The effect of ratio chitosan-bentonite and processing time on the characterization of chitosan-bentonite composite

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Abstract. Chitosan/bentonite composite was synthesized to modify and enhance its characteristics to adsorb both anionic and cationic substances. The influence of several factors on synthesis of the chitosan/bentonite composite were investigated. The study focused on obtaining the best operating conditions that would produce homogenous chitosan/bentonite composite. The effect of weight ratio of bentonite to chitosan, reaction times and pre-treatment were investigated. The composite were characterized by Fourier transform infrared spectroscopy, X-ray diffraction and Scanning electron microscopy. The optimum chitosan/bentonite composite was obtained at weight ratio of bentonite to chitosan 1 : 2 and 12 hours reaction. On these conditions, more chitosan can interact with the matrix of bentonite to form chitosan – bentonite composite.

1. Introduction

Chitosan is the second largest biopolymer after cellulose. Chitosan is interesting because of its low cost, availability of amino and hydroxyl groups in the structure, which are potential to react [1]. However, the chitosan has limitation in their application due to its low surface area, and mechanic resistance [2]. In order to overcome the limitation, several works have been conducted on the development of chitosan based materials such as membranes [3], fibers [4], films [5] and scaffolds [2]. Chitosan film have prepared by Dotto et al., (2013) to remove dyes from aqueous media. The film showed high adsorption capacities, good mechanical properties and easy for separation. Esquerdo et al. have developed chitosan scaffolds which has good characteristics for adsorption, including porosity of 92% and specific surface area of 1135 m²g⁻¹. Chitosan based materials with good mechanical and functional characteristics, able to remove anionic and cationic dyes, are scarce. An alternative is the development of chitosan/bentonite composite, once chitosan is polycationic and bentonite has anionic groups in its structure. Another study showed that Gunister have prepared and characterized chitosan-montmorillonite composite [6]. They used chitosan which has an average molecular weight of 400,000. The composite was prepared by mixing chitosan solution in different concentration into montmorillonite suspension. chitosan is attached on the surface of clay particles. XRD analyses displayed that organic molecules did not enter enough sufficiently into the layers of clay structures. The effects of polymers on the montmorillonite dispersions are widely studied [7-10]. Because of that, in this study we focused on the bentonite pre-treatment. Bentonite used in this study were both
intercalated and without treatment. By intercalating process, the interlayer of bentonite might be wider and the chitosan could enter into the layers of bentonite structure. This work aimed to synthesized and characterized a composite based on chitosan and bentonite. Chitosan/bentonite composite was prepared and characterized by potential test of the suspension, Fourier transform infrared spectroscopy (FTIR), and X–ray diffraction (XRD).

2. Experimental

2.1. Materials
Natural bentonite was collected from Pacitan, East Java, Indonesia. Bentonite was ground and sieved through 140 mesh. After sieving, Bentonite was intercalated by using HDTMA-Cl 1% as surfactant. Chitosan was produced by deacetylation of chitin in sodium hydroxide solution at 125°C for 3 h process. After deacetylation process, chitosan was washed by water and then dried.

2.2. Preparation of Chitosan – Bentonite
A definite amount of bentonite was dispersed in water and then chitosan in 1% acetic acid solution was added into the dispersion. The dispersion was mechanically stirred for 6 – 24 h at room temperatures. The composites having weight ratio of bentonite to chitosan 2 : 1; 1 : 1; and 1 : 2 were prepared. After processing, the composite was filtrated and dried in the oven.

2.3. Characterization of Chitosan-Bentonite Composite
The potential measurements were carried out using potential Instruments to identify the potential of ions in the suspension system. Bentonite has been identified as mainly smectite group minerals using X-ray diffraction (XRD) and FTIR analysis methods. X-ray diffraction (XRD) measurements were performed by a PANalytical PW 3373/00 X’Pert X-ray diffractometer, Netherlands which used CuKa, 1.54 Å radiation at 40 kV and 30 mA. Fourier transform infrared spectroscopy (FTIR 8400S Shimadzu,Japan) was performed using the KBr pellet with a concentration of 1 % in the range of 4000 - 400 cm\(^{-1}\). All of the spectra were recorded at room temperature with a resolution of 4 cm\(^{-1}\) for 45 scans. Spectral outputs were recorded in transmittance mode as a function of wave number.

