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Synthesis of Copolymer of Chitosan with Acrylamide as an Adsorbent for Heavy Metal Waste Treatment

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Abstract. The aim of this research is to chemically modify chitosan to improve and enhance the ability as an adsorbent. Chitosan is a natural polymer produced from chitin deacetylation. The best performance of chitosan as an adsorbent is in acidic solutions. Chemical modification was carried out by chitosan copolymerization with acrylamide. Copolymer synthesis was done by using microwave oven with the weight ratio of chitosan and acrylamide of 1: 4. The characterization of chitosan copolymer with acrylamide (chitosan-g-acrylamide copolymer) was conducted by FTIR spectroscopy and Scanning Electron Microscope (SEM). The analysis of the functional group by FTIR spectroscopy shows that the copolymer has been successfully synthesized. The surface analysis with SEM shows that the morphology of the copolymer surface is more homogeneous compared to that of chitosan.

1. Introduction

Chitosan is a biopolymer produced by the chitin deacetylation process. Chitin is a compound widely found in shrimp shells [1]. Chitosan is polycationic, so that it can be applied in various fields such as metal adsorbents, dyes, and cosmetics. Chitosan is biodegradable, biocompatible and non-toxic compound. Chitosan has biological and chemical properties. Chitosan has antimicrobial activity so it is widely used in biomedicine. Chitosan can interact very well with inorganic solutes (metal ions) and dyes, due to the presence of reactive groups such as -OH and -NH₂ [2].

However, chitosan has disadvantage of only dissolved in acidic solutions, insoluble in water and unstable in acidic solutions, so that their use is limited mainly as an adsorbent [3]. Therefore, researchers have done a chemical modification of chitosan [4,5]. Chemical modification of chitosan has been done to improve and enhance the ability of chitosan as an adsorbent, such as adding cross-linked material such as glyoxal, formaldehyde, and ethylene glycol [6]. Cross-linked material can stabilize chitosan in acidic solutions and improve its mechanical properties. Another method that has also been carried out by researchers to improve the ability of chitosan as an adsorbent is by copolymerization, namely grafting between chitosan with some vinyl monomers such as acrylic acid, methyl acrylate, acrylonitrile, vinyl chloride, acrylamide and others [7].

Copolymerization of the graft into chitosan is one of the most effective method to improve the performance of chitosan. Graft copolymers are used to improve the physical and chemical properties of natural and synthetic polymers for agricultural, biomedicine and other fields. There have been many studies on the graft copolymerization including copolymerization of chitosan with acrylonitrile, acrylamide, acrylic acid using cerium ammonium nitrate as an initiator, methyl acrylate using the initiator of potassium periodatcuprate(III) [3]. Copolymerization of chitosan with acrylamide has also



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been carried out by previous researchers, among others using the initiator of ammonium persulfate [9], and copolymerization of chitosan with acrylamide using gamma rays for the adsorption of Cu and Ni metals [8].

In this research, copolymerization of chitosan graft has been carried out into acrylamide, where copolymerization is conducted using the ammonium persulfate initiator. The copolymerization process is done by using microwave radiation heating using a microwave oven which is commonly used at home. Polymer synthesis using microwave has the advantage of short reaction time compared to the conventional heating. The results of chitosan graft copolymerization with acrylamide will later be applied for treatment of heavy metal waste, such as Pb metal, which is not included in this paper.

2. Materials and Methods

2.1. Materials

The materials used in this research are chitosan with 87.5% deacetylation degree obtained from the local market, acrylamide (Merck, Germany), ammonium persulfate (AR, China), 2% acetic acid, technical methanol obtained from local market in Indonesia and distilled water. All chemicals are used directly without further purification.

