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The Utilization of Modified Chitosan from Shrimp Shell As Photodegradation of Pesticides Paraquat Dichloride

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Abstract
In this study, the chitosan modification of shrimp shell has been made by impregnated the chitosan from shrimp shell with Ti/ZrO_2 and ZrO_2 to formed composite of chitosan-Ti/ZrO_2 and chitosan-ZrO_2. These composites were made by immobilization technique and characterized by FTIR and SEM-EDX. The chitosan-Ti/ZrO_2 and chitosan-ZrO_2 composite were used as a catalyst to degrade the pesticide paraquat dichloride in the presence of UV light (λ = 257 nm). The photodegradation process of paraquat dichloride takes place under 10 watts UV light irradiation and was measured using spectrophotometer UV. The maximum degradation percentage of pesticide paraquat dichloride photodegradation by chitosan-Ti/ZrO_2 and chitosan-ZrO_2 composites are 61.97% and 57.97% within 30 minutes irradiation time.

Keywords
Chitosan, Chitosan-ZrO_2,Paraquat Dichloride, Photodegradation

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1. INTRODUCTION

Paraquat dichloride (PQ) is a widely used pesticide in agriculture for the treatment of broadleaf and grassy weeds in various types of crops (Khodkar et al., 2019). Despite agricultural benefits, it is highly toxic to humans and animals and has the potential to cause membrane damage through lipid peroxidation by a free radical attack. Its toxicity to terrestrial and aquatic environments also raises serious concerns. Thus, it is very essential to treat wastewaters generated as a result of the production and application of PQ before disposal to secure the health of humans, wildlife and the aquatic environment (Eleburuike et al., 2016).

Several methods were used in treating wastewater such as coagulation, photodegradation, ozonation, biological treatment, filtration, etc (Kandisa et al., 2016; Safari et al., 2019; Siregar et al., 2021). The advantages of using photodegradation are, there is no sludge produced and foul odors are greatly reduced, safety application of the reactions being performed at atmospheric pressure and near ambient temperature and requires only dissolved oxygen in water (Wang et al., 2020b). Heterogeneous photocatalysis, which is one of the AOPs, is accepted as an efficient, cost-effective and environmentally friendly method of decontaminating water that has been polluted with pesticides and other organic compounds (Fil, 2016).

Shrimp shell from household waste is often not used and just becomes garbage, whereas shrimp shell waste can be used as an adsorbent and applied in waste treatment (Younes et al., 2012). Shrimp shell waste can be taken to produce chitin and synthesized into chitosan. Chitosan is a derivative of chitin, this compound is included in the biopolymer, it obtained from the alkaline deacetylation process of chitin (Teli and Sheikh, 2012). The yield of shrimp chitosan was also 15.4% more when compared to crab and squilla chitosan (Kumari et al., 2017).

Chitosan tends to be more reactive and easily dissolves in aqueous solutions. Chitosan can dissolve in organic and inorganic solvents because it has a free primary amino acid group spread evenly in its molecular chain, so chitosan is better used than chitin (Mohadi, 2015; Nwabor et al., 2020). To improve the ability to subscribe to organic compounds, chitosan was synthesized further by the addition of semiconductor compounds that have the photocatalytic ability, such as TiO_2, ZrO_2, etc. The titanium dioxide (TiO_2) nanotubes were synthesized using different N-containing ligands and in this research, the oxide of Ti/ZrO_2 and ZrO_2 immobilize into chitosan to form chitosan-Ti/ZrO_2 chitosan-ZrO_2 composites (Mohadi et al., 2018).

According to previous research, composites materials mean the addition of properties into a combined material that can act as a photocatalyst which is then called a photocatalyst and on the other hand can be play a role as an adsorbent to overcome the weaknesses of conventional photocatalysts (Siregar et al., 2021). The composite means the addition of properties into a combined material that can act as a photocatalyst which is then called a photocatalyst and other hands can be as an adsorbent to overcome the weaknesses of conventional photocatalysts (Safari et al., 2019; Wang et al., 2020a). The chitosan-Ti/ZrO_2 chitosan-ZrO_2 composites have been made with various approaches to produce materials that are more effective in reducing hazardous waste both in industrial waste and organic compounds waste, because chitosan is an adsorbent for the waste substance, while Ti/ZrO_2 and ZrO_2 as photocatalytic agents. From the description, it is necessary to research the ability of chitosan-Ti/ZrO_2 chitosan-ZrO_2 composites to reduce the concentration of paraquat dichloride pesticides in an aqueous medium by adsorption mechanism and besides that, it is also expected that chitosan-Ti/ZrO_2 chitosan-ZrO_2 composites from shrimp shell waste can be used to degrade paraquat dichloride pesticides by the photocatalytic process.

