



Photocatalysis degradation of 2,4-dichlorophenoxyacetic acid in water environment using synthesized TiO₂ nanoparticles

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ARTICLE INFO

Received: 6/5/2022

Accepted: 20/6/2022

Published: 22/6/2022

Keywords:

2,4-D, TiO₂, nanomaterial, photocatalysis,

ABSTRACT

The present study investigated the photodegradation of 2,4-Dichlorophenoxyacetic acid (2,4-D) in a water environment using synthesized titania nanoparticles (TiO₂-NPs). The TiO₂-NPs fabricated by sol-gel method were distinguished by X-ray diffraction (XRD) and Transmission electron microscopy (TEM), Infrared spectroscopy (IR), and zeta potential measurements. The results indicated that TiO₂ - NPs were nanospheres of appropriately 30nm with a major anatase phase. Synthesized TiO₂-NPs have the point of zero charge (PZC) of around 6.0. The efficient conditions for photocatalysis degradation of 2,4-D under sunlight were considered and found to be 120 min, pH 11, and 1 mM KCl. Under ideal conditions, the photodegradation efficiency of 2,4-D reached greater than 72 %. Our results suggest that TiO₂-NPs would be promisingly applied for eliminating 2,4-D from an aqueous solution.

Introduction

The contamination of surface and ground waters by pesticides has become a serious environmental and health concern. The 2,4-dichlorophenoxyacetic acid (2,4-D) is one of the most successful widely used herbicides [1]. The 2,4-D derivatives may easily enter water bodies resulting in extreme residues in environment [2]. The degradation of 2,4-D in water is relatively slow, with a half-life up to 170 days depending on the particular condition [3]. Various techniques for removal of 2,4-D such as biodegradation [4], photocatalytic degradation [5, 6], advanced oxidation [7, 8], flocculation/coagulation

and adsorption [6, 9, 10]. Heterogeneous photocatalysis offers a more economically viable route for its decomposition by utilizing widely distributed solar energy.

Due to the low toxicity, low-cost, high photostability, and high efficiency, the application of TiO₂ for the photocatalytic decontamination of water has been intensively investigated over the past few decades [10, 11]. Obviously, the photoactivity of TiO₂ -NPs is strongly reliant on its structures, morphological properties, crystallinity, and surface charge [12, 13]. In the contemporary work, we explored photoactivity of synthesized TiO₂-NPs by sol-gel method in 2,4-D

degradation under sunlight irradiation for purpose of environmental remediation.

Experimental

Materials

TiO₂ nanoparticles were sol-gel synthesized by using Tetrabutylorthotitanate (TBOT) (C₁₆H₃₆O₄Ti, Merck, Germany). The proper volume of solution KCl, HCl, and KOH (p.A, Merck, Germany) was added to adjust and measure the ionic strength and pH of a solution. Ultrapure water was provided by an 18.2 MΩcm resistivity ultrapure water system (Labconco, USA). An HI 2215 pH meter (Hanna, USA) was applied to measure pH value. Other chemicals with analytical grade were bought from Merck.

Synthesis of TiO₂ nanoparticles from TBOT

Firstly, a solution of 70 mL of ethanol was put in a beaker, and then 35 ml of TBOT with 0.46 mL concentrated nitric acid was added to form an oxidation inhibitor (called A solution). This solution was thoroughly stirred to make a sol. Another 70 mL ethanol with was mixed well with 10 mL ultrapure water (called B solution). After that, the B solution was added into A solution with stirring until the sol became a gel. Secondly, the gel was dried in a drying cabinet at 95 °C for 24 h. In the next step, the dry gel was ground to a powder. Finally, the powder was calcined at 500 °C for 2 h before cooling to room temperature in a desiccator. Finally, the powder was well grinded to form nanosized TiO₂. [11].

Characterization methods

The synthesized TiO₂- NPs were depicted by X-ray diffraction (XRD), Transmission electron microscopy (TEM), and zeta potential measurements. A Bruker D8 Advance X-ray Diffractometer was utilized to conduct the XRD pattern. Hitachi High-Technologies Corporation S4800-NIHE, Japan was used to collect The TEM image. An Affinity-1S spectrophotometer (Shimadzu, Japan) was applied to attain Fourier transform -Infrared spectroscopy (FT-IR) analysis in the range of 400 - 4000 cm⁻¹ wavenumber. IR spectra were recorded with 4 cm⁻¹ resolution at room temperature and atmospheric pressure. Charging properties of synthesized TiO₂-NPs at different pH in the solution of

1 mM KCl were defined by a Zetasizer Nano ZS (Malvern, England) using Smoluchowski's equation [10].