2.2. Synthesis of copolymers

The study was conducted with a weight ratio between chitosan and acrylamide of 1: 4. A 0.5-gram chitosan was placed into 2% acetic acid solution and stirred with magnetic stirrer until dissolved for 20 minutes in a Teflon container. Then, 2 grams of acrylamide were dissolved in 10 ml of distilled water, then poured into a Teflon container containing chitosan and stirred until the mixture was homogeneous. After that, 5% ammonium persulfate was added from the total weight of the sample and the mixture was stirred until homogeneous. Then, the Teflon container was placed into microwave oven by adjusting the microwave power that is 30%, 50%, and 70% by adjusting the reaction time every 2 minutes until the gel was formed. The time of gel formation was noted. After the reaction was complete, the formed gel was poured into a container containing excessive methanol to precipitate the product while stirring. The precipitate that has been obtained was washed with methanol for several times to remove the formed homopolymer. The precipitate was filtered, placed into a petri dish and then dried in a vacuum oven at 40 °C to a constant weight. Copolymers were then characterized using FTIR and SEM, while the percentage of grafting can be determined by equations (1) and (2), where W_0 , W_1 and W_2 are initial mass of chitosan, mass of copolymer, and mass of acrylamide, respectively [11]:

$$\%G = (W_1 - W_0) / W_0 \times 100\% \quad (1)$$

$$\%E = (W_1 - W_0) / W_2 \times 100\% \quad (2)$$

2.3. Characterization

2.3.1. *Fourier transformation infrared (FTIR) spectroscopy.* FTIR analysis was performed on samples of chitosan, acrylamide and chitosan copolymers with acrylamide in the form of KBr pellets and measured at wavelengths of 400 - 4000 cm using FTIR SHIMADZU-8400.

2.3.2. *Scanning electron microscopy (SEM).* Scanning Electron Microscope (SEM) analysis was also performed on samples namely chitosan, acrylamide and chitosan copolymers with acrylamide using SEM JEOL JSM 6510 LA. Samples were measured in a powder form.

3. Result and Discussion

3.1. Synthesis of copolymer

Synthesis of chitosan copolymers with acrylamide was carried out using a microwave oven commonly used at home. Chitosan used in this work was originated from shrimp shells with deacetylation degree

of 87.5% that obtained from the local market. Copolymers were synthesized with a ratio of chitosan and acrylamide of 1:4. The initiator used for the synthesis of chitosan and acrylamide copolymers was ammonium persulfate. Copolymer synthesis was carried out with variations of power namely 30%, 50%, and 70%. The reaction is stopped until the solution is thickened or form a gel. This indicates that the copolymer has been formed. The initially white solution turns into a thick yellow solution. To stop the reaction, the gel obtained is poured into excessive methanol to form a precipitate. The precipitate formed were dried in a vacuum oven at a temperature of 40 °C until constant weight is obtained.

The time needed to form copolymers on various microwave power was varied. The average time required for the formation of the copolymer in microwave with 30%, 50% and 70% power, respectively were 24, 12, and 8 minutes. The greater the microwave power used, the faster the formation of copolymers. Due to greater power, the radicals were formed faster, so that of the copolymer. With the greater power, the reaction rate will be greater so that the time needed for the formation of copolymers is faster. Energy transfer is faster with the increasing of microwave power. In addition, the higher power microwave radiation indicates a higher temperature. Observations of the sample during the reaction show that with the increasing of microwave power, the time taken for the sample to boil is also faster. The time needed to boil each of the microwave with power of 30%, 50% and 70%, are 8, 4, and 2 minutes, respectively.

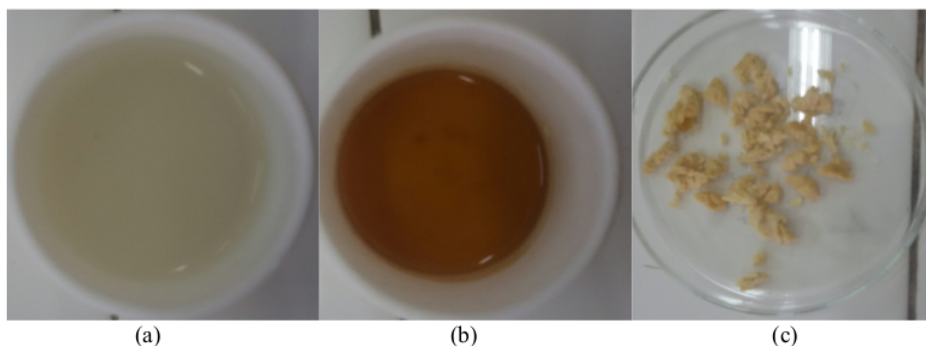


Figure 1. Sample (a) before the copolymerization reaction, (b) after the copolymerization reaction, and (c) after precipitated with methanol.

