SYNTHESIS OF NANOCOMPOSITE CHITOSAN-TiO_2 AND ITS APPLICATION AS PHOTODEGRADATION AGENT OF METHILEN BLUE IN AQUEOUS MEDIUM

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ABSTRACT

Synthesis of nanocomposite chitosan-TiO_2 have been done. Nanocomposite made of chitosan was isolated from crab shell namely α-chitosan and squid pens as β-chitosan. Nanocomposite was synthesized by combining the function of chitosan as supporting material with TiO_2 particle that have high photocatalytic activity. The nanocomposite characterized by FTIR and SEM/EDX analysis show the functional groups of chitosan and and also surface morphology of nanocomposite chitosan-TiO_2. The FTIR spectra shows adsorption band of O-Ti-O at 677-695 cm^{-1}, and characteristic adsorption band of chitosan at wavenumbers 1600 cm^{-1} for -NH_2 and 3400 cm^{-1} for -OH. From SEM/EDX analysis can be seen that TiO_2 has been distributed evenly on surface of chitosan. The nanocomposite was applied for photodegradation of methylene blue in aqueous medium on UV light radiation. The optimum percent photodegradation at wavelength 660 nm by the nanocomposite α-chitosan-TiO_2 and β-chitosan-TiO_2 are 59,48% and 59,82%, respectively.

Key words*: chitosan, nanocomposite, methylene blue, photodegradation.*

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1. Introduction

Chitosan is a natural biopolymer with abundant resource. Chitosan is derived from chitin, including compounds produced from deacetylation process by high concentrations of NaOH [1], where the majority of chitin and its derivatives produced by animals crustaceans [2]. The structure of chitin and chitosan have difference lies in the comparison of the amine group ($-NH_2$) with an acetyl group ($-CH_3CO$) is called the degree of deacetylation [3].

Muzzarelli and Jeuniaux [4] have reported that the chitin produced from crustacean shells of animals, such as shrimp or crab α-chitin structure, while the structure of the β-and γ-chitin chitin respectively generated by squid pens and fungi. Chandumpai *et al*. [5] for their studies have compared the content of chitosan produced from shrimp shells with squid pens, where the percentage of chitosan produced from squid pens and shrimp shell powder around 25-30% and 15-20% of the dry weight, respectively.

The non-biodegradable organic compounds in the environment as well as dye wastes generated from the textile industry is a major problem in aquatic environments One of the many examples of the dyes used in the textile industry is methylene blue. This compound is quite stable so it is difficult to degraded in nature and harmful to the environment especially in very large concentrations because it can increase the value of Chemical Oxygen Demand (COD) in surface water [6].

Various techniques or methods to reduce pollution from textile waste have been developed, including the method of adsorption. However, this method is not so effective because and when its accumulated in the adsorbent somehow will lead to new problems in the future [7]. As an alternative, in this research the use of photodegradation method by photocatalyst materials with irradiated by ultraviolet light able to decompose the dye waste. In this study the metal oxide TiO_2 that has a high photocatalytic activity dispersed into chitosan which acts as a supporting material to form nanocomposite chitosan-TiO_2 that has high photocatalytic activity and applied as photodegradation agent of methylene blue in aqueous medium.

2. Materials and Methods

2.1 Materials

Crab shells and squid pens taken from Cinde traditonal market in Palembang. Crab shells and squid pens samples washed and dried under sun light for four days. The dry crab shells crushed by a mortar, while the squid pens crushed by grinder and then sieved to 80 mesh. The chemical reagents as well as sodium hydroxide, hydrochloric acid, titanium dioxide, methylene blue, silver nitrate were used directly after purcased from Merck with out any further purification. The instrumental laboratory that used in this research were UV-Vis spectrophotometer Shimadzu UV-2600, spectrophotometer FT-IR 8201PC, and SEM-EDX JEOL JED-2300.

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2.2 Methods

2.2.1 Preparation of chitosan from crab shells and squid pens

The research studies in the laboratory indicate that the squid pens contain only small amounts of the mineral content of about 0.03%, so that the demineralization process can be eliminated, so preparation of chitosan from squid pens started by deproteinasi step while for crab shell started from demineralization according to Chandumpai *et al.* methods [5].