Photocatalytic degradation experiments

To optimum conditions for the photodegradation experiment, 5 ppm 2,4-D was mixed with 10 mg/ mL photocatalyst TiO₂-NPs. Then the suspension was transferred into the glass reactor before adjusting to a certain pH and kept under sunlight for UV irradiation for 2 h. After that, the suspension was transferred into 15mL Fancol tubes and centrifuged to separate solid particles and supernatant. The solutions were then quantified by UV-Vis spectroscopy using UV-1650 spectrophotometer (Shimadzu, Japan).

The photocatalytic degradation was conducted with pH range from 3 to 11. The effect of TiO₂ -NPs dosage was studied from 1.0 to 30.0 mg/mL compared without catalyst. The reaction temperature was remained unchanged at 24 ± 1°C by photoreactor. All experimentations were repeated triplicates.

Spectroscopic method

The 2,4-D concentration was determined by the spectroscopic method using a UV-Vis spectrophotometer (UV-1650PC, Shimadzu, Japan) using 1 cm optical path length quartz cuvettes.

The degradation of 2,4-D was assessed by comparing the variation in the amount of 2,4-D in solution before and after taking the process. The degradation efficiency of 2,4-D (% D) was computed by using Equation (1):

$$\%D = (C_i - C_t) \times 100 / C_i \quad (1)$$

where D is the degradation efficiency, C_i and C_t are the initial 2,4-D concentrations and concentrations of 2,4-D at the time t, respectively.

Results and discussion

Characterizations of TiO₂ nanoparticles

XRD pattern of synthesized TiO₂ nanoparticles was depicted at 2θ = 25.3°, 37.8°, and 48.1°. These peaks confirm that the main morphology of TiO₂ is the anatase phase. In addition, some extremely shorter peaks at 2θ = 27,2; 36,2; 54,3 would relate to rutile phase. The fineness peaks indicated that the nanosized materials were well crystallized. The indexation shows that these peaks similar are to those identified on as-

synthesized TiO₂. Thus, the XRD diagram reinforces that the phase of TiO₂ in our study is predominantly anatase phase and the rutile phase was a tiny amount. Our results agreed with previous works of other scientists [12, 13].

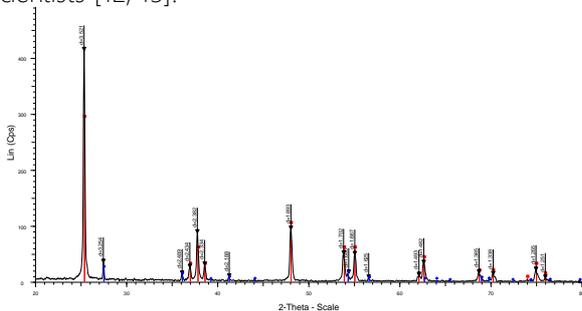


Figure 1: XRD pattern of synthesized TiO₂ nanoparticles

The TEM image shows that TiO₂ particles were spherical with a regular diameter of approximately 30 nm. The nanoparticles appeared to be relatively homogeneous and uniform in size.

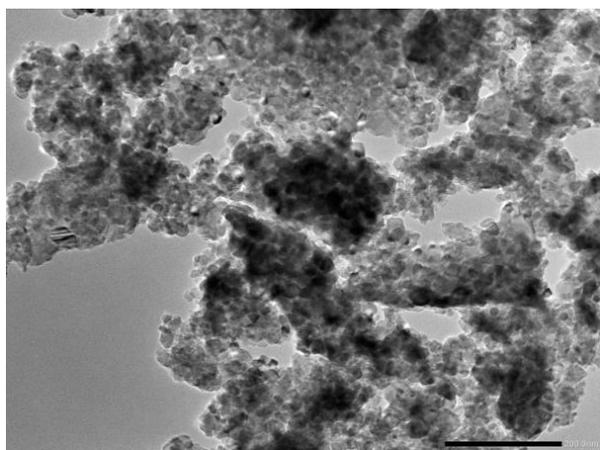


Figure 2: TEM image of TiO₂ nanoparticles at 200nm resolution

Figure 3 shows the IR spectra of TiO₂-NPs with a large banding and a sharp peak at 3743.83 and 1647.21 cm⁻¹ that ascribed to -OH vibration. Also, double peaks at 1249.87 and 1197.79 cm⁻¹ advocate the existence of hydroxide groups. Meanwhile, the minute peaks at 474.49 and 428.20cm⁻¹ refer to the octahedra structure [14].