Synthesis of chitosan copolymer with acrylamide is a graft copolymerization in which acrylamide is grafted into the chitosan. The number of acrylamide monomers that can be grafted into chitosan can be determined by calculating the results of grafting (%G) and grafting efficiency (%E) based on equations (1) and (2). The results of grafting (%G) and grafting efficiency (%E) synthesis of chitosan and acrylamide copolymers at various microwave powers are presented in Table 1. Table 1 showed that %G and %E were decreased with the increasing of microwave power used. Due to the greater radiation power, the greater homopolymer reaction occurred thus %G and %E were decrease. A decrease in %G with the increasing of microwave power in the synthesis of chitosan-grafting-polyacrylamide was also reported by previous researchers, namely chitosan-polyacrylamide copolymers, which is carried out in various power of 60, 70, 80, 90 and 100%. The results showed a decrease in %G with the increasing of microwave power of 80% and 100%, due to more homopolymerization reactions [10].

Table 1. Effect of variation of microwave power on %G and %E.

Power of Microwave	%G	%E
30%	399.18	99.79
50%	367.06	91.76
70%	309.00	72.25

Chitosan copolymerization with acrylamide is free radical polymerization using the ammonium persulfate initiator. The mechanism of chitosan copolymerization with acrylamide which has been proposed by Machalova *et al* (2006) is presented in Figure 2. Based on the polymerization of free radicals in the initial stages of the reaction, the initiator undergoes initiation to form radicals. Radicals are formed due to heat generated in a microwave oven. Furthermore, a propagation reaction occurs where radicals from the initiator attack the chitosan functional groups and free the H atoms contained in the NH₂ and OH groups contained in chitosan. Thus, chitosan will form radicals. The chitosan radical then attacks the acrylamide monomer to forms another radical. In the final stage, the termination stage, there is a bond formed between the radicals from the polymer that has been grafted.

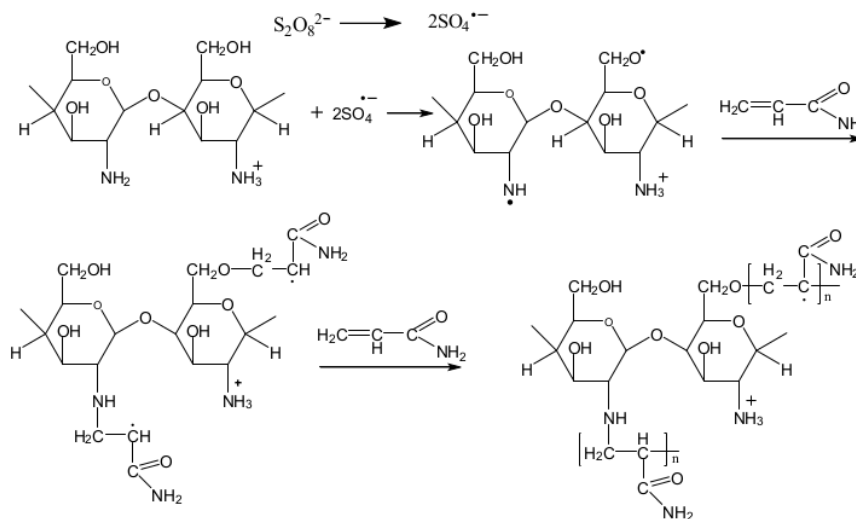


Figure 2. Mechanism of copolymerization of chitosan with acrylamide [14].