2.2.1.1 Demineralization

Amount of 50 g of 80 mesh crab shell put into a 500 mL beaker glass, then adding 1 M HCl solution with a ratio of 1:10 (w/v) between shell crab and HCl. The mixture is stirred with a magnetic stirrer at room temperature for 3 hours and then filtered with Whatman 41 μm filter paper while continously washed with purewater until no residual chloride ion remain in the samples. The washing process is stopped if no turbid solution formed when the filtrate drops with $AgNO_3$ solution and the pH was neutral. The residue dried in an oven with a temperature max of 70°C until dry to constant weight.

2.2.1.2 Deproteinasi

After demineralization step the samples continue to the proteinasi process, where the residue from demineralization step was put into a 500 mL beaker glass and added with 1 M NaOH solution at a ratio of 1:10 (w/v) between the shells of crabs and NaOH solution. The mixture was heated and stirred at 60°C on a hotplate for 1 hour and then filtered with Whatman 41μm filter paper. The residue were found on the filter paper was washed with purewater water until neutral pH, and then dried in an oven with a temperature of 70°C until dry to constant weight, the product namely chitin.

2.2.1.3 Deacetylation

Chitosan is produced by deacetylation of chitin, which product from deproteinasi step was put into the glass beaker and added 50% NaOH solution at a ratio of 1:10 (w/v) between the crab shells and NaOH solution. The mixture is heated and stirred at a temperature above 90°C on hotplate for 2 hours. The mixture was filtered with Whatman 41 μm filter paper and the residue was washed with distilled water until the residue namely chitosan in neutral pH. Chitosan was dried in an oven at a temperature of 70°C until dry to constant weight. Chitosan has been obtained then characterized by FT-IR spectrophotometer to identify the functional groups of chitosan, and determine the degree of deacetylation product by base line method.

2.2.2 Synthesis of Chitosan-TiO_2 nanonanocomposite from crab shells and squid pens

Amount of 10 g of chitosan from crab shell and squid pens was added into 100 mL of 0.1 M HCl solution in 250 mL beaker glass, while continously stirring until it dissolved evently and the TiO_2 particle was added with a ratio of 1: 1 (w/w) between chitosan and TiO_2. The mixture then filtered with Whatman 41μm filter paper to obtain the nanocomposite chitosan-TiO_2 as residue on the filter paper then continue washed with purewater until the filtrate water in neutral

pH, then the residue dried in an oven at temperature of 70°C until dry to constant weight. The same procedure was also performed for chitosan from squid pens. After drying process, the nanocomposite chitosan-TiO_2 is characterized by FT-IR spectrophotometer and SEM-EDX.

2.2.3. Determination of the activity of nanocomposite chitosan-TiO_2 on photodegradation and adsorption of methylene blue in aqueous medium

Amount of 30 mL of methylene blue solution with a concentration of 5 mg/L was mixed with 0.1 g of nanocomposite chitosan-TiO_2 with contact time at 60 minutes with two different conditions, i.e. with and without illuminated by UV light. After 60 minutes of interaction the mixture was separated using a centrifuge at 5000 rpm for 5 minutes to separate the nanocomposite chitosan-TiO_2 with methylene blue solution. The methylene blue photodegraded or adsorbed by the nanocomposite chitosan-TiO_2 measured using UV-Vis spectrophotometer Shimadzu UV-2600 at a working wavelength of 660 nm. The concentration of methylene blue solution is varied as well as 10, 20, 40, and 60 mg/L. From the absorbance values the percentage of photodegradation and adsorption of methylene blue can calculated. The same procedure was also performed for nanocomposite chitosan-TiO_2 from squid pens, and TiO_2.

3. Results and Discussion

3.1 Caracterization of Chitin, Chitosan and nanocomposite Chitosan-TiO_2 from Crab shells and squid pens by FT-IR Spectrophotometer

Crab shell powder and squid pens that have been prepared deproteinasi process, which is an early stage to obtain chitosan. Yield produced on stage deproteinasi reached 60.15% for shell crab, squid bone while the yield obtained approximately 65.04%. In the demineralization process, a process of removal of the primary minerals found in crab shells as calcium carbonate ($CaCO_3$) which resulted in yield of 40.02%. The final step to obtain chitosan process called deacetylation. In the process, the yield of chitosan derived from chitin of crab shells was 70.71%, while the yield obtained for chitin of squid pens about 85.73%.

