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Photocatalytic degradation of pesticides by titanium dioxide and titanium pillared purified clays



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Abstract Titanium dioxide was synthesized by the sol–gel method and titanium pillared purified clay was prepared with two titanium contents: 1.15 and 10.5 mmol of Ti per gram of clay. The composites were synthesized by immobilizing TiO₂ onto surfactant-pillared clay via ion exchange reaction between clay with cation surfactant, cetyl-trimethyl ammonium bromide (CTMABr). The composition and texture of the prepared photocatalysts were characterized with X-ray powder diffraction (XRD), FT-IR spectroscopy, transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDX). The adsorption performance and photocatalytic activities of the prepared samples were investigated using 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxypropionic acid (2,4-DP) as models of organic pollutants. The results were obtained that these photocatalysts can effectively degrade selected pesticides. The removal efficiency increases with the Ti content in the pillared clay.

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1. Introduction

The development of the agrochemical industry has dramatically increased in the last few decades due to widespread intensive agricultural activities. Increasing pesticides application and improper wastewater disposal methods are of particular concern for the freshwater (surface and groundwater), coastal and marine environments. Among these pesticides, a large amount of chlorinated compounds are currently produced and reach the environment. Contamination by chlorinated

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compounds is currently one of the most serious environmental problems and constitutes the most important family of toxic non-biodegradable compounds (Roques, 1996).

2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxypropionic acid (2,4-DP) are aryloxyalkanoic acids. The herbicides of this family, used especially on cereals agriculture (BCPC, 1997), are the most widely used pesticides around the world (Bovey and Young, 1980). In 2001, 2,4-D was the pesticide the more used in USA in the commercial sector and the gardening sector with weights of respectively, 3.6–5.0 and $7.3\text{--}8.2 \times 10^6$ kg (EPA, 2004). 2,4-D is toxic to broad-leaved plants. This herbicide is absorbed by roots and translocates to the growing points of roots where it inhibits the growth of the plants. Due to low soil sorption and high potential of leachability, its residues are often reported in the surface and ground water (Pichat et al., 1993). It is a well known endocrine disrupter (Colborn et al., 1993).

In view of this, it is advisable to develop technologies that promote the easy degradation of such bio-recalcitrant organic compounds. A promising way to perform the mineralization of these type of substances is the application of advanced oxidation processes (AOPs). These AOPs are characterized by the generation of very reactive and oxidizing free radicals in aqueous solutions which achieve a great destruction power. Among the different technologies proposed as AOP, heterogeneous photocatalysis is an efficient technique to destroy organic pollutants in water (Schiavello, 1987; Zhang et al., 2001; Augugliaro et al., 2002; Péreza et al., 2006; Gafar Muhamad, 2010; Abdennouri et al., 2010; Barka et al., 2010). This technique is based upon the use of UV-irradiated semiconductors (generally titania). When TiO_2 is irradiated with photons whose energy is equal to or greater than its band gap energy ($E_G = 3.2$ eV) i.e. with $\lambda = 390$ nm, electron-hole pairs are created. In aqueous system, holes react with H_2O or OH^- adsorbed at the surface of the semiconductor to produce OH^\bullet radicals which are the most oxidizing species in this process (Vulliet et al., 2003). Although heterogeneous photocatalysis was classified as an expensive treatment option, the cost can be minimizing and optimize from different aspects, one is to apply methodologies for catalyst separation and recycling.

The intercalation of titanium into the interlayer of clays is one of the most promising methods for synthesizing titanium pillared clays as well as improving the photocatalytic activity for the degradation of organic pollutants in water (Bhattacharyya et al., 2004; Zhu et al., 2005). The aims of the present work are to synthesise titanium dioxide and titanium intercalated purified clays and to investigate their photocatalytic activity for the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxypropionic acid (2,4-DP) in aqueous solution.

