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Photocatalytic Degradation of Alpha Cypermethrin Based on ZSM-5/TiO₂ Hybrid Composites

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ABSTRACT

Zeolite Socony Mobil-5 (ZSM-5) was successfully synthesized by a hydrothermal method from the silicon dioxide (SiO₂) precursor prepared from rice husk ash. Titanium dioxide (TiO₂) nanoparticles were decorated on ZSM-5 substrate by a sol-gel method. ZSM-5/TiO₂ materials were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscope (TEM), and Brunauer-Emmett-Teller (BET) surface area analysis. ZSM-5 was successfully synthesized in crystal structure with an average crystallite size of 3-5 μm. TiO₂ nanoparticles with the size of 3-5 nm were distributed on the surface of ZSM-5. ZSM-5/TiO₂ materials were used as a photocatalyst to remove alpha – cypermethrin, a kind of the pesticide residues. The results showed that the removal efficiency was 90% with the initial concentration of alpha - cypermethrin of 160 mg L^{-1}. ZSM-5/TiO₂ would be a very potential material for using as a photocatalyst for the treatment of persistent organic pollutants.

Introduction

The development of agriculture is accompanied by the use of many kinds of pesticides [1-3]. Therefore, pesticide residues are increasing in water and soil sources and need to be treated [2]. Pesticide residues are known as persistent organic pollutants (POPs) and they are difficult to degrade in nature in a short time. Alpha-cypermethrin ($C_{22}H_{19}Cl_2NO_3$) is a kind of POP widely used as a caricide and insecticide for controlling certain insect pests in crops [1, 4]. Alpha-cypermethrin has very low toxicity to humans, plants and animals. However, it is very toxic to aquatic life. However, more

and more pesticide residues have been discharged into the aquatic environment without treatment. Therefore, it is necessary to have a solution for POPs treatment to avoid pollution and long-term consequences.

Currently, adsorption and oxidation are two common methods, widely used for the removal of POP. The photocatalytic method has many advantages because it is not the use of harmful chemicals and is based on photocatalyst [3, 5]. The end products of oxidation are less toxic compounds such as water, carbon dioxide, and nitrogen [3]. The most popular and commercially available photocatalyst is TiO₂ with the average diameter TiO₂ nanoparticles about 25 nm (called P25)

[6, 7]. Normally, due to the size effect, nanomaterials often exhibit catalytic activity with a diameter of less than 10 nm. Therefore, there are many studies to prepare TiO_2 nanoparticles with fine size and application as photocatalysts. Furthermore, TiO_2 is often incorporated into hybrid materials to increase its catalytic activity [8, 9].

ZSM-5 is a type of zeolite with a medium-sized pore size [8-10]. Due to its large specific surface area, ZSM-5 is a suitable supporting material for nanocatalysts [11, 12]. The high surface area of ZSM-5 can enhance light harvesting and adsorption for POPs [13]. ZSM-5 can act as a support to generate adsorption and catalytic sites [9, 14]. Recently, there have been a few studies on the preparation of ZSM-5/TiO_2 for the removal of POPs [8, 9, 13, 15]. However, the preparation of ZSM-5/TiO_2 hybrid materials for the removal of pesticide residues has not been performed. In this study, silica prepared from rice husk ash was used as a raw material source for the synthesis of ZSM-5. Rice husk ash is the by-products of agriculture containing the highest silica (more than 90%) [16, 17]. TiO_2 nanoparticles were prepared by sol-gel method in situ ZSM-5. ZSM-5/TiO_2 hybrid materials were used to remove alpha-cypermethrin.

Experimental

Materials

Sodium hydroxide (NaOH), hydrochloric acid (HCl), tetrapropylammonium bromide $(CH_3CH_2CH_2)_4N(Br)$, sodium hydroxide, P25 and titanium butoxide were purchased from Aldrich Sigma. Alpha-cypermethrin was obtained from India Company. A locally collected source (at Cai Rang District, Can Tho city, Vietnam) of rice husk ash was obtained for the preparation of SiO_2.

Methods

Preparation of ZSM-5 and ZSM-5/TiO₂

ZSM-5 was prepared by a hydrothermal method with SiO_2 obtained from rice husk ash according to the previous reports [11, 12]. Briefly, SiO_2, Al $(OH)_3$, TPABr, and water were mixed in - a 35:1:10:500 molar ratio to form a mixture under stirring at 50 °C and 90 minutes, respectively. The mixture was placed in a hydrothermal reactor and carried out the reaction at 200 °C and 24 hours. The precipitate was filtered and dried before calcination at 500 °C for 5 h to obtain ZSM-5.

