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Synthesis of Chitosan Sulfate From Crab (Scylla serrata) and its application as adsorbent

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ABSTRACT

Synthesis of chitosan sulfate from crab (Scylla Serrata) shell and its application as Remazol Yellow FG dye adsorbent has been studied. This experiment was conducted to study the effectiveness of chitin from crab shell to be converted into chitosan sulfate and to study the adsorption of chitosan sulfate by Remazol Yellow FG dye. Isolation of chitin from crab shell was done by deproteination and demineralization process. Chitin had been converted into chitosan using demineralization process. Chitosan sulfate was made by reacting chitosan with 1 M ammonium sulfate solution. Characterizations of the chitosan are involving determination of degree of deacetylation. Functional group of chitin, chitosan and chitosan sulfate were determined by FTIR spectroscopy. The dye adsorption of chitosan sulfate was analyzed with UV-Vis spectroscopy. The result showed that rendement of chitin, chitosan and chitosan sulphate were 28.57%, 52.5% and 92%. The degree of deacetilation of chitin and chitosan were 80 – 90% and 70 – 80%. Remazol Yellow FG was adsopr 76.5%.

Keyword: *: Remazol yelow FG, crab shells, chitosan sulfate*

1. INTRODUCTION

Since the appearance of dyes in effluents is a major concern, it was their adverse effects to many forms of life. The deliverance of dyes in the environment is the matter of concern for both toxicological and esthetical reasons (Metivier-Pignon, Faur-Brasquet & Cloirec, 2003). For example in industries, they produce textile, paper, plastics, etc., to use dyes in their products and also to consume substantial volumes of water.

The colour is a part of contaminant to be recognized in wastewater. The presence of very small amounts of dyes in water is highly visible and undesirable (Robinson, McMullan, Marchant & Nigam, 2001; Banat, Nigam, Singh & Marchant, 1996). Remazol yellow FG (RY FG) dye is the most commonly used for dyeing cotton, silk and batik. It can cause eye burns which may be responsible for permanent injury to the eyes and skin of human and animals. Therefore, the treatment of effluent containing such dye is of interest.

Adsorption is the major techniques of dye removal which the procedure of choice and gives the best results as it can be used to remove different types of coloring materials (Jain, Gupta, Bhatnagar & Suhas, 2003; Ho & McKay, 2003; Derbyshire, et al, 2001). Nowdays, many approaches have been studied for the development of effective adsorbents. Many adsorbents, including natural materials, biosorbents, and waste materials from agriculture and industry, have been proposed by several

workers. These materials could be used as adsorbents for the removal of dyes from solution (Rafatullah, et al, 2010).

In the present study a chitosan, the second most widely available polysaccharide after cellulose, was synthesized from chitin in the crab shell which has been chemically modified and effectively used for the adsorption of RY FG dye. Chitosan is obtained from deacetylation of chitin, which is a major component of crab shells. Chitosan proves to have wide applications in various fields (Kumar, 2000). It has interesting properties such as biocompatibility and biodegradability, and its degradation products are non-toxic (Crini, 2005).

Chitosan synthesized from crab shell which a bargage in the Muara Kapuas Restaurant in Yogyakarta was produced chitin. It is the form of flakes or powder (Kahu, Daravanan & Jugalde, 2014). The property of chitosan is insoluble in ammonium sulfate. Since it has free amino groups, it would be to react with sulfate ion by forming the corresponding salt. Although, sulfate, being divalent, crosslinks the protonated chitosan chains, forming sulfate-crosslinked chitosan. Such crosslinking in chitosan has been reported by Mayyas (2012) who has prepared SCC for medicinal applications by treating chitosan hydrochloride gel and sodium sulfate.

2. RESEARCH METHOD

Materials. Crab shell from Muara Kapuas Restaurant, Yogyakarta, Indonesia, ammonium sulfat, Remazol Yellow FG, hydrocloric acid, sodium hydroxide were purchased from Merck, Indonesia.