2. Materials and methods

2.1. Materials

All of the reagents used in this work were of analytical grade and used without further purification: $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (Aldrich, 98%), CH_3COOH (Fluka, 99.8%), HCl (SdS-French, 37%), $\text{C}_2\text{H}_5\text{OH}$ (Prolabo, 99.85%), CH_3OH (Prolabo, 97%), CTMABr: cetyl-trimethyl ammonium bromide ($\text{C}_{19}\text{H}_{42}\text{NBr}$) (Amresco, 99%), H_2O_2 (Panreac, 33%), AgNO_3 (PROLABO

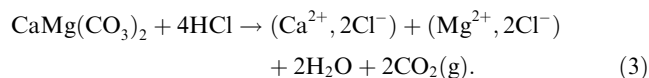
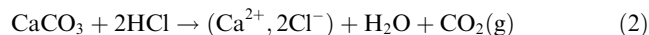
and HNO_3 (LOBA CHEMIE). 2,4-Dichlorophenoxyacetic acid ($\text{C}_8\text{H}_6\text{Cl}_2\text{O}_3$) and 2,4-dichlorophenoxypropionic acid ($\text{C}_9\text{H}_8\text{Cl}_2\text{O}_3$) used as model pollutant compound were obtained from Fluka, their chemical structures are given in Fig. 1. All the solutions were prepared with pure water obtained from a Millipore Milli-Q system.

2.2. Clay purification

The raw clay was collected from Safi region in Morocco. Its chemical composition determined by X-ray fluorescence spectrometry, (mass%), was: SiO_2 , 45.99; Al_2O_3 , 17.13; Fe_2O_3 , 5.82; CaO , 5.17; MgO , 3.26; K_2O , 4.61; Na_2O , 0.15; P_2O_5 , 0.21; SO_3 , 0.20. The clay powder was purified according to the following procedure: clay dispersion was placed in a graduated cylinder for allowing particles $> 2 \mu\text{m}$ in size to settle down and the fine fraction, whose size was $< 2 \mu\text{m}$ was extracted at the time of the static sedimentation of the particles in suspension based on this equation:

$$t = 191.5 \times \frac{X}{d^2}, \quad (1)$$

where “ t ” is the necessary time (min), for a particle of diameter “ d ” (μm), to reach a depth of X (cm). Carbonates of calcium and magnesium were eliminated by hydrochloric acid (0.1 N) at the ratio of 10 mL/g according to the following reactions:



The organic matter present in the clay sample was oxidized by addition of H_2O_2 (33%) at the ratio of 10 mL/g under agitation during 2 h at ambient temperature.

After centrifugation, purified clay was washed with distilled water until it was free of Cl^- ions according to a test with AgNO_3 . The adsorption sites of the clay were activated by nitric acid (0.8 N) at the ratio of 10 mL/g. Activated clay was recovered by centrifugation, washed with water and dried at 40°C for 72 h. The cation exchange capacity of purified clay measured by exchange with methylene blue (Czimerova et al., 2006) was 0.517 mmol/g.

2.3. Preparation of TiO_2 and pillared clays

The TiO_2 used in this study as prepared by the sol-gel method by dissolving $\text{Ti}(\text{OC}_3\text{H}_7)_4$ in methanol/ethanol solution with molar ratio 1:1:10, respectively. The obtained solution was maintained at 75°C for 3 h and the appropriate amount of water was added drop wise into the hot solution. The sample was then dried at 110°C overnight and was calcined at 500°C for 120 min.

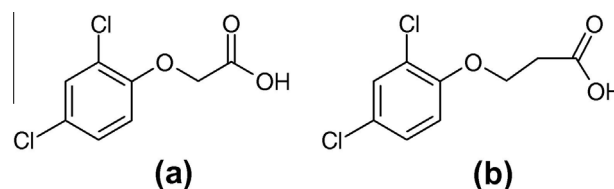


Figure 1 Molecular structures of 2,4-D (a) and 2,4-DP (b).

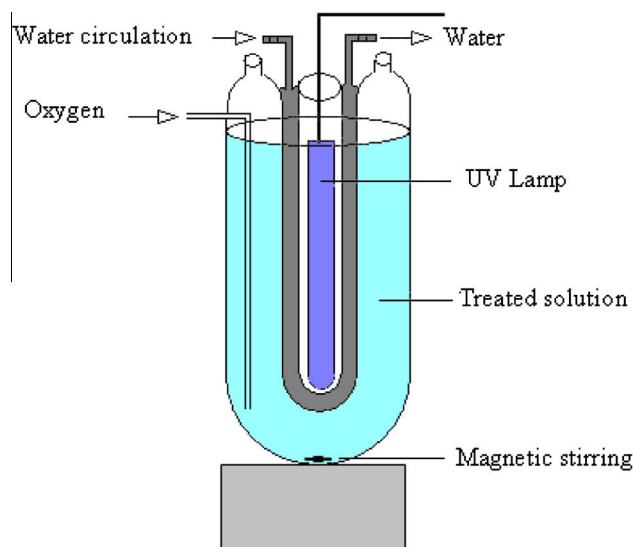


Figure 2 Schematic diagram of the photocatalytic reactor.