The ZSM-5/TiO_2 catalyst was prepared by a sol-gel method. Titanium (IV) butoxide and isopropyl alcohol were mixed in a 1:5 volume ratio, under stirring for 30 minutes to obtain a solution. ZSM-5 (0.5 g) and 1 mL of nitric acid were added into 10 mL of the solution, under stirring for 3 hours at 90 °C to hydrolyze titanium (IV) butoxide on the surface of ZSM-5. The obtained gel was dried 60 °C for 12 hours. Finally, the obtained solid was calcined at 400 °C for 3 hours.

Characterization of ZSM-5 and ZSM-5/TiO₂

Crystalline phase of ZSM-5 zeolite and ZSM-5/TiO_2 was investigated by a X-ray diffraction (XRD, D8 Phaser, Bruker, Germany) over 2 theta (2θ) range from 10° to 70° with a scanning speed of 0.05°/min using $CuK\alpha$ radiation (λ = 1.5406 Å). The surface morphology of ZSM-5 zeolite was observed under scanning electron microscope (SEM, Hitachi, S-4800) at an accelerating voltage of 10 kV after gold coating. The formation of silica was observed by Fourier transform infrared spectroscopy (FTIR, FTS-3500, Bio-Rad, USA) using KBr pellets with the scanned spectra of 4000 – 400 cm^{-1}. The distribution of TiO_2 nanoparticles within the ZSM-5 was determined by a transmission electron microscope (TEM, JEOL JEM-1400, Japan) with an accelerating voltage of 100 kV. The specific surface areas of the ZSM-5 and ZSM-5/TiO_2 were measured and determined by the Brunauer-Emmett-Teller (BET) method from nitrogen adsorption-desorption data with equipment (Quantachrome Instruments, Nova Station B)

Removal of alpha-cypermethrin

Given photocatalysts (80, 100, 120, 140 mg) were added in 100 mL of 160 mgL^{-1} aqueous solution of alpha-cypermethrin. The solution was contained in the quartz reactor and was kept in the dark for 30 minutes, under stirring for the adsorption. The mixture was then illuminated with a UVA lamp with a wavelength (360 – 400 nm) at room temperature for the photocatalytic reaction. At a given interval, 2 mL of solution was taken for evaluating alpha-cypermethrin concentration. The concentration of alpha-cypermethrin in solution was measured by a UV/VIS spectrophotometer (UV-Vis, Pharo 300, Merck, Germany), at the maximum wavelength λ_{max} = 276 nm [1, 4]. The removal efficiency of alpha-cypermethrin (η) was calculated by the following equation: $\eta = (C_0 - C_t)/C_0 \times 100\%$. where C_0 is the initial alpha-cypermethrin concentration and C is the remaining alpha-cypermethrin concentration in the solution at a given time for treatment.
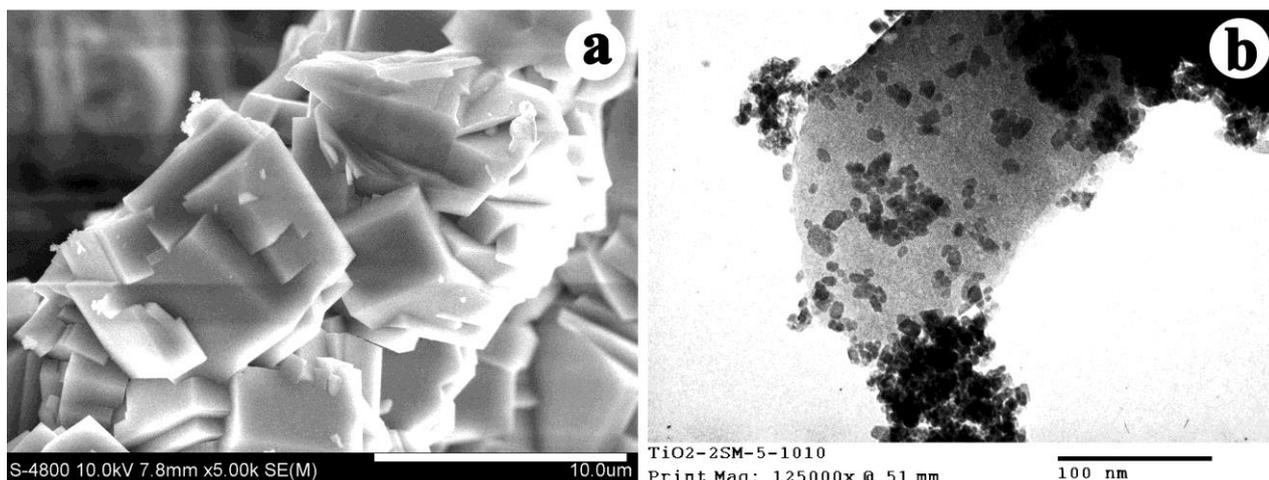
Figure 1: (a) SEM image of ZSM-5; (b) TEM image of ZSM-5/TiO₂

