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STUDY ON REMOVAL OF LINDANE IN WATER ENVIRONMENT BY PHOTOCATALYST USING TIO$_2$ NANOPARTICLES

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Nguyen Thi Hang [1,2], Nguyen Thu Hien[1], Nguyen Thi Thuy Linh[1], Pham Tien Duc [1*], Le Thanh Son[1*], Nguyen Van Huong [3], Bui Quang Minh[3]
1. Faculty of Chemistry, VNU University of Science, Vietnam National University, Hanoi
2. Department of Infrastructure and Urban Environmental Engineering, Hanoi Architectural University
3. Center for Research and Technology Transfer, Vietnam Academy of Science and Technology
*Email: sonlt@vnu.edu.vn; tienducpham@hus.edu.vn

TÓM TẮT

NGHIÊN CỨU LOẠI BỎ LINDANE TRONG MÔI TRƯỜNG NƯỚC BẰNG PHƯƠNG PHÁP QUANG XÚC TÁC SỬ DỤNG VẬT LIỆU NANO TiO$_2$

Thuốc diệt cỏ cơ clo, lindane được nghiên cứu xử lý bằng phương pháp quang xúc tác sử dụng vật liệu nano titan oxit (TiO_2-NPs). Vật liệu TiO_2-NPs chế tạo trong phòng thí nghiệm bằng phương pháp sol-gel và được xác định các đặc trưng bằng phương pháp nhiễu xạ tia X (XRD) và kính hiển vi điện tử truyền qua (TEM). Vật liệu TiO_2-NPs có thành phần pha chủ yếu là anatase với kích thước khoảng 30 nm. Điều kiện xử lý lindane tối ưu bao gồm pH 6,0; lượng vật liệu 0,25 mg/ml, thời gian 90 phút. Trong các điều kiện tối ưu, hiệu suất xử lý lindane sử dụng liệu TiO_2-NPs đạt trên 80%. Nghiên cứu cũng khẳng định phân hủy lindane chủ yếu do quá trình quang xúc tác với sự có mặt của các gốc tự do hơn là hấp phụ lindane trên bề mặt vật liệu TiO_2-NPs.

Từ khóa: *Lindane, TiO_2, Vật liệu nano, Xử lý nước, Xúc tác quang.*

1. INTRODUCTION

Lindane is an isomer of the gamma hexachlorocyclohexane (γ-HCH). Lindane can remain in water and soil for a long time. Lindane and other organochlorine pesticides are no longer used in the world due to the signed Stockholm. The colloidal particles may be removed form the air by rain or degraded by other compounds found in the atmosphere. In soil, sediments, and water, lindane is broken down to less toxic substances by algae, fungi, and bacteria, but this process can take a long time [1].

Various techniques have been used to remove lindane, such as biological, chemical, and physical degradation [2-7]. Among them, advanced oxidation process (AOP) using nanomaterial combining with UV light photocatalyst is one of the most effective for lindane removal in water environment [5]. AOPs are technologies which involve the generation of $OH^{\cdot}$ radicals for the purpose of oxidizing organic contaminants to their non-toxic products [8]. The $OH^{\cdot}$ radicals ensure the effective degradation of organic compounds into simple and biodegradable forms. Different solution conditions such as pH, reaction time, and material dosage are highly affected to removal efficiency.

Since TiO_2 is a very well-known semiconductor photocatalyst that can absorb an appropriate UV radiation from a light source (greater than its ban gap) to generate an electron/hole pair [8]. The TiO_2 nanoparticles

(TiO_2-NPs) are of interest for photocatalytic application because of the electronic and optoelectronic properties coupled with high surface area and quantum size effect [9]. Upon UV radiation absorption, TiO_2 produces conduction band electrons (e_{cb}^-) and valence band hole (h_{VB}^+). Many organic pollutants were removed by photogradation using TiO_2-NPs [10-12]. Recent studies investigated lindane degradation by photocatalysis using commercial TiO_2-NPs or nanocrystalline TiO_2 [13]. In addition, lindane removal through adsorption using TiO_2-NPs was also studied. However, clarification of the photocatalyst degradation or surface adsorption of lindane using TiO_2-NPs has not been reported.