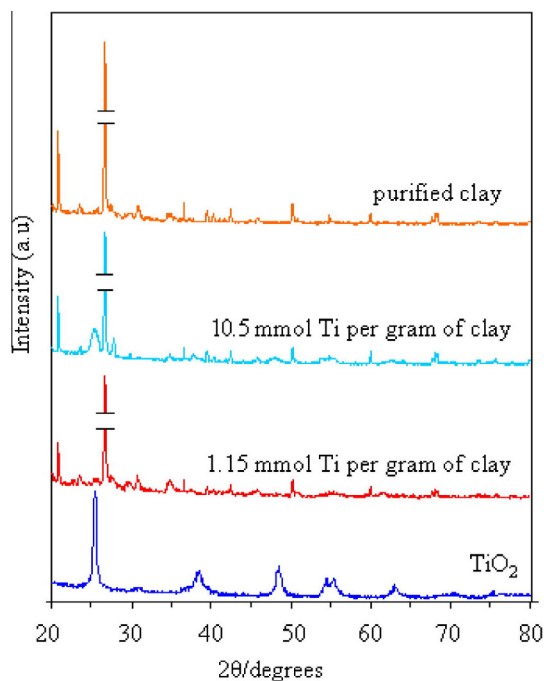


Figure 3 XRD patterns of TiO_2 , purified clay, 1.15 and 10.5 mmol of Ti per gram of clay.

Pillared clays at two ratios of titanium (1.15 and 10.5 mmol of Ti per gram of clay) were prepared according to the following procedure: 2.0 g of clay was dispersed into 200 mL of distilled water and the suspension was stirred for approximately 24 h. 4.0 g of CTMABr surfactant was added into the clay dispersion. To this mixture, a solution of $\text{Ti}(\text{OC}_3\text{H}_7)_4:\text{CH}_3\text{COOH}:\text{H}_2\text{O}$ with a molar ratio of 1:10:40 was added drop wise with continuous stirring. The obtained precipitates were recovered from the mixture by centrifuging, dried and calcined at 500 °C for 24 h.

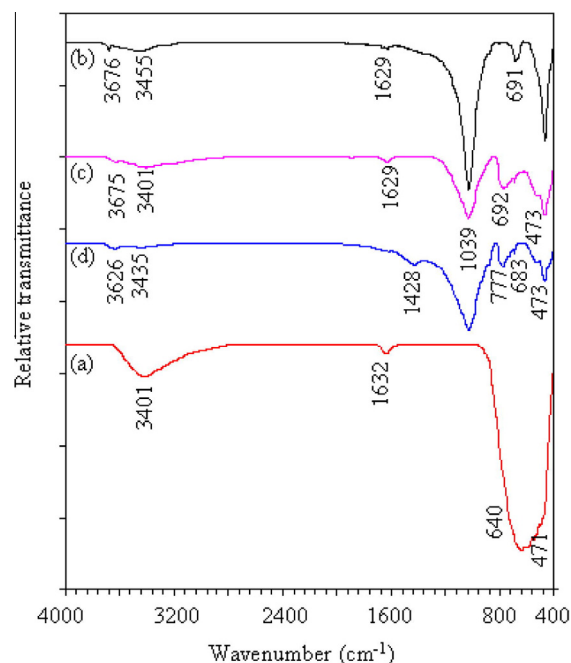


Figure 4 IR spectra of synthesized TiO_2 (a), purified clay (b) and pillared clay samples at 1.15 (c) and 10.5 mmol of Ti per gram of clay.