Results and discussion

Characteristics of ZSM-5/TiO₂

The morphology of ZSM-5 and ZSM-5/TiO₂ are shown in Fig 1. ZSM-5 materials were rectangular cubes with a size of 3-5 µm (Fig 1a). This result proved that ZSM-5 was in crystal form. The results were completely consistent with the results of previous research. In Fig 1b, the obtained TiO₂ nanoparticles are spherical and uniform with the size from 3 - 5 nm. However, the distribution of TiO₂ nanoparticles on the surface of ZSM-5 was not uniform.
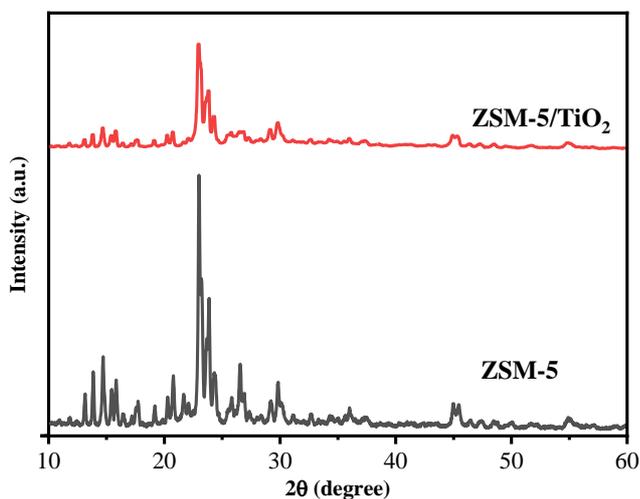
Figure 2: XRD patterns of ZSM-5 and TiO₂/ZSM-5

Fig 2 shows the XDR patterns of ZSM-5 and TiO₂/ZSM-5. The characteristic peaks of ZSM-5 were at the scanned angles of 2θ = 14°, 14.2°, 15.1°, 16°, 23.4°, 24.2°, 25.6°, and 30.2° that were corresponded to (101), (111), (102), (112), (131), (022), (051), (313), (323), and (062) planes, respectively. When decorating TiO₂ nanoparticles on the surface of ZSM-5, characteristic diffraction peaks of ZSM-5 were also obtained with lower intensity than that of pure ZSM-5. This can be explained by TiO₂ nanoparticles covering on the surface of ZSM-5, reducing the intensity of characteristic diffraction peaks. The intensities of the characteristic peaks of TiO₂ were overlapped by the characteristic peaks of ZSM-5. In addition, there was no appearance of strange peaks, indicating that obtained ZSM-5/ TiO₂ was high purity. The results were consistent with previous studies.
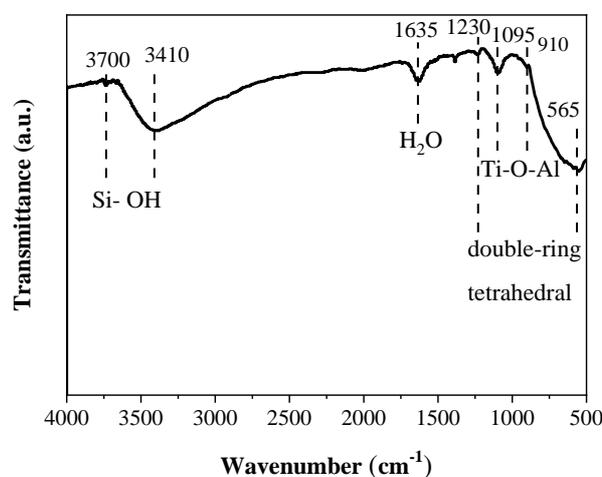
Figure 3: FT-IR spectrum of TiO₂/ZSM-5

