficiency than Degussa P25 and also better dispersion of the TiO_2 photocatalyst on the halloysite nanotubes (Fig. 4, Fig. 2c). The Degussa P25 decomposition efficiency reaches a maximum of 33.2% after 240 minutes of irradiation, while the halloysite 40% - TiO_2 60% nanocomposite shows 39.5% degradation efficiency in 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. 5).

4. Conclusions

In this study we have examined the photocatalytic performance of new hall-TiO_2 nanocomposites. We synthesized hall10%-$TiO_2$90% and hall40%-$TiO_2$60% nanomaterials. The characterization of the new composites showed that the anatase form of TiO_2 was apparent and well dispersed onto the halloysite nanotubes. The two materials have high specific surface areas of 188 m^2/g and 222 m^2/g, for the hall40%-$TiO_2$60% and the hall10%-$TiO_2$90% respectively. The photocatalytic decomposition of TEB was performed under UV illumination for 240 minutes. The results indicated that the new hall-TiO_2 nanocomposites can be used as effective catalysts for the photo-decomposition of TEB in water in comparison to Degussa P25. Indeed, the decomposition efficiency of Degussa P25, hall40%-$TiO_2$60% and hall10%-$TiO_2$90% was 33.2%, 39.5% and 47.4% respectively. In addition, the maximum 47.4% of Tebuconazole content has been decomposed within first 150 minutes under UV irradiation while no further photocatalytic activity was observed the last 90 minutes of UV exposure.

References

Bekiari V. and Avramidis P. (2014), Data quality in water analysis: validation of combustion-infrared and combustion-chemiluminescence methods for the simultaneous determination of Total Organic Carbon (TOC) and Total Nitrogen (TN), *International Journal of Environmental Analytical Chemistry*, **94**, 65-76.

Calza P., Baudino S., Aigotti R., Baiocchi C., Branca P. and Pelizzetti E. (2002), High-performance liquid chromatographic/tandem mass spectrometric identification of the phototransformation products of tebuconazole on titanium dioxide, *Journal of Mass Spectrometry,* **37**, 566–576.

De Hermann Prestes T., De Oliveira Gibbon D., Lansarin M.A. and Moro C.C. (2010), Tebuconazole photocatalytic degradation kinetics, *Química Nova,* **33**, 798–801.

Eaton A. D. (2005), Standard Methods for the Examination of Water and Wastewater, 21st *American Public Health Association, American Water Works Association, Water Environment Federation,* ed. (Washington DC, APHA-AWWA-WEF).

FAO/ECE. (1991), Legislation and Measures for the Solving of Environmental Problems Resulting from Agricultural Practices (With Particular Reference to Soil, Air and Water), Their Economic Consequences and Impact on Agrarian Structures and Farm Rationalization. *United Nations Economic Commission for Europe (UNECE) and FAO, Agri/Agrarian Structures and Farm Rationalization* report **No. 7**.

Konstantinou I. K. and Albanis T. A. (2003), Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways, *Applied Catalysis B: Environmental*, **42**, 319–335.

Papoulis D. Komarneni S., Panagiotaras D., Stathatos E., Christoforidis K. C., Fernández-García M., Li H., Yin S., Sato T. and Katsuki H. (2014), Three-phase nanocomposites of two nanoclays and TiO_2: Synthesis, characterization and photacatalytic activities, *Applied Catalysis B: Environmental*, **147**, 526-533.

Papoulis D., Komarneni S., Panagiotaras D., Stathatos E., Toli D., Christoforidis K. C. Fernández-García M., Li H., Yin S., Sat, T. and Katsuki H. (2013 a), Halloysite–TiO_2 nanocomposites: synthesis, characterization and photocatalytic activity. *Applied Catalysis B: Environmental*, **132-133**, 416-422.

Papoulis D., Komarneni S., Panagiotaras D., Nikolopoulou A., Hui L., Yin S., Sato T. and Katsuki H. (2013 b), Palygorskite–TiO_2 nanocomposites: Part 1. Synthesis and Characterization, *Applied Clay Science*, **83-84**, 191-197.

Papoulis D., Komarneni S., Panagiotaras D., Nikolopoulou A., Christoforidis K.C., Fernandez-Garcia M., Hui Li., Yin S. and Tsugio S. (2013 c), Palygorskite–TiO_2 nanocomposites: Part 2. Photocatalytic activities in decomposing air and organic pollutants, *Applied Clay Science*, **83-84**, 198-202.

Reichenberger S., Bach M., Skitschak A. and Frede H.G. (2007), Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness: a review, *The Science of the Total Environment*, **384**, 1-35.

RIVM. (1992), The Environment in Europe: A Global Perspective. *National Institute of Public Health and Environmental Protection (RIVM)*, Netherlands.

Stamatis N., Antonopoulou M. and Konstantinou I. (2015), Photocatalytic degradation kinetics and mechanisms of fungicide tebuconazole in aqueous TiO_2 suspensions, *Catalysis Today*, **252**, 93–99.

WHO - World Health Organization (1993), Guidelines for Drinking-Water Quality, **vol. 1**, Recommendations. (Second Edition), WHO, Geneva.