2.4. Photocatalytic reactor and light source

Photocatalytic experiments were performed in a cylindrical batch reactor with 10 cm in diameter and 20 cm in height (Fig. 2). The reactor was made from quartz glass, which made possible the transfer of the irradiation. The reactor was exposed to a luminous source composed of a medium pressure mercury-lamp (400 W), placed in an axial position inside a cooling water jacket system. Constant agitation was assured by means of a magnetic stirrer placed at reactor base.

2.5. Procedure and analysis

The reactor was initially loaded by 800 ml of 2,4-D aqueous solution at 20 mg/L. The mass of the photocatalyst was 120 mg. The mixture was maintained in the dark for 30 min under stirring to reach adsorption equilibrium, and then irradiated. Samples taken at different times were centrifuged at 3000 tr/min for 10 min. The residual concentration was determined from its UV-Vis absorbance characteristic with the calibration curve method at the wavelength of maximum absorption ($\lambda_{\text{max}} = 283 \text{ nm}$). GBC UV/Vis 911 spectrophotometer was used.

3. Results and discussion

3.1. Characterization of the samples

3.1.1. XRD analysis

Fig. 3 shows X-ray powder diffraction patterns of the purified clay, synthesized TiO_2 and pillared clay samples at 1.15 and 10.5 mmol of Ti per gram of clay. The characteristic

diffraction peak corresponding to (1 0 1) reticular plane of anatase form was detected at 25.37° (2θ). Other anatase diffraction peaks appeared at 37.97° , 47.67° , 54.86° , 62.77° and 75.62° (2θ). These peaks are observed in XRD patterns of both the samples 1.15 and 10.5 mmol of Ti per gram of clay. The intensity of the diffraction peaks of anatase increased with increasing Ti/clay mass ratio. Generally, the intercalation of layered clays with pillars results in a shift to lower 2θ of the peak corresponding to (0 0 1) reticular plane. This peak could not be detected in this experiment, because of the limit of the instrument employed.

3.1.2. FT-IR spectroscopy

Fig. 4 shows FT-IR spectra of purified clay, synthesized TiO_2 and pillared clay samples at 1.15 and 10.5 mmol of Ti per gram of clay. Stretching vibrations of water molecules in purified clay may contribute to $-\text{OH}$ peaks at 3500 cm^{-1} . On pillaring, the band broadens due to the introduction of more $-\text{OH}$ groups of the pillar, which is interpreted as an effect of pillaring (Kurian and Sugunan, 2003). Pillared clay has low amount of adsorbed/coordinated water due to the non-swelling nature. The band around 1040 cm^{-1} is due to asymmetric stretching vibrations of SiO_2 tetrahedra. This band shifts to low

wavenumbers with the increase in Ti content in pillared clay. The absorption band at 473 cm^{-1} could be attributed to bending of Si-O vibration, as a result of pillaring, intensity of this band decreases with the increase in Ti content in pillared clay.

3.1.3. TEM-EDX

TEM images of purified clay, synthesized TiO_2 and pillared clay samples are presented in Fig. 5. From the TEM photograph we can obviously see that the prepared TiO_2 was nanometer scale particles. The morphology of the composites was strongly modified by the intercalation of titanium. Small aggregated TiO_2 particles are randomly dispersed on the flat plates of pillared clay. More particles are observed with an increase in the amount of Ti. Indicating the increase of immobilized TiO_2 results in less ordering of the layered clay structures, consistent with the results obtained from XRD experiments.

3.2. Photocatalytic performance

3.2.1. Persistence of 2,4-D under UV irradiation

In the same operating conditions used for the photocatalytic degradation, the photolytic degradation was studied using