Isolation Chitin from Crab Shell. In typical experiment, Crab shells obtained from Muara Kapuas Yogyakarta, Indonesia. It processed the washing and drying process in order to facilitate the storage. The shells of crabs destroyed until soft (in powder form). Process demineralization begins with a 5% HCl solution. One hundred grams of powder crab shell incorporated into the solution and stirred evenly for 1 to 2 hours at room temperature with a weight ratio of powder crab (gram): 5% HCl volume (mL) is 1: 10. After that the bark powder crab drained with filter paper and washed with distilled water until at pH ± 7, the results of residue is filtered and dried by heating oven at 80 ºC. This demineralization process aims to eliminate the minerals contained in the shells of crabs, especially calcium. The next step is the process deproteination. Fourteen grams of powder cakang crab demineralized at reflux in a 5% NaOH solution at temperature 65 ºC - 80 ºC while stirring using a magnetic stirrer evenly for 1.5 hours to 2 hours with crab powder weight ratio (gram): 5% NaOH volume (mL) is 1: 10. After the drained crab shell powder with paper filter and washed with distilled water until at pH ± 7, the result of the residue is filtered and dried by heating in the oven at temperature of 80 ºC. After a constant weight, it is ready to be used for FTIR analysis. (Yield: 28.57%).

Chitosan Synthesis. In the synthesis of chitosan, deacetylation of chitin process is carried out which have been previously generated. Two grams of crab chitin powder was dissolved in 25 ml 45% w / v NaOH and it is mixed with agitation. Then a solution was placed in a microwave with long light of 2 minutes. Product filtered and washed with distilled water until the pH ± 7. Results of residue after filtered dried by heating an oven at a temperature of 100 ºC. After heavy constant dryness then it is ready to be used for FTIR analysis. (Yield: 52.5%).

Chitosan Sulfate Synthesis. Chitosan was obtained from the previous stage is added ammonium sulphate 0.1 M with a ratio of 2: 5 (w kitosan /v amonium sulfate) then it was in shaker for 4 hours as practiced by Mahatmanti (2001). Mix filtered with Whatman filter paper 42, the precipitate was washed with distilled water until neutral and dried for 4 hours in the oven at temperature of 60 ºC. (Yield: 92%).

Adsorption Remazol Yellow FG. Adsorption properties are determined by the adsorption solution of Remazol Yellow FG by chitosan sulfate on the optimum conditions of the procedure by Anggraini (2007) [13], followed by desorption at the same conditions. The solution Remazol Yellow FG with concentration and pH optimum of 10 ml was added 50 mg of chitosan sulfate, then it will be shaker during the optimum time at room temperature. The mixture was filtered through Whatman filter paper 42, the filtrate obtained measured by Uv-Vis spectroscopy at wavelengths optimum. The precipitate adsorbent filtration results in a procedure was added 10 ml of distilled water, then it will be shaker at

the optimum time at room temperature. The mixture was filtered with Whatman filter paper 42, the filtrate obtained was analyzed by Uv-Vis spectroscopy at wavelengths optimum.

3. RESULTS AND DISCUSSION

3.1. Isolation chitin from cerb shell and chitosan synthesis

The yield of chitin obtained from crab shells amounted to 28.57%, it is similar from the literature where crab contains chitin of 18.70 to 32.90% by Marganov (2003). The yield of chitin from crab shells is relatively small, it is due to the mineral content crab shells from 53.70 to 78.40% (Marganov, 2003).

The shells of crabs that have been stored do not need to be boiled. The cooking process in the shop itself already includes the boiling process. The shells of crabs were destroyed until tender (in powder form). It aims to facilitate the processing of the subsequent steps occurrence of mineral separation process which is shown by the formation of CO_2 gas in the form of air bubbles at the time of HCl was added to the sample (Hendry, 2008). Crab shell contains more minerals, as indicated by the formation of a lot of air bubbles upon addition of HCl into the sample, so the addition of HCl done gradually so that the sample does not overflow. The reaction is as the follow:

$$CaCO_3(s) + 2HCl(l) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$
$$Ca_3(PO_4)_2(s) + 6HCl(l) \rightarrow 3CaCl_2(aq) + 2\ H_2PO_4^-(aq) + H_2O(g).$$

Demineralization phase aims to eliminate the inorganic mineral $CaCO_3$ and $Ca(PO_4)_2$ that exist in the shells of crabs. The major minerals in the shells of crabs are in a minor amount. To eliminate the HCl which may still lagging be washed with distilled water until neutral. In this study, demineralization is done by using HCl 5% (1.6 M) for 24 hours at a temperature of ±40 ºC using heating hot plate, it proves that the temperature and reaction time affects the yield of chitin obtained and filtering factor for using Buchner filter with ordinary filter paper which specific pore size, when there is a powder that smaller pore size will not be filtered and vented which is why the yield is less.