FTIR was used to determine the functional groups of ZSM-5/ TiO₂ materials. The FTIR spectrum of ZSM-5/ TiO₂ is shown in Fig 3. The broad peaks at 565 cm⁻¹ and 1230 cm⁻¹ were attributed to pentasil double-5-ring bending vibration. The adsorption bands at 3700 cm⁻¹ and 3410 cm⁻¹ confirmed the stretching vibration of Si-OH. 1630 cm⁻¹ represented by the OH. The adsorption bands at 1095 cm⁻¹ and 910 cm⁻¹ were attributed to vibration of Ti-O-M (M=Al, Si). The peak at 1635 cm⁻¹ represented the vibration of molecule adsorbed water.
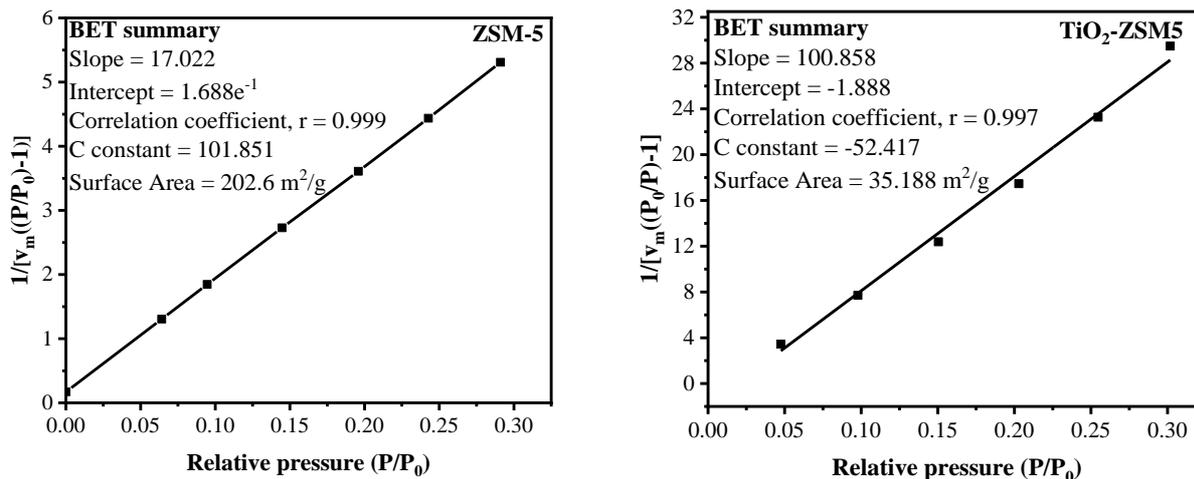
Figure 4: BET plot of the nitrogen adsorption on the: ZSM-5 and ZSM-5/TiO₂

Fig 4 shows the isothermal adsorption result of nitrogen gas on ZSM-5 and TiO₂/ZSM-5 materials. The BET adsorption equation was used to determine the surface area of the materials and is expressed as:

$$\frac{1}{v\left[\left(\frac{P_0}{P}\right)-1\right]} = \frac{c-1}{v_m c}\left(\frac{P}{P_0}\right) + \frac{1}{v_m c}$$

where, P and P_0 are the equilibrium and saturation of nitrogen; v is the volume of adsorbed nitrogen; v_m is the monolayer adsorbed nitrogen quantity; c is the BET constant. The results show that the specific surface area of ZSM-5 was 202.6 m²/g. When TiO₂ was modified into the structure of ZSM-5, the specific surface area of ZSM-5/TiO₂ was reduced to 35.188 m²/g. This could be explained that TiO₂ nanoparticles covered and reduced the surface area of ZSM-5. However, the presence of TiO₂ can play an important role in the photocatalytic application. To evaluate the photocatalytic potential, ZSM-5/TiO₂ was used as the photocatalyst for the degradation of alpha-cypermethrin.

Degradation of alpha-cypermethrin

Kinetics of photocatalytic reaction of alpha-cypermethrin

Kinetics of photocatalytic reaction of alpha-cypermethrin using ZSM-5/TiO₂ hybrid composites are shown in Fig 5. The two phases of alpha-cypermethrin treatment were adsorption and photocatalytic reaction. When the experiments were carried out in dark (30 min) conditions, the percentage removal of alpha-

