Effect Croslinking on Characteristics of Silica Chitosan Composite from Vulcanic Ash of Sinabung Mount and Shrimp Husk by Sol Gel Method

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Abstract: This research was carried out to determine the effect of glutaraldehyd croslinking on the synthesis of silica chitosan composites from the Na_2SiO_3 precursor of volcanic ash of Sinabung and chitosan from shrimp husk by sol gel method. The synthesis of the silica-chitosan composite by mixing the 20 mL Na_2SiO_3 precursors with (2% : 3%) (w/v) chitosan in the aid of glutaraldehyde as crosslinking agent and without glutaraldehyde. Modifications with sol gel is done because it is more simple and rapid progress as well as the binding reaction of the ligands mobilized. Prepared Silica Chitosan Composit using glutaraldehyd labeled (Si-g-ChC) and Silica Chitosan Composit without glutaraldehyd labeled (SiChC) . The characteristic of the composit material (Si-g-ChC) and (SiChC) used by FTIR and XRD.

1 INTRODUCTION

The volcanic ash of Sinabung mount has the main content of Silica (SiO_2) which is very abundant based on previous research (Barasa et al., 2013; Kusmartini et al., 2017; Simatupang et al., 2016). This potential SiO_2 content can be used as a basic ingredient in making silica-based adsorbents (Barasa et al., 2013). Silica can be used as an absorben because of its high porosity, high mechanical strength, high thermal stability, high pore surface area, stable surface in acidic medium, non-fluffy, resistant to microbes and low prices. Previous research shows that the silica gel be successful synthesized by using of volcanic ash base on Sinabung mount. The silica gel consists of –OH from Si-OH and Si-O from Si-O-Si. The silica gel is well generated on this research is amorphous, average pore radius of $1.5469x10^{-1}$ Å, the surface area of silica gel is 374,994 m²/g which is it possible to be applied as an adsorbent (Simatupang et al., 2018). The susceptibility of using silica gel is the low ability of its surface to interact with heavy metal ions so that silica gel is unable to function as an effective adsorbent for heavy metal ions (Astuti et al., 2012).

Abundant shrimp husk waste can be used as