In the present study, for the first time, photodegradation of lindane compared with adsorption technique in water environment using synthesized TiO_2-NPs was investigated. Some effective parameters for lindane removal by photocatalyst were systematically optimized. The mechanism of lindane removal using TiO_2-NPs is also suggested on the basis of degradation kinetic and the change in surface charge.

2. EXPERIMENTAL

2.1. Materials and Chemicals

Tetrabutyl orthotitanate (TBOT), Formula $Ti(OCH_2CH_2CH_2CH_3)_4$, namely CAS 5593-70-4, with molecular weight 340.32 g/mol (Merck, Germany).

The 1,2,3,4,5,6-Hexachlorocyclohexane (γ-Isomer), namely CAS 58-89-9) for gas chromatography, GC (with purity > 99.0%), with a molecular weight of 290.81 g/mol was purchased from Tokyo Chemical Industry (Tokyo, Japan).

Solution pH was monitoring by a pH meter (HI 2215, Hanna, USA). Other chemicals with analytical or GC grade were supplied from Merck. Ultrapure water with resistivity 18.2 MΩ.cm was produced from an ultrapure water system (Labconco, Kansai City, MO, USA).

UV lamp with capacity of 11W/220V, 254 nm was purchased from Ningbo Yawei Water Purifier Manufacture Co., Ltd, China.

2.2. Synthesis and characterization methods

The synthesis of TiO_2 nanoparticles was performed by sol-gel method, followed by heat treatment at 500°C. Firstly, we prepared a solution of ethanol, TBOT and concentrated nitric acid. A solution of ethanol and water with the ratio 7:1 and TBOT were well mixed until forming a sol-gel. This sol-gel was dried at 95 ^{0}C in 24 h. This dry powder was calcinated at 500 ^{0}C for 2 h before cooling to room temperature in a desiccator. Finally, this white powder was masticated to get TiO_2 nanoparticles.

The XRD pattern was carried out on X-ray diffractometer (Bruker D8 Advance, Germany) with Cu, K_α radiation ($\lambda = 1.54178$ Å) to confirm phase structure TiO_2-NPs. The mean of particle size and morphology of TiO_2-NPs were determined by high transmission electron microscopy (TEM) using JEM-2100 (Jeol, Japan).

2.3. Photodegradation study

The experiments were performed in a 50 ml glass vial, with a total reaction solution of 25 ml. The TiO_2 –NPs were dispersed in water with concentration of 0.1 mg/mL. The 200 ppb lindane solution was added in TiO_2 –NPs solution. Then, the suspension was adjusted to suitable pH and continuously rotated at about 50 rpm to remain a solution homogeneity under UV-light. The UV lamps was performed in a bench-scale photochemical system equipped with 4 lamps, each lamp has 11 W of voltage and emit light primarily at 254 nm. The UV lamps were turned on at least 30 min prior to the experiments for uniformity of the UV fluence rate. After photodegradtion, the solution was centrifugated in 10 min using an ultra-speed centrifuge (MR23i, JOUAN, France) with maximum 15000 rpm. A 2 ml sample was taken to be extracted by 2 ml n-hexane and quantified by gas chromatography - electron capture detector (GC-ECD). The analytical procedure by GC-ECD is decribed in our previously published paper [14]. Briefly, we used a DB-5 (5% phenyl and 95% methyl polysiloxane) capillary column of 30 m x 0. 25 mm x 0.25 µm to separate lindane in the GC system. The Nitrogen (99.99%) with a flow rate of 1.2 ml/min was used as mobile phase.

The ECD detector was set at 300 °C while injector temperature of 250 °C with splitless mode was operated. The limit of detection (LOD) was 0.09 µg/L while limit of quantification (LOQ) was 0.3 µg/L, respectively. All experiments were carried out in triplicates.