cypermethrin was very slow (about 2.5%) due to the adsorption. Then, the photocatalytic reaction took place over the next 120 minutes. The reaction rate increased very quickly and reached the maximum value of 90% removal of alpha-cypermethrin (after 120 minutes of reaction). When the catalyst content increased from 80 mg to 140 mg, the percentage removal of alpha-cypermethrin increased and reached the maximum value with a catalytic content of 100 mg. This can be explained that when the catalytic content was greater than the critical value (100 mg), the excess catalysts could cover the surface of the catalyst. Moreover, the result of these two processes was a decrease in the ability to alpha-cypermethrin removal. Thus, 100 mg of ZSM-5/TiO₂ was chosen for further experiments.
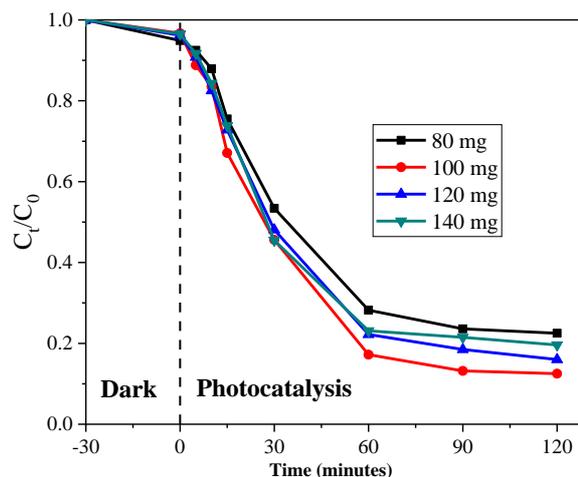
Figure 5: Kinetics of photocatalytic reaction of alpha-cypermethrin using ZSM-5/TiO₂ hybrid composites with different amount of the catalysts

Comparison the photocatalytic activity of ZSM-5/TiO₂ material with P25

Fig 6 shows the kinetics of the photocatalytic reaction of alpha-cypermethrin using ZSM-5/TiO2 hybrid composites and P25. The removal of alpha-cypermethrin also took place in 2 stages: adsorption and photocatalytic reaction. At the adsorption stage, the efficiency of alpha-cypermethrin treatment was higher when using the ZSM-5/TiO5 catalyst. This can be explained by the large specific surface area of ZSM-5 as well as the adsorption capacity of ZSM-5 in comparison to P25. However, the removal efficiency of the adsorption stage was not high (about 2.5%). At the photocatalytic reaction, the removal efficiency of alpha-cypermethrin increased significantly corresponding to 90% using the ZSM-5/TiO2 catalyst and 57.8% using the P25 catalyst. The increase in the catalytic activity of TiO2 can be attributed to two major reasons. One was due to the size effect of TiO2 (TiO2 size (about 3 - 5 nm) on the ZSM-5 surface was smaller than P25 (about 25 nm). The other was the interaction between ZSM-5 and TiO2. Therefore, ZSM-5/TiO2 would be a potential photocatalytic catalyst.
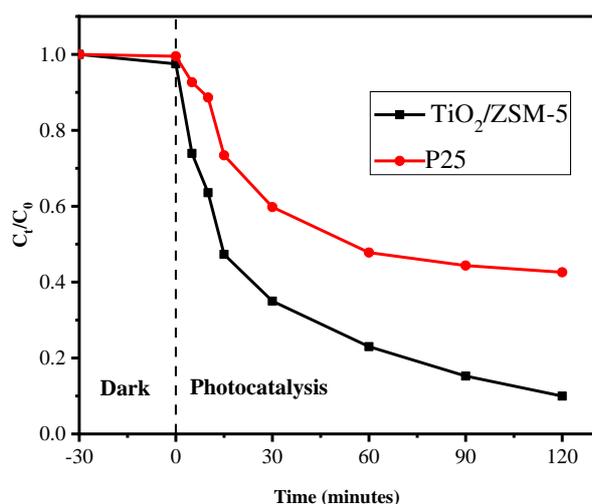
Figure 6: Kinetics of photocatalytic reaction of alpha-cypermethrin using ZSM-5/TiO2 hybrid composites and P25

Conclusion

ZSM-5 was successfully synthesized by the hydrothermal method from SiO2 source extracted from rice husk ash. TiO2 nanoparticles were prepared using a titanium (IV) butoxide precursor based on ZSM-5. ZSM-5/TiO2 hybrid composites were successfully synthesized with TiO2 nanoparticle diameters from 3 to 5 nm on ZSM-5 substrate. ZSM-5/TiO2 hybrid composites were used for the removal of alpha-cypermethrin. Results showed that 90% of alpha-cypermethrin was removed after 30 minutes of adsorption and 120 minutes of photocatalytic reaction with ZSM-5/TiO2 catalyst. Compared to commercial TiO2 (P25), the synthesized material had better catalytic activity. Therefore, ZSM-5/TiO2 hybrid composites would be a potential material for the treatment of persistent organic pollutants.

Acknowledgements

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