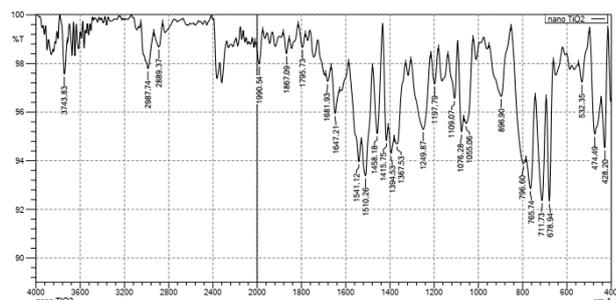


Figure 3: The IR spectra of TiO₂-NPs

The photochemical applications of TiO₂-NPs are strongly impacted by its surface properties. The physicochemical properties of TiO₂ are shown in Fig. 4. Generally, the surface charge of TiO₂ significantly contributes to photocatalytic activities, particularly for the kinetics of photo-oxidation of organic compounds. Typically, a more efficient generation of hydroxyl radicals by TiO₂ is achieved in a weak alkaline medium owing to the presence of an optimal concentration of OH⁻, which is advantageous for the photocatalytic degradation of organic compounds in aqueous solution [10].

In our study, the change in charging behaviors of TiO₂-NPs coinciding with a variation of pH value at 1 mM KCl was observed clearly. Figure 6 illustrates that the point of zero charge (PZC) of synthesized TiO₂-NPs was around 6.0 which is similar to reported values [15].

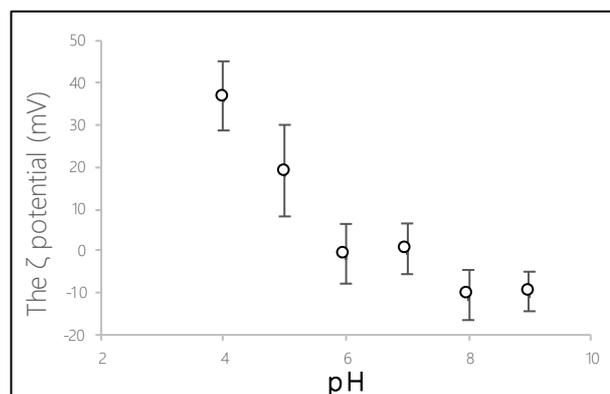


Figure 4: The ζ potential of TiO₂-NPs at variant pH value in KCl 1 mM

In this study, at pH < 6.0, the TiO₂ surface is positively charged, meanwhile, at pH > 6.0, it is negatively charged. The negative charge of TiO₂-NPs in basic solution is crucial to 2,4-D adsorption ability onto TiO₂-NPs surface.

By comparing the data obtained from different physicochemical techniques involving XRD, TEM, IR, and zeta potential measurement, we strengthen that TiO₂ nanoparticles (TiO₂-NPs) were successfully synthesized in this study.

Photodegradation of 2,4-D using TiO₂-NPs

Effect of pH

The pH value plays a crucial role in the photoactivity of TiO₂-NPs in 2,4-D treatment. The fact is that pH is likely to change surface charge of TiO₂ - NPs as well as to

form free radical $\text{OH}\cdot$. The present study investigated the pH range 3.0-11.0 in UV irradiation time 120 min, photocatalyst dosage 10 mg/mL, 1 mM KCl. Figure 5 shows that the removal efficiency of 2,4-D with TiO_2 -NPs under UV irradiation reaches the two highest values at 69.6 % at pH 5.0 and 72.27 % at pH 11.0.

The effect of pH on the 2,4-D degradation can be explicated by considering both characteristics of nano photocatalyst material and 2,4-D herbicide at different pH media. Regarding TiO_2 -NPs photocatalyst material, the increase in the pH value leads to a significant change in the surface charge and reaches the point of zero charge (PZC) at pH 6.0. In acidic media, TiO_2 -NPs are positively charged while 2,4-D exists in the form of negative ions. Therefore, the adsorption ability on the surface of TiO_2 -NPs rises thanks to electrostatic interaction. The results showed that there was intensive degradation of 2,4-D at pH 5.0.

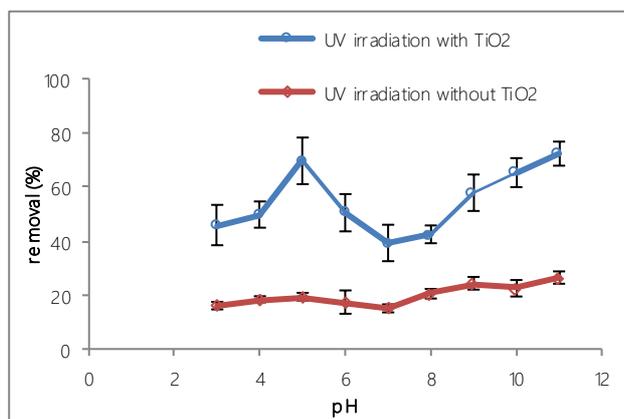


Figure 5: Photodegradation of 2,4-D under UV irradiation of sunlight with and without TiO_2 -NPs