Other factors that influence the amount of yield of chitin is a sequence of stages of manufacture chitin, chitin isolation done in three stages, namely the process of demineralization and deproteination. Ernawati (2008) study the isolation of chitin done through deproteinasi phase followed by a phase of demineralization. This is because the minerals formed shield (protector) which are hard on the shells of the crabs, generally mineral harder than protein, so by removing the minerals, the stage can be optimized alkaline with deproteination and removed the proteins, as protector made of minerals which have been lost. Deproteination aims to break the bond between the protein and chitin, by adding sodium hydroxide. Proteins were extracted in the form of Naproteinat where Na^+ ions bind to the end of the negatively charged protein chain so as to precipitate.

Chitin from deproteination results was deacetlation by adding concentrated NaOH 45%. At the chitin ratio of 1:12 (w / v) between chitin with a solvent. The mixture was stirred and heated at 100 °C for 2 min and low of power. This condition is used for the structure of the cells of chitin which is thick and strong intramolecular hydrogen bond between the hydrogen atom in the amine group and the oxygen atom of the carbonyl group. The process of deacetylation in strong base causes the loss of an acetyl group on chitin through break the bond between the carbon in acetyl group with nitrogen in the amine group. In alkaline conditions, deacetylation of chitin (-$NHCOCH_3$) into chitosan (NH_2) occurs as shown in Figure 1. The yield of chitosan obtained from chitin amounted to 52,5% with deacethylation degree of 80%.

FTIR spectra from Figure 2. is crab shell (a), chitin (b) and chitosan (c) showed uptake patterns that appear on the same wavelength is 3434.24 cm^{-1} shows the vibration OH widened. Other uptake is at 2924.20 cm^{-1} stretch C-H aliphatic fused to the tape as a helping helping OH N-H. As for the N-H bending vibration appears at wave number 1637.63 cm^{-1}, CH absorption of chitin shells of crabs bend at 1419.06 cm^{-1}. Their absorption at 1033.72 cm^{-1} shows the vibration of C-O-C in the chitosan ring. The

changes which occur after the deacetylation stage is the emergence of group C=O at 1796 cm^{-1} indicating group of C = O of chitosan.