3. Results and Discussions

3.1 The Effect of Bentonite : Chitosan Ratio on the Composite
The Bentonite which is used to synthesize the composite were both fresh bentonite and also bentonite that has been intercalated with HDTMA-Cl. To study the effect of ratio bentonite to chitosan, the samples were characterized on the weight ratio of bentonite to chitosan 2:1, 1:1 and 1:2. The potential
test was conducted on samples for bentonite suspensions, chitosan solutions and chitosan-bentonite composite suspension system, separately. The potential test is performed to determine the ions changes in the suspension system before and after the composite formed. The potential test data was shown in the Table 1.

**Table 1.** The potential data for bentonite suspension, chitosan solution, bentonite chitosan before and after composite processing

| Bentonite – Chitosan ratio, g/g | Bentonite suspension | Chitosan solution | Before processing | After processing | Δ Potential |
|--------------------------------|----------------------|-------------------|-------------------|-----------------|-------------|
| B:C = 1:2                      | 244                  | 318               | 562               | 349             | 213         |
| B:C = 1:1                      | 260                  | 318               | 578               | 359             | 219         |
| B:C = 2:1                      | 263                  | 319               | 582               | 357             | 225         |
| B-HDTMA:C = 1:2                | 246                  | 318               | 564               | 354             | 210         |

Table 1 showed that the potential of bentonite suspension increased when the amount of bentonite added increased. Otherwise, because the amount of chitosan solution used was unchanged in number so that the potential of chitosan solution remained constant. Theoretically, the number of charge in the suspension system increase because of both materials. But, Table 1 showed that the potential of the system after process was lower than that of system before process. It meant that there is phenomena that the charges of both materials combine (negative charge attributed to bentonite and positive charge attributed to chitosan) so that the potential system after process reduced. The reducing charge because of the charge combination between bentonite and chitosan was described by potential difference (Δ Potential). Potential difference in this study might explain the amount of chitosan was attached on to bentonite in composite system. The higher the potential difference, the higher the composite developed. The potential difference (Δ Potential) of the composites increase with increasing the amount of fresh bentonite added into the composite system. The maximum potential difference was obtained at the weight ratio of bentonite to chitosan 2:1. Although the value of the highest potential difference was obtained by the weight ratio bentonite to chitosan 2:1, but the increase of potential difference is not proportional to the amount of added bentonite. Increasing bentonite as much as four time just gives insignificant increasing in potential difference of composite. In comparison, the ratio of bentonite to chitosan is 1:2 has been obtained from a composite with a potential difference is quite good value. Otherwise, the intercalated bentonite gives the lowest value of potential difference on the composite. The presence of HDTMA on the bentonite gives the limitation of chitosan molecule to interact with the bentonite system. HDTMA was attached in the multilayer of bentonite at pretreatment process and blocked the chitosan molecules to enter the bentonite multilayer system.
Figure 1 shows that chitosan peaks look similar to bentonite and chitosan–bentonite composite peaks in the range of 3400 - 3600 cm\(^{-1}\). It is the characteristic of the -OH vibrating stretching asymmetric -OH bond at 3447.20 cm\(^{-1}\).

On the FTIR spectrum, the peak in the range 500-700 cm\(^{-1}\) is Si-O bending vibration. The peak is attributed to bentonite that changed in the absorption before and after the process. The change in the peak indicated the evolution in the condition of the bentonite pores. The bentonite pores were more open than the pores of the initial bentonite. This is due to the inclusion of the chitosan molecules into the layer structure of bentonite.

![FTIR spectra of chitosan, fresh bentonite and chitosan-bentonite composite for 6 h processing](image)

**Figure 1.** FTIR spectra of chitosan, fresh bentonite and chitosan-bentonite composite at different ratio for 6 h processing

Figure 1 also gives the FTIR spectra of material based chitosan-bentonite for different ratio of bentonite to chitosan. According the FTIR spectra, the ratio of bentonite:chitosan 1:2 was the optimum ratio rather than other weight ratio. It looks at the peak in the range 1500-1550 cm\(^{-1}\). The peak at this wavenumber is the highest absorbance compared to the peak of other weight ratio of bentonite-chitosan. It referred to the higher amount of chitosan in the composite system. Eventhough, the weight ratio bentonite to chitosan 1:2 was optimum result compared to other system, but this result was not as expected. It caused that the amount of bentonite at that ratio is the smallest so that the number of bentonite pores provided is also limited. The limitation of the bentonite pore will limit the number of chitosan molecule to occupy the bentonite space. The weak peak in the range 1500-1550 cm\(^{-1}\) is a
bending vibration of N-H bond of the amine group in chitosan. This weak peak indicates that the number of chitosan molecules that enter into the bentonite pore is still limited. It was probably caused by the high molecular weight of chitosan used and did not suitable to the bentonite pore size. The peaks in the range 850-1450 cm\(^{-1}\) are sharper than that of chitosan-bentonite composite. It might be the occurance of the binding system of the chitosan and bentonite.