The FT-IR Spectrum of raw crab shells and squid pens, chitosan and the nanoparticle are show in Fig. 1. The crab shells and squid pens before treatment still has an acetyl group by the appearance of absorption at wave number 1070 cm^{-1} indicating the presence of -CO group stretching vibration and wave number 2900 cm^{-1} which indicates the stretching vibration -CH_3. The typical absorption for chitosan from crab shells in the wavenumber of 3448.72 cm^{-1} which indicates the presence of hydrogen bonding of the-OH group that overlaps with the –NH region, while for raw squid pens, visible-OH group stretching vibration at 3410.15 cm^{-1} region [7].

The deacetylation of chitin tranform to chitosan has succesfull which indicates disappearance of the C=O group in 1680-1660 cm^{-1} indicates missing or have reduced the C=O group of chitin, as well as the appearance of absorption at 871.82 cm^{-1} for the FT-IR spectrum of chitosan from crab shells and 894.97

cm^{-1} for the FT-IR spectra of chitosan from squid pens which indicates vibrations of the NH_2 group of chitosan [8]. The results of the calculation method based on the degree of deacetylation by the base line method on FT-IR spectra, the degree of deacetylation of chitosan from crab shells was 76.6% and for chitosan from squid pens was 70.42%.

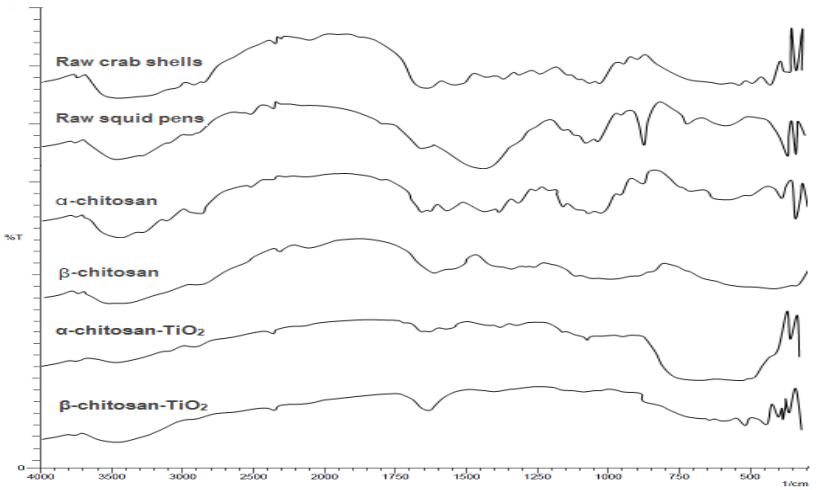

Figure 1. FT-IR spectra of crab shells,squid pens, chitosan and nanoparticle chitosan-TiO_2.

Interpretation of the FT-IR spectra of nanocomposite chitosan-TiO_2 from crab shell or squid pens indicated by the absorption at around 3000-3750 cm^{-1}. This indicates that there is a primary -OH group and the NH_2 group which is active in the chitosan. The adsorption of O-Ti-O for nanocomposite chitosan-TiO_2 from crab shells appear on the 694.37 cm^{-1}, whereas for nanocomposite chitosan-TiO_2 from squid pens absorption of O-Ti-O appeared at 678.94 cm^{-1} region. The typical absorption in the wavenumber region below 1000 cm^{-1} shows the absorption for inorganic compounds, especially Cu metaloxide according to EDX data in Fig. 2.

3.2 Characterization of Nanocomposite of Chitosan-TiO_2 by SEM/EDX

The SEM images (Fig. 3) of nanocomposite chitosan-TiO_2 show that TiO_2 nanoparticles are distributed evenly over the surface of chitosan to form nanocomposite chitosan-TiO_2.