Nevertheless, the rapid degradation of 2,4-D in alkaline media may result from the availability of hydroxyl ions (OH^-) on the surface of TiO_2 , which contributes to the abundant amount of free hydroxyl radicals ($\text{OH}\cdot$) [4, 9].

$$\text{TiO}_2 (h^+) + \text{H}_2\text{O} \rightarrow \text{OH}\cdot + \text{H}^+ + \text{TiO}_2 \quad (2)$$

$$\text{TiO}_2 (h^+) + \text{OH}^- \rightarrow \text{OH}\cdot + \text{TiO}_2 \quad (3)$$

As a result, the maximum removal of 2,4-D reaches the peak of 72.27% at pH 11.0. Our result is reasonable with other previous works that used TiO_2 -NPs for the degradation of organic compounds [3, 5]. According to these previous results, the addition of TiO_2 -NPs strongly enhances the degradation of 2,4-D. However, after 90 min of irradiation, the maximum degradation of 2,4-D was only at around 50% [4, 15]. Meanwhile, our maximal removal (72.27%) is considerably higher than these similar experiments using TiO_2 -NPs as a photocatalyst. This would cause by the highly

homogeneous synthesized TiO_2 -NPs in our experiment.

Figure 5 also shows a relatively low photodegradation efficiency of 2,4-D (less than 30%) under UV irradiation without TiO_2 NPs. In the absence of photocatalyst, a process known as photolysis may associate with the preferential formation of intermediates of reaction.

Effect of photocatalyst dosage

Figure 6 exhibits the increase in 2,4-D degradation that occurred when the dosage of TiO_2 photocatalyst was raised from 0 –30 mg/mL. The better photoactivity according to the increase of TiO_2 dosage could be the result of the higher surface area of material that would be offered, which favors the adsorption of more molecules of 2,4-D. The higher amount of photocatalyst is, the higher number of photons is converted to chemical energy, and more radicals $\text{OH}\cdot$ and other strong oxidizing ingredients will be produced, which could accelerate the degradation of organic compounds [16].

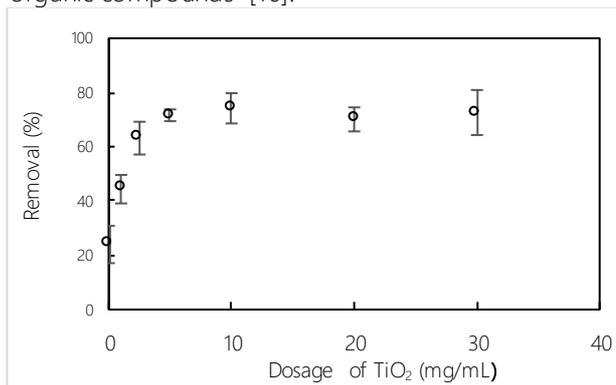


Figure 6: Effect of dosage of photocatalyst on 2,4-D degradation ($C_{i,2,4-D} = 5$ ppm, pH 11, and 1 mM KCl). Error bars show standard deviations of triple repeats

The optimum dosage of TiO_2 was 10 mg/mL while the degradation efficiency of 2,4-D was found about 74.2%. Also, there was an insignificant change in 2,4-D degradation as the amount of TiO_2 photocatalyst was more than 10,0 mg/mL. This can be clarified by the excess of TiO_2 particles may result in the opacity of the suspension and prevent 2,4-D molecules from exposing UV rays from sunlight [16]. Hence, the optimum TiO_2 dosage is 10 mg/mL and it is kept unchanged for extensive research.

Conclusion

The TiO₂ nanoparticles were successfully synthesized and characterized by various physicochemical methods. The results confirmed that TiO₂ - NPs were nanospheres of appropriately 30nm with a major anatase phase. Synthesized TiO₂-NPs have the point of zero charge (PZC) of around 6.0. The 2,4-D removal efficiency with TiO₂-NPs under UV irradiation reached the highest value of 72.27% at pH 11.0 with the optimal dosage of 10 mg/mL TiO₂. Our study indicates that 2,4-D photodegradation by using TiO₂-NPs is significantly more effective than that without TiO₂-NPs, and TiO₂ is a potential photocatalyst for 2,4-D removal in a water environment using natural irradiation sources.

Acknowledgement

This research is funded by Ministry of Science and Technology of Vietnam under grant number ĐTDL.CN-62.19.

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