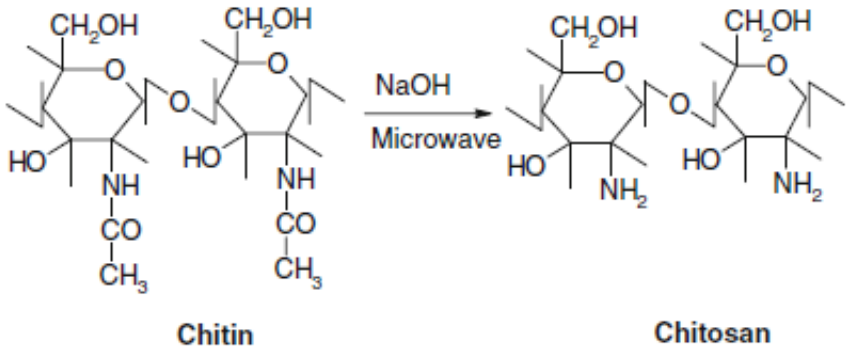

Figure 1. Deacethylation Chitin to Chitosan

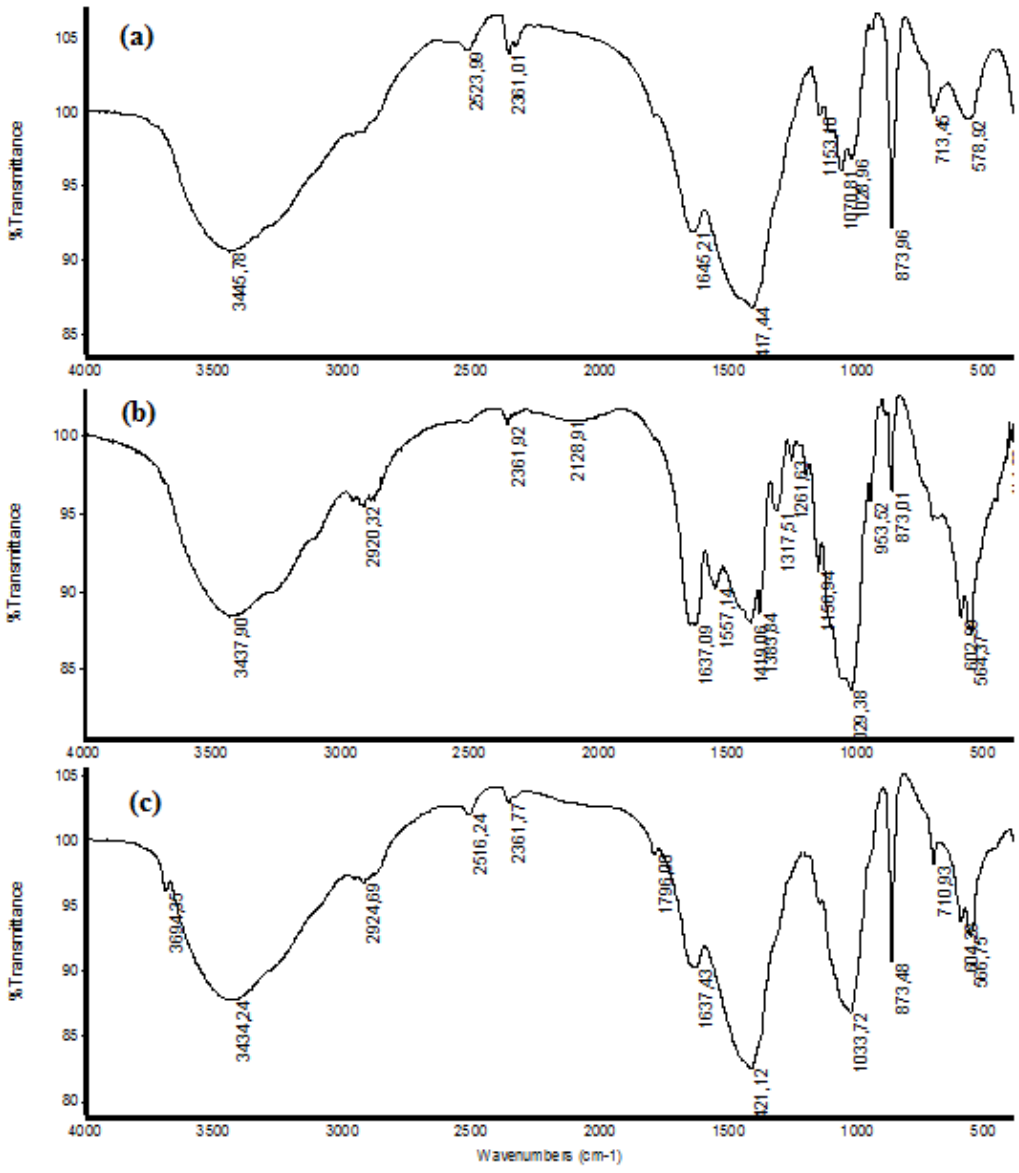

Figure 2. Infrared Spectra of (a) crab shell, (b) chitin, and (c) chitosan

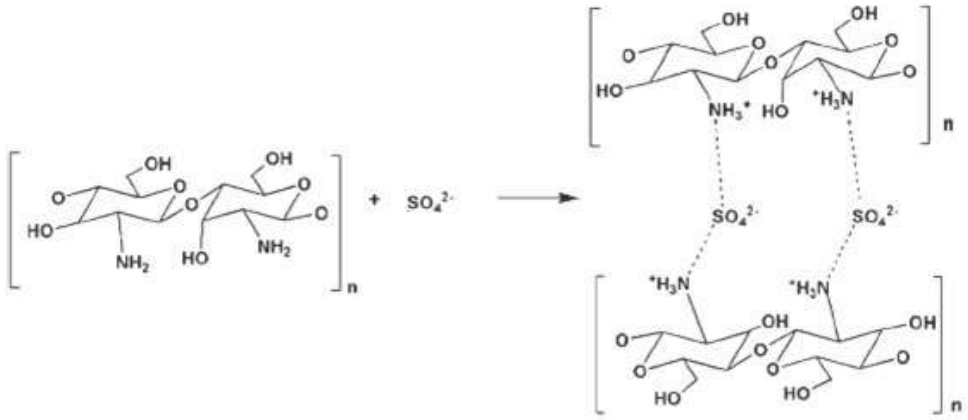

Figure 3. Conversion reaction of chitosan to chitosan sulfate

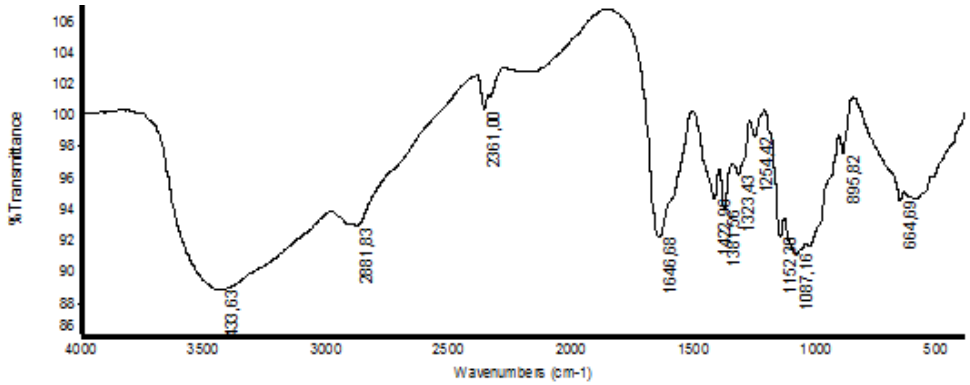

Figure 4. Infrared spectra of chitosan sulfate

3.2. Chitosan sulfate synthesis

The yield of chitosan sulfate obtained from chitosan amounted to 92%. Conversion chitosan into chitosan sulfate is basically binding electrostatic sulfate ions on chitosan reactive group (amine group) into force $NH_3^+OSO_3^{2-}$(Figure 3). This conversion is done to increase the adsorption capacity chitosan because of the presence of sulfate ions, the amine group on the chitosan will be more cationic, besides the presence of sulfate groups then it will be expected to bind the cationic groups. Sulphate ions are used for the ion which has electron rich. Active cluster reactivity chitosan sulfate is more stable than chitosan because the protonated amine group has undergone a permanent presence attachment of the sulphate ions. Chitosan sulfate was determination of functional groups with FTIR spectra in Figure 4.