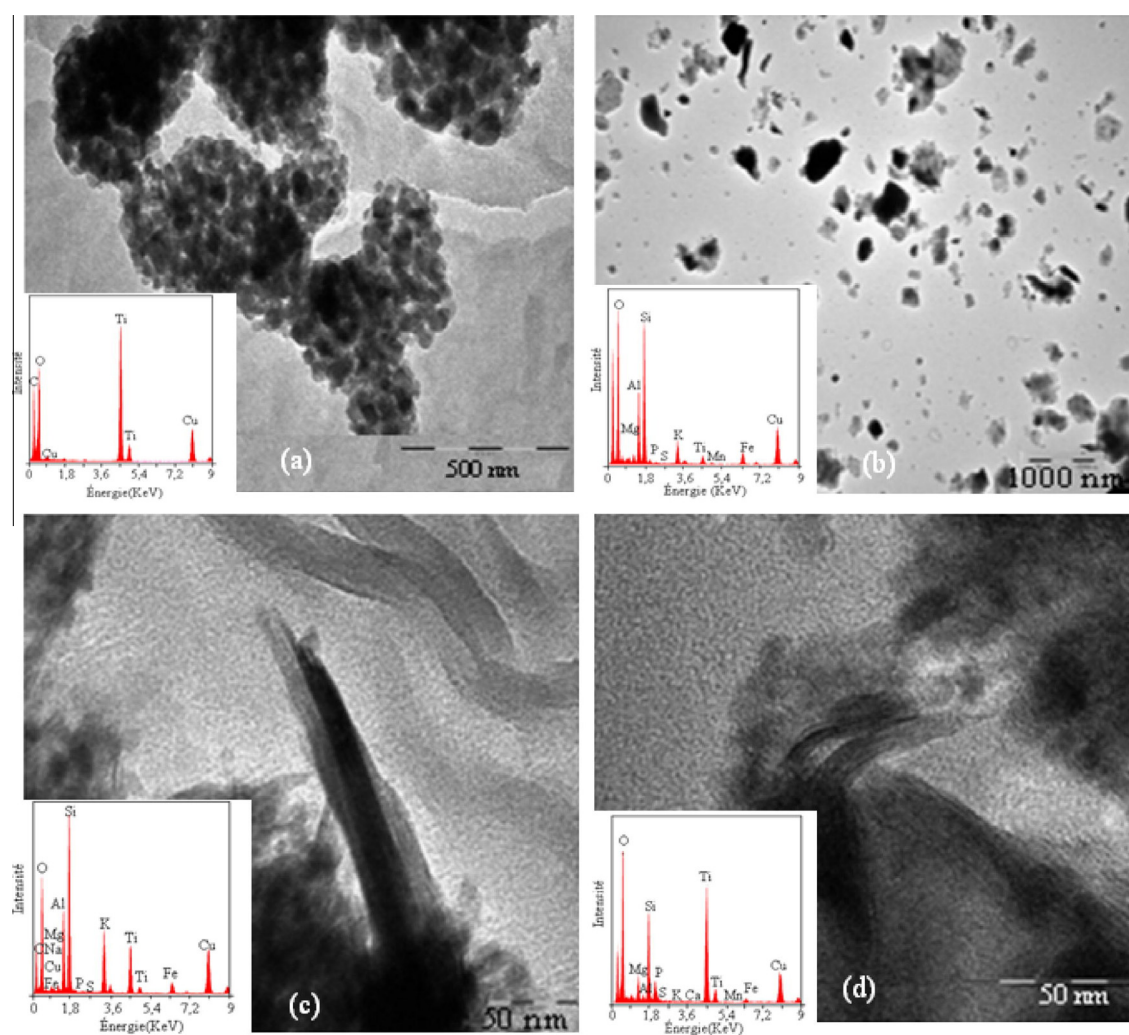


Figure 5 TEM-EDX of synthesized TiO_2 (a), purified clay (b) and pillared clay samples at 1.15 (c) and 10.5 mmol (d) of Ti per gram of clay.

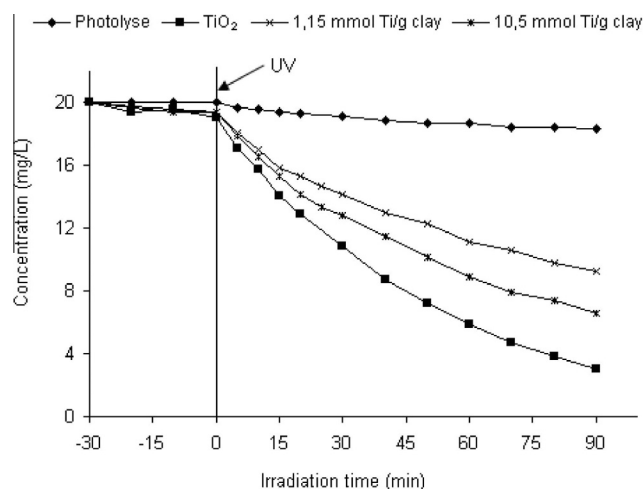


Figure 6 Variation of 2,4-D concentration versus irradiation time without and with the photocatalysts.