The degradation of lindane was evaluated by comparing the concentration of lindane in solution before and after photodegradation. The removal efficiency of lindane was calculated by using Equation (1):

Removal (%)= $(C - C_t) \times 100 / C_i$ (1)

where C_i and C_t are the initial lindane concentrations and concentrations of lindane at the time t, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of TiO_2 nanoparticles

The XDR pattern of synthesized TiO_2 is indicated in Figure 1. The sharp peaks appeared with high intensity at 2θ (degree) = 25.25, 37.9, 48, 53.85, 55, 62.8, corresponding to the d = 3.524, 2.380, 1.894, 1.701, 1.668, 1.482 demonstrate that the high purity crystalline of anatase is obtained.

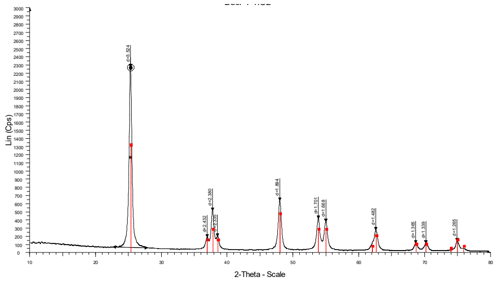

Figure 1. XRD pattern of synthesized TiO_2

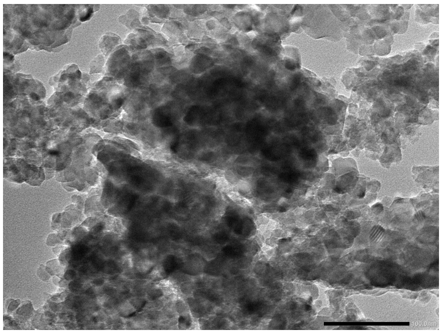

Figure 2. The TEM image of synthesized TiO_2

Figure 2 shows the transmission electron microscopy (TEM) image of the TiO_2 particles. All particles are like-cubic shape with the mean size of about 30 nm. This result confirms that our synthesized TiO_2 are nanomaterials.

3.2. Effective parameters for lindane degradation

For degradation of lindane, some effective parameters are important, such as solution pH, contact time and catalyst dosage.

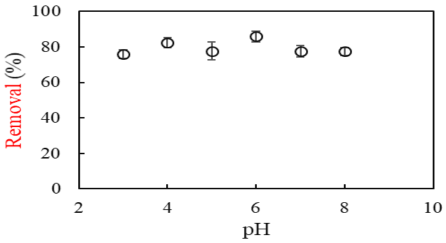

Figure 3. Effect of pH on lindane degradation using TiO_2 -NPs

The solution pH in one of the most effective parameter for the lindane degradation using photocatalyst. The pH strongly affects to the presence of radical and charging behavior of TiO_2-NPs. Figure 3 shows that highest lindane degradation efficiency of about 86 % is observed at pH 6. The degradation decreased at acidic and basic media due to the prevention of radical $OH^{\cdot}$ at high or low pH [10] .

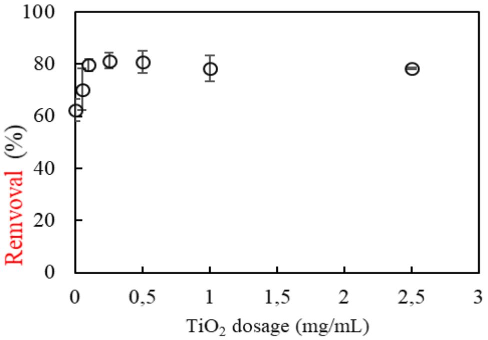

Figure 4. Effect of TiO_2 dosage on lindane degradation using

Figure 4 shows that an increase of TiO_2 dosage from 0 to 0.25 mg/mL caused a significant increase in degradation efficiency. However, further increase in catalyst dosage didnot make a change in degradation. This might be due to a fast flocculation of TiO_2-NPs. Therefore, the best TiO_2 dosage for lindane degradation is 0.25 mg/mL.