Absorption band at wavenumber 3433.63 cm^{-1} shows the OH stretch vibration and vibration NH_2 helping overlaps (Silverstein, Bossler & Morril, 1986). Vibration C-H methylene (CH_2) are shown in wave number 2881.63 cm^{-1}. Absorption at 1422.26 cm^{-1} support their -CH_3 bound the amide. Absorption at 1646.62 cm^{-1} showed absorption -C=O amide and their N-H bending vibrations that indicate the presence of an amine (NH_2). Uptake C-N shown in wavenumbers 1080.16 cm^{-1} (Fessenden & Fessenden, 1989). Uptake S=O shown in wave numbers of about 1100 cm^{-1} (Sudjadi, 1983). In the solid phase is lower uptake 10-20 cm^{-1} (Silverstein, Bossler & Morril, 1986), so that the absorption spectra are shown in the area 1087.16 cm^{-1}.

3.3. Adsorption Remazol Yellow FG

The optimum condition of Remazol Yellow FG 6 dye adsorption by chitosan sulfate was pH 4, concentration of 20 ppm and the interaction time 15 minutes by Anggraini (2007). As we calculated, the adsorption of chitosan sulfate was 15.32 ppm. Chitosan sulfate can adsorp 76.5% Remazol yellow FG soluted. Interaction between Remazol Yellow FG with chitosan sulfate can occur because sulfonate group Remazol Yellow FG soluble in water turns into ions anionic, so it can attack the amine group in chitosan sulfate has protonated first by sulfate groups.

4. CONCLUSION

The result of this study showed that rendement of chitin, chitosan and chitosan sulphate were 28.57%, 52.5% and 92%. The degree of deacetilation of and chitosan 80%. Chitosan sulfate can adsopr 76.5% Remazol Yellow FG in the optimum condition.

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