800 ml of 2,4-D and 2,4-DP at 20 mg/L. The solution was irradiated without photocatalysts. The results are illustrated in Figs. 6 and 7. Kinetics of pesticides photolytic degradation show that, after 90 min of irradiation, a very low diminution of the concentration was observed. From this result, we can neglect the interference of the photolytic degradation with the photocatalytic degradation.

3.2.2. Preliminary adsorption in the dark

Sorption is an important parameter in determining the photocatalytic degradation rate. The adsorbed molecules on the surface of the semiconductor particles act as an electron donor, injecting electrons from its excited state to the conduction band of the semiconductor under UV irradiation. Adsorption tests in the dark were carried out in order to evaluate the adsorbed quantities of 2,4-D and 2,4-DP on the photocatalyst surface. Table 1 indicates that the adsorbed quantities do not exceed 5% of the initial quantity in the solution. The adsorbed quantities of 2,4-D and 2,4-DP on pillared clay increases with the augmentation of Ti content. This result can be explained by the availability of more adsorption sites at the surface of the composite due to nanometric TiO₂ loading.

3.2.3. Photocatalytic degradation

The photocatalytic performance of the TiO₂ and pillared clay samples for the degradation of 2,4-D and 2,4-DP is shown in Figs. 6 and 7. The figures indicate that the synthesized photocatalysts can effectively degrade selected pesticides. The photocatalytic activity of pillared clay samples was increased by the increasing in Ti loading. The figures also indicate that the photocatalytic activity of TiO₂ is higher than that of the pillared clay samples. This result could be due to the poor accessibility to the TiO₂ surface and amorphous phase of the TiO₂ pillars (Ding et al., 1999). Moreover, the size of TiO₂ particles is several nanometers (Fig. 5a), much smaller than that of the pillared clay samples leading to high photocatalyst surface exposed to irradiation. However, the pillared clay samples can be readily separated from the suspension after the reaction because they sediment in minutes when the stirring was stopped, while the TiO₂ sample could not sediment easily, and lead to a potential

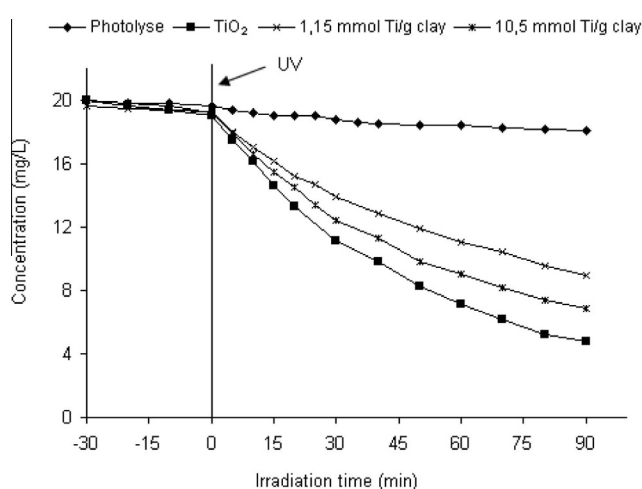


Figure 7 Variation of 2,4-DP concentration versus irradiation time without and with the photocatalysts.

Table 1 Adsorbed quantities of used pesticides (mg/g) on the photocatalysts after 30 min.

Photocatalyst	TiO ₂	1.15 mmol Ti/g clay	10.5 mmol Ti/g clay
2,4-D	6.35	3.77	3.90
2,4-DP	6.41	4.89	5.03

difficulty in downstream separation. The pillared clay samples form large granules which could easily be recovered from aqueous solutions by filtration or sedimentation and permit its reuse. This is an important advantage in practice.

4. Conclusion

TiO₂ nanomaterial and titanium pillared clay with two Ti contents were synthesized and characterized. Their photocatalytic activities were investigated for the photocatalytic degradation of 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenoxypropanoic acid. The results were found that these photocatalysts can effectively degrade selected pesticides. The adsorption performance and photocatalytic activities of prepared samples were proportional to Ti loading amounts onto pillared clay.

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