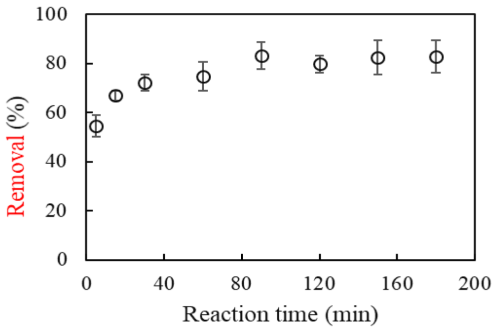

Figure 5. Effect of reaction time on lindane degradation using TiO_2-NPs

The degradation efficiency of lindane is also affected by the time using UV radiation (or reaction time). Basically, the higher degradation efficiency is achieved with increasing contact time. In our case, lindane degradation grew up when increasing reaction time from 0 to 90 min. However, there was insignificant difference in decomposition of lindane when reaction time was from 90 to 180 min (Figure 5). The degradation efficiency was higher than 80% and remained in the contact time range of 90 - 180 min.

3.3. Degradation mechanism

Degradation mechanisms of lindane using TiO_2-NPs are discussed in detail on the effect of initial concentration of lindane and the change in surface charge before and after degradation.

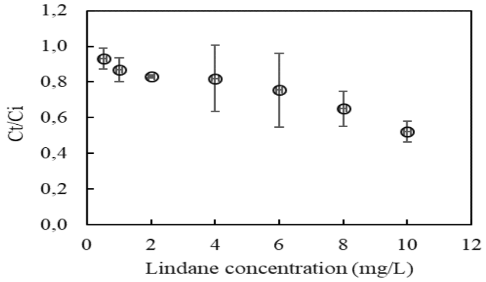

Figure 6. Effect of initial concentration on lindane degradation using TiO_2-NPs

Figure 6 shows the effect of initial concentration on lindane degradation in the range of 0.5 to 10 mg/L. The rate of degradation of lindane decreased with the increase the initial concentration from 0.5 to 2 ppm but decreased with the increase the initial concentration from 4 to 10 ppm. The degradation efficiency of lindane decreased with increasing the initial concentration. This might be due to its high resistance to oxidation via $OH^{\cdot}$ radical interaction. The formation of a large number of by-products which competed with lindane for the reactive radicals and the concentration of which increased with increasing the initial concentration of lindane [15].

The results are in good agreement with the change in surface charge monitoring by ζ potential measurements in which charging behavior of TiO_2-NPs changed insignificantly after lindane degradation (not shown in details) [16].

When adsorption of lindane on TiO_2 surface takes place, ζ potential of TiO_2-NPs change significantly due to the surface interaction and aggregation of TiO_2-NPs

will induce the change of the particle size of TiO_2-NPs [17, 18]. However, in our case, after lindane removal, the changes in particle size and the surface charge were negligible.

The highly surface charge of TiO_2-NPs can induce the photocatalytic activities, as the kinetics of photo-oxidation of organic compounds. Typically, a more efficient generation of $OH^{\cdot}$ radicals by TiO_2 is achieved in a weak alkaline medium owing to the presence of $OH^{\cdot}$ radicals, which is promoted for the photocatalytic degradation of contaminated compounds, especially the organic pollutants in aqueous solution. It implies that in our case adsorption of lindane on TiO_2-NPs surface may take place, the photocatalytic degradation is the main mechanism.

4. CONCLUSION

We have investigated degradation of lindane using titania nanoparticles (TiO_2-NPs). The TiO_2-NPs were mainly anatase with particle size of 30 nm which were confirmed by XRD and TEM measurements. Some effective conditions for lindane degradation was optimized and found to be pH 6.0; TiO_2 dosage 0.25 mg/mL, reaction time 90 min. Under optimum conditions the removal of lindane using TiO_2-NPs reached greater than 80%. Our study demonstrates that photocatalyst degradation in the presence of strong radical is the main mechanism while adsorption of lindane on TiO_2-NP surface is negligible.

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