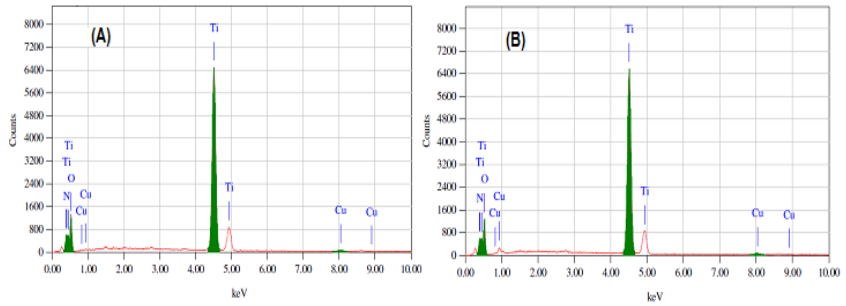

Figure 2. Data analysis of Energy Dispersive X-ray of (a) nanocomposite of α-chitosan-TiO_2 from crab shells (b) nanocomposite of β-chitosan-TiO_2 from squid pens.

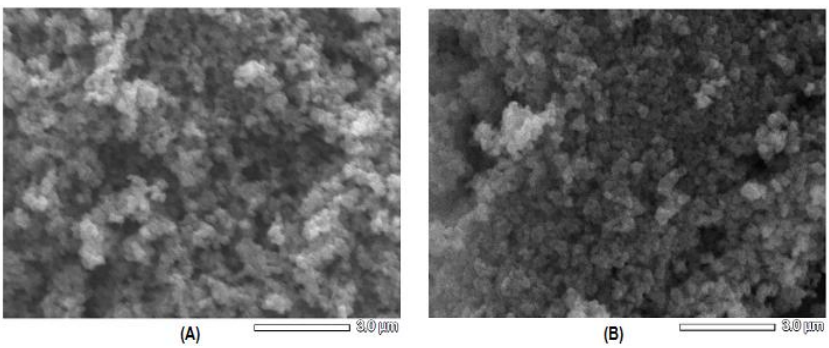

Figure 3. Scanning Electron Microscope (SEM) with magnification x10.000 for (a) nanocomposite α-chitosan-TiO_2 from crab shells (b) nanocomposite β-chitosan-TiO_2 from squid pens.

The SEM image also agree to the EDX data (Fig. 3) of nanocomposite chitosan-TiO_2 from crab shells and squid pens. The nanocomposite chitosan-TiO_2 from crab shells and squid where most of the surface covered by white TiO_2 nanoparticles.

3.3 Chitosan-TiO_2 nanonanocomposite and TiO_2 activity on photodegradation and adsorption of Methylene Blue

The wavelength used is obtained from the highest absorbance measurement value of 6 mg/L methylene blue solution in a wavelength region from 550 to 720 nm. The measurement results indicate that the value is highest absorbance at a wavelength of 660 nm with the absorbance value of 0.476. Photodegradation activity of nanocomposite chitosan-TiO_2 and TiO_2 can be seen from the percentage of photodegradation methylene blue that shows in Fig. 4.

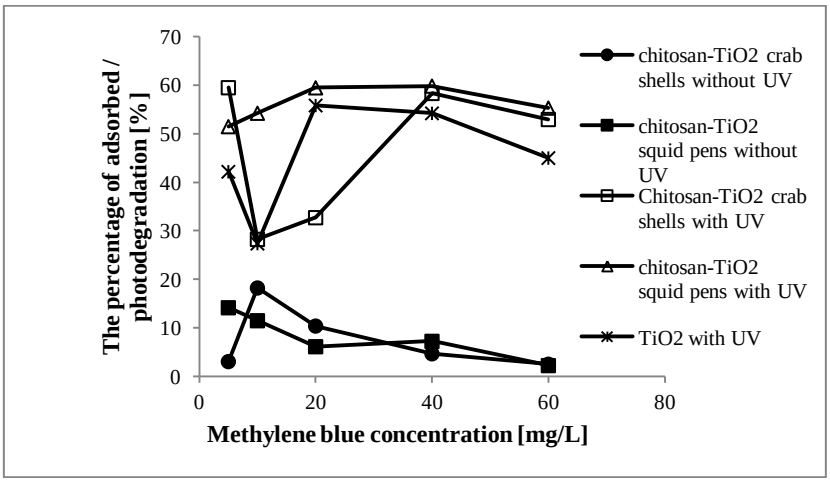

Figure 4. The concentration vs percentage of photodegradation of methylene blue by nanocomposite chitosan-TiO_2 and TiO_2 with and without UV irradiation.