2. MATERIALS AND METHODS

The chemical reagents such as sodium hydroxide, hydrochloric acid, titanium dioxide, zirconyl chloride octahydrate were in analytical grade and used directly after being purchased from Merck without any further purification. The analytical instruments were Fourier Transform Infra-Red (FT-IR) spectroscopy Shimadzu Prestige-21, SEM-EDX JEOL JED-2300 and UV-Vis spectrophotometer Double Beam Shimadzu UV-1800.

2.1 Preparation of Chitosan from Shrimp Shell

The preparation of chitosan from shrimp shells was conducted by demineralization and deproteination processes (Teli and Sheikh, 2012). As much as 100 g of 60 mesh shrimp shell was put into a 500 mL beaker glass, then adding 1 M HCl solution with a ratio of 1:10 (w/v). The mixture is stirred at room temperature for 3 hours at 60°C, then filtered and the residue dried in an oven at 70°C until dry to constant weight. After the demineralization step the samples continue to the deproteination process, where the residue from demineralization step was put into a 500 mL beaker glass and added with 0.1 M NaOH solution at a ratio of 1:10 (w/v). The mixture was heated and stirred at 60°C for an hour and then filtered. Chitosan was dried in an oven at a temperature of 70°C until dry to constant weight. Chitosan has been obtained then characterized using FT-IR and SEM-EDX.

2.2 Preparation of Chitosan-Ti/ZrO_2 and Chitosan-ZrO_2 Composites

An amount of 1.8 g of chitosan was added to 0.1 M HCl solution slowly and stirred with a magnetic stirrer until it dissolved completely. Then added ZrO_2 with a ratio of 1:1 (w/w) with chitosan. The solution is then precipitate and filtered using filter paper, from this process will be obtained chitosan-ZrO_2 composite deposits. The residue is washed with distilled water until the pH is neutral. Then dried at 70°C using an oven, this step is repeated until the weight of chitosan-ZrO_2 composite was constant. Chitosan-ZrO_2 composite was then characterized by FT-IR to see its function group, and the surface morphology of Chitosan-ZrO_2 composites was characterized by SEM-EDX. A similar procedure has been conducted to formed chitosan-Ti/ZrO_2 which is the ratio of chitosan : TiO_2 dan $ZrOCl_2$ is 1:1. Then the obtained material has been characterized by FT-IR and SEM.

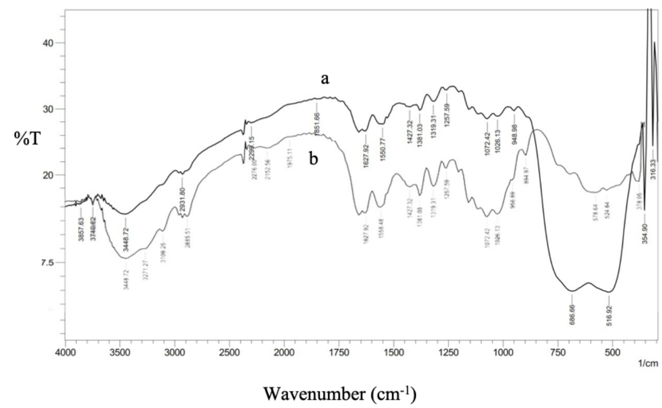

Figure 1. FT-IR Spectra for Chitosan-Ti/ZrO_2 (a) and Chitosan-ZrO_2 (b) Composite

2.3 Determination of Adsorption and Photodegradation Capacity of Chitosan-Ti/ZrO_2 and Chitosan-ZrO_2 Composite

A total of four standard solutions of paraquat pesticides with a volume of 30 mL in various concentrations of 5, 10, 20, and 40 mg/L interact with 0.1 g chitosan-Ti/ZrO_2 and chitosan-ZrO_2 composite for 30 minutes. The interaction was carried out in two different conditions, namely with or without irradiation of UV light. After 30 minutes the mixture was separated by centrifuge for 5 minutes at 5000 rpm. The filtrate was then measured using a UV spectrophotometer with 257 nm as the maximum absorbance wavelength.

3. RESULTS AND DISCUSSION

The chitosan modification that has been synthesized from shrimp shells was characterized by FT-IR Spectrophotometer and SEM-EDX to see the functional groups and the degree of deacetylation and the morphology of composite materials. FT-IR spectrum data from chitosan-Ti/ZrO_2 and chitosan-ZrO_2 composite were measured at a wavelength of 400 cm^{-1} - 4000 cm^{-1} as shown in Figure 1.

Figure 1 showed that the chitosan-Ti/ZrO_2 (a) and chitosan-ZrO_2 (b) composite has similar broad vibration between 3000-3750 cm^{-1} which indicates the presence of -OH and -NH_2 groups which are active as chitosan. The presence of -NH_2

stretching is mentioned in 3749.62 cm^{-1} and -OH stretching vibration at 3448.72 cm^{-1}. Similar peaks of composite materials were also found at 2900-2930 cm^{-1} which indicated that the presence of -CH group (Younes et al., 2012). The bending vibration of the –NH amide group of the chitosan-Ti/ZrO_2 (a) and chitosan-ZrO_2 (b) composite appeared at1627.92 cm^{-1}. The metal oxide vibrations of composites material appeared in 500-700 cm^{-1}, which indicated O-Ti-O at 686.66 cm^{-1}, and O-Zr-O from chitosan-ZrO_2 composites will appear in an area of about 500 cm^{-1} temporarily from Figure 2. The absorbance at a wavelength of 570.93 cm^{-1}. Typical absorbance seen at wavenumbers below 1000 cm^{-1} indicates specific for inorganic compounds.

SEM analyses are important to investigate the structural properties of the composites. The morphologies of chitosan-Ti/ZrO_2 and chitosan-ZrO_2 composite were presented in Figure 2.

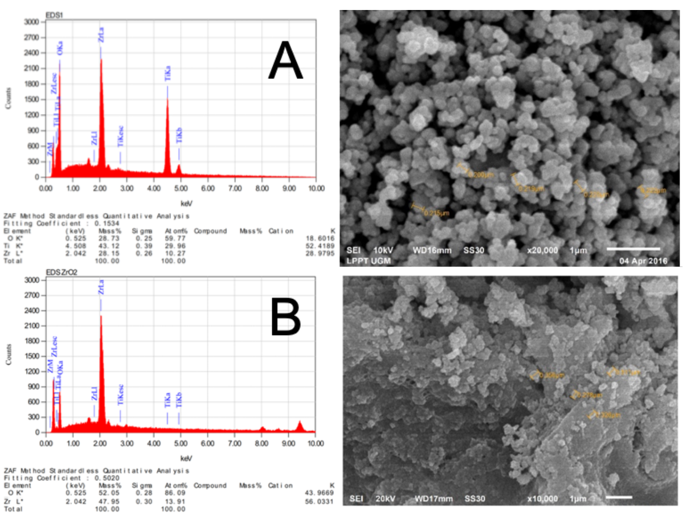

Figure 2. SEM-EDX Data for Chitosan-Ti/ZrO_2 (a) and Chitosan-ZrO_2 (b) Composite

SEM images of chitosan-Ti/ZrO_2 (a) composite showed round-shaped particles on their surface, which indicates the TiO_2 particles. The chitosan-ZrO_2 (b) surface preserves the same round-shape structure which indicates the ZrO_2 has been distributed but unevenly on the surface of chitosan. According to EDX results, Ti and Zr content in the composite materials was found in good agreement with Zr doping amount (Demircivi and Simsek, 2018).

3.1 Photodegradation of Paraquat Chloride Pesticides Using Chitosan-ZrO_2 Composite

For effective photocatalytic degradation reactions of the composite materials can be achieved by the preliminary adsorption of the pollutant. Therefore, to investigate the adsorption equilibrium of the catalysts, dark adsorption experiments were conducted by g 10 mg composite materials with 30 mL of varying concentration of to paraquat dichloride pesticide solution

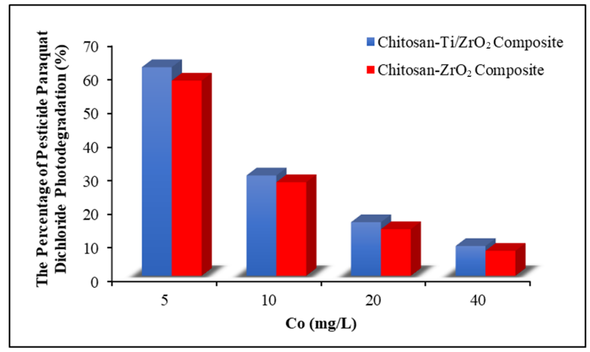

Figure 3. Percentage of Photodegradation of Pesticide Paraquat Dichloride by Chitosan-Ti/ZrO_2 (a) and Chitosan-ZrO_2 (b) Composites at Various Concentrations

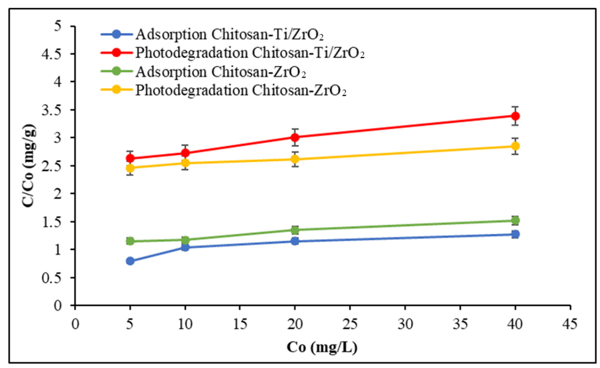

Figure 4. Graph of Comparison Between Removal Efficiency of Pesticide Paraquat Dichloride by Composite Materials using Adsorption and Photodegradation Treatment

under UV light radiation for 30 min shaking as shown as Figure 3.

The removal efficiency of chitosan-Ti/ZrO_2 (a) and chitosan-ZrO_2 (b) composite were found as 61.97 and 57.97% within 30 min at a lower concentration. The results of both composites materials showed that the photodegradation ability was decreased with concentration increasing of paraquat dichloride pesticides in an aqueous medium, this was possible due to weak interaction of the UV light with composite material when the concentration of absorbate is increased. These findings showed that the pesticide paraquat dichloride can be removed by composites materials. As the comparison, the study of comparison between adsorption and photodegradation using both composite materials onto pesticide paraquat dichloride has been presented in Figure 4.

Figure 4 showed that the removal efficiency of composite material has good ability using photodegradation treatment than adsorption treatment with the removal efficiency up to 3.39-2.85 mg/g for chitosan-Ti/ZrO_2 and chitosan-ZrO_2 composite, respectively. These findings showed that

Table 1. Comparison the Results in Paraquat Dichloride Pesticides Degradation

Degradation Agent	Percentage Degradation	Degradation time	References
W-TiO_2 (tungsten-doped P_{25} TiO_2)	98%	6 h	(Kaur et al., 2019)
TiO_2	60%	3.5 h	(Moctezuma et al., 1999)
Sphingomicrobium marinum	59.96%	2 h	(Teerakun et al., 2020)
CeO_2- modified TiO_2 nanotubes	51%	3 h	(Eleburuike et al., 2016)
TiO_2 thin film	48%	3.5 h	(Ali and Hassan, 2008)
TiO_2 nanostructured	35%	4 h	(Razali et al., 2013)
TiO_2-ZnO	51.22%	4 h	(Ali and Hassan, 2008)
ZnO	57.64%	2 h	(Arfi et al., 2017)
Chitosan-Ti/ZrO_2 composite	61.97%	30 minutes	This work
Chitosan-ZrO_2 composite	57.97%	30 minutes	This work

photodegradation treatment is twice bigger than the adsorption process with an adsorbed capacity of only 1.52-1.27 mg/g. These phenomena assumed that the UV light degradation of pesticide paraquat dichloride to become small molecule than before to the small molecule can more easily adsorb (Arfi et al., 2017). Furthermore, in this study, the comparison of similar studies is shown in Table 1. Table 1 showed that this study has a good percentage degradation with fast irradiation time.

4. CONCLUSIONS

The preparation of chitosan modified to formed chitosan-Ti/ZrO_2 and chitosan-ZrO_2 composites have been successfully prepared. FTIR spectra were showed similar peaks and characteristics of chitosan and metal oxide. The morphologies of SEM showed similar irregular round-shaped particles on the composite materials. The removal efficiency of chitosan-Ti/ZrO_2 and chitosan-ZrO_2 composite were found as 61.97 and 57.97% within 30 min at 5 mg/L. Moreover, the pesticide paraquat dichloride photodegradation using chitosan-Ti/ZrO_2 and chitosan-ZrO_2 composite take less reaction time and higher degradation ability compared to the results of other studies.

5. ACKNOWLEDGEMENT

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