3.2. Characterization of copolymers

3.2.1. FTIR Spectroscopy Analysis. FTIR spectroscopic analysis was carried out on chitosan, acrylamide and chitosan-acrylamide copolymers and the spectra are shown in Figure 3. FTIR spectra for copolymers were taken from the results of copolymer synthesis at 70% microwave power. Figure 3 (a) shows the FTIR spectra of the chitosan. The absorption peak with high intensity at 3427.51 cm^{-1} is the stretching vibration from OH and NH₂ groups. The absorption at 2920.23 cm^{-1} and 2881.65 cm^{-1} shows the stretching vibration of C-H. The absorption peak at 1660.71 cm^{-1} is the C=O vibration of carboxylate group of chitosan, while the absorption peak at 1596.99 cm^{-1} is the absorption of N-H. Vibration stretching of C-N appears at the absorption peak of 1427.32 cm^{-1} .

Figure 3 (b) is an FTIR spectra of acrylamide. The emergence of absorption peaks at 3352.26 cm^{-1} and 3178.69 cm^{-1} is the peak of NH₂ vibration stretching from acrylamide. The absorption peak at 1674.21 cm^{-1} is the C = O absorption band of amide (I). The C-N absorption band of acrylamide

appeared at 1429.25 cm^{-1} . While the absorption peak of N-H bending vibration of acrylamide appeared on 1610.56 cm^{-1} . The presence of the C = C double bond of acrylamide appeared on the absorption peak around $900\text{-}990\text{ cm}^{-1}$ and 3057 cm^{-1} .

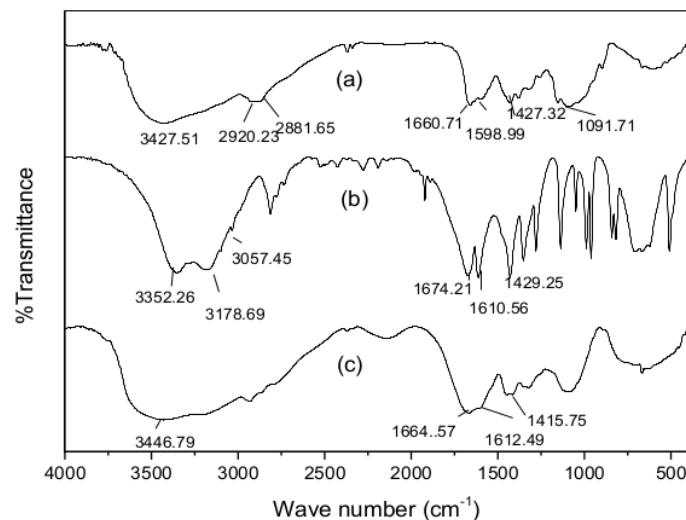


Figure 3. Spectra FTIR of (a) chitosan, (b) acrylamide, (c) copolymer of chitosan-acrylamide.

FTIR spectra of chitosan-acrylamide copolymers can be seen in Figure 3 (c). From the spectrum of the copolymer in Figure 3 (c), it is observed that the double bond C=C does not appear at wavelengths around $900\text{-}990\text{ cm}^{-1}$ and $3075\text{-}3095\text{ cm}^{-1}$. This shows that the copolymerization reaction has taken place. Moreover, the spectra show the formation of copolymers is the shift in the absorption of C=O amide from 1674.21 cm^{-1} to 1664.57 cm^{-1} . There was a broad peak at wave number of 3446.79 cm^{-1} due to OH absorption. The broad absorption peak is also caused by an overlap between the N-H vibrations of chitosan and NH_2 from acrylamide. In addition, an indication of chitosan-acrylamide copolymers has been formed is the peak of C-N absorption at wave number of 1415.75 cm^{-1} . Based on previous research showing that the peak of the adsorption of chitosan-acrylamide copolymer appeared in 3434.71 cm^{-1} which is OH stretching from polyacrylamide and chitosan. While the adsorption band at 1411.69 cm^{-1} is C-N stretching vibration from the chitosan-acrylamide copolymer [12]. Based on the FTIR spectra, the chitosan and acrylamide copolymers have been successfully synthesized using microwave oven.

The FTIR spectra of the copolymer that has been synthesized with microwave power variations of 30, 50, and 70% can be seen in Figure 4. From the spectra, it can be seen that the absorption peaks of the copolymers produced in the microwave power variation have identical absorption peaks. FTIR spectra in Figure 4 shows that the copolymer has been successfully synthesized in various microwave power.

3.2.2. SEM Analysis. Scanning Electron Microscope (SEM) analysis is a surface analysis that can shows the surface morphology of a material. The results of SEM analysis can be seen in Figure 5. SEM analysis was carried out for chitosan, acrylamide, and chitosan-acrylamide copolymers. The SEM analysis results (Figure 5) show the surface differences of chitosan, acrylamide and chitosan-acrylamide copolymers. Based on Figure 5 (c), chitosan-acrylamide copolymers with porous surfaces were observed. The formation of these pores is due to the grafting between chitosan and acrylamide.

This porous surface indicates that chitosan-acrylamide copolymers can be used as adsorbents. Based on Figure 5, it can be seen that the surface of the copolymer is more homogeneous compared to that of chitosan.

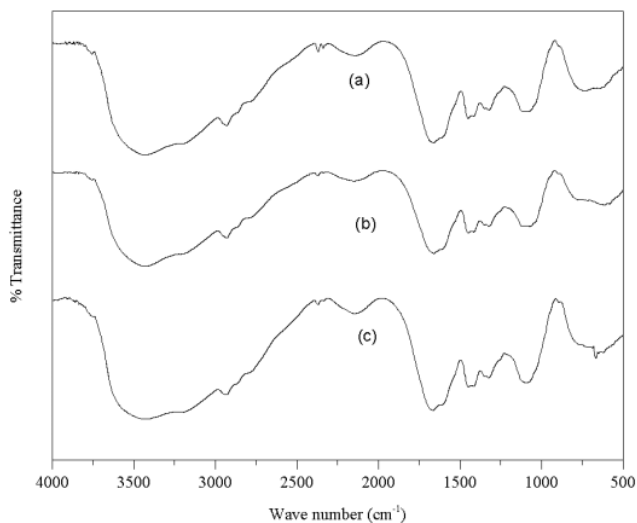


Figure 4. FTIR Spectra of chitosan-acrylamide copolymers synthesized by various microwave power of (a) 30%, (b) 50% and (c) 70%.

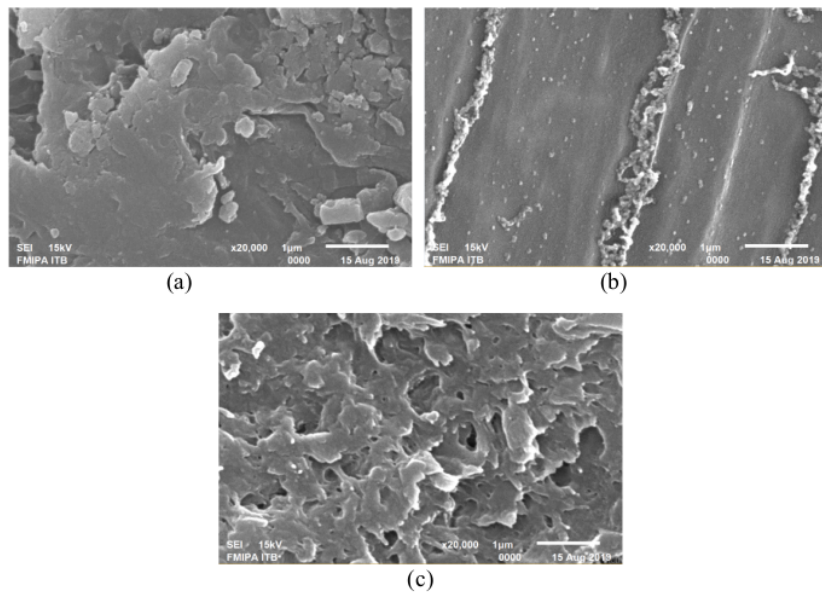


Figure 5. SEM (a) chitosan (b) acrylamide (c) copolymer of chitosan-acrylamide

4. Conclusion

The chitosan copolymerization with acrylamide using ammonium persulfate initiator was successfully synthesized in a microwave oven. The decrease in %G and %E as the microwave power increases was caused by the occurring of more homopolymer reactions.

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