Nanocomposite of chitosan-TiO_2 synthesized from crab shells and squid pens both have good activity to photodegrade of methylene blue. Chitosan nanocomposite-TiO_2 from crab shells capable to photodegrade ofmethylene blue with irradiated of UV light were 59.48%; 28.26%; 32.73%; 58.31%; and 52.94% for each concentration of methylene blue 5, 10, 20, 40, and 60 mg/L. Chitosan nanocomposite-TiO_2 from squid pen indicate percent photodegrade of methylene blue were 51.47%; 54.23%; 39.46%; 59.82%; and 55.29% for each concentration of methylene blue 5, 10, 20, 40, and 60 mg/L. The optimum conditions of nanocomposite chitosan-TiO_2 from crab shells and squid pens was at concentration of 40 mg/L methylene blue with a percentage photodegradation of 59.48% and 59.82%, respectively. The metal oxide TiO_2 also able to degrade of methylene blue, and the optimum conditions for it at a concentration of 20 mg/L with a percentage of 55.82% photodegradation.

Figure 4 shows also the percentage adsorption of nanocomposite chitosan-TiO_2 as adsorbent in adsorption of methylene blue without UV light irradiation. To compare the activity of nanocomposite chitosan-TiO_2 in degrading methylene blue with and without UV light irradiation. The nanocomposite of chitosan-TiO_2 was interact with methylene blue solution than stored in dark room (unirradiated by UV light), the percentage of adsorption of methylene blue where 3.10%; 18.26%; 10.42%; 4.71%; and 2.57% for initial concentrations of 5, 10, 20, 40, and 60 mg/L. In this condition the photodegradation process does not occur, but only the adsorption process by the fungtional group of chitosan of nanocomposite chitosan-TiO_2 to give low percentage of methylene blue were adsorbed.

The adsorption activities by nanocomposite chitosan-TiO_2 of squid pen are also shown in Fig. 4. Where, nanocomposite chitosan-TiO_2 of squid pen is able to adsorb methylene blue without UV light irradiation with the adsorption percentage of 14.19%; 11.52%; 6.17%; 7.28%; and 2.28%. The adsorption capacities of nanocomposite chitosan-TiO_2 both from squid pen and crab shell are able to reduce concentration of methylene blue in the solution. The adsorption process occur effectively only at lower concentration and reduce gradually in higher initial concentration of methylene blue 20, 40 and 60 mg/L, this indicates that adsoption prosess occur as monolayer and all functional group of chitosan have bending of adsorbate molecule. While, the photodegradation process more dominant occurs at higher initial concentration of methylene blue. Nanocomposite chitosan-TiO_2 of squid pen has a slightly higher percentage of photodegradation capacity than the nanocomposite chitosan-TiO_2 from crab shells. This is caused by the structure of β-chitosan from squid pen which tend to be more open structure compare to the α-chitosan of crab shell, it causes TiO_2 particles on the composite surface of β-chitosan of squid pen has easily access to photodegrade of methylene blue than the α-chitosan of crab shell.

4. Conclusions

Based on the research that has been done, it can be concluded that chitosan-α that have been isolated from crab shells produce yield of 70.71%, while the chitosan-β that have been isolated from squid pens generate yield of 85.73%. The degree of deacetylation of the chitosan-α to shell crab is 76.6%, while the degree of deacetylation of the chitosan-β for squid pens is 70.42%. The photodegradation of methylene blue by nanocomposite chitosan- TiO_2 from crab shells and squid pens produce optimum photodegradation activity at concentrations of 40 mg/L with a percentage of photodegradation of nanonanocomposite was 59.48% and 59.82%, respectively.

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