**3.2 Effect of The Processing Time on The Composite**

To study the effect of the processing time on the composite, the samples were characterized on the ratio of bentonite to chitosan 1:2 for 3 to 24 h processing. The potential test data are shown in the Table 2 and the FTIR spectras of material are shown in Figure 2.

**Table 2.** The potential data for bentonite suspension, chitosan solution, bentonite chitosan before and after composite processing at different processing times

| Processing Time, h | Potential, mV |  |
|--------------------|---------------|---|
|                    | Bentonite suspension | Chitosan solution | Before processing | After processing | Δ Potential |
| 3                  | 246           | 319             | 565              | 351              | 214         |
| 6                  | 244           | 318             | 562              | 334              | 228         |
| 12                 | 246           | 319             | 565              | 340              | 225         |
| 24                 | 246           | 318             | 564              | 346              | 218         |

**Figure 2.** FTIR spectra of chitosan, fresh bentonite and chitosan-bentonite composite at different processing times for bentonite : chitosan ratio 1:2
Figure 2 shows that the optimum condition of composites processing are for 12 h processing. The result was supported by the potential test datas that showed that processing time gave a high potential difference of the composite. It can be seen on Figure 2 at peak in 1500-1550 cm\(^{-1}\) that indicating the vibration of N-H bonds of the chitosan.

The data indicated that chitosan has interacted with the bentonite better than that of other processing time. At the time of 3-6 h, the chitosan probably have not attached strongly with the bentonite, while the 24 h processing time, the chitosan might occurrence desorption due to the prolong of processing time.

3.3. The Characterization of Chitosan-Bentonite Composite by XRD

In this section, the focus of the study was to determine how the effect of the variations on the bentonite-chitosan ratio and the length of processing time on the main peak shifting at \(2\theta = 5.828\). The shifting peaks can be used to determine whether the chitosan molecule entered into the bentonite multilayers structure.

| Samples                | \(2\theta\), degree | \(D_{001}\) spacing, Å | I-count |
|------------------------|---------------------|------------------------|---------|
| Fresh Bentonite        | 5.83                | 15.15                  | 695     |
| Composite B:C =1:2; 6 h| 5.91                | 14.93                  | 485     |
| Composite B:C =1:1; 6 h| 5.92                | 14.91                  | 347     |
| Composite B:C =2:1; 6 h| 5.86                | 15.05                  | 476     |
| Composite B:C =1:2; 12 h| 6.03                | 14.64                  | 407     |

Figure 3. X-ray Diffractogram of fresh bentonite and chitosan-bentonite composite at different bentonite-chitosan ratio for 6 hours processing

The main peak shifting and \(d_{001}\) spacing changing are shown in Figure 3. It can estimate how large the bentonite pore size formation. The XRD Diffractogram of the samples showed the shifting of the main peak of the composite slightly to the right that showed the distance between the bentonite layers were getting smaller. The shifting peak was not significant, this indicated that only a small number of
Chitosan molecules entered into the pores of bentonite and was unable to change the bentonite interlayer distance. The chitosan molecules did not enter into the bentonite structure due to a high molecular size of chitosan molecules. However, the data FTIR has supported that chitosan has interacted with the bentonite even though the interaction might be on the outer surface of bentonite.

According to the Figure 4, it can be observed that the composite results of both samples (6 and 12 hours process) shifted the main peak slightly to the right compared with fresh bentonite. The main peak shifting was not significant indicates that the number of entering chitosan was very low. Chitosan molecules did not change the bentonite interlayer distance. Both of samples looked like similar result. The main peak shifting was not significant.

4. Conclusions
In this research, the optimum conditions of the synthesis of composite chitosan - bentonite were at weight ratio of bentonite / chitosan 1: 2 and processing time of 12 h. On these conditions, more chitosan can interact with the matrix of bentonite to form chitosan-bentonite composite. The chitosan molecules probably located on the outer surface of the bentonite and not enter in the layer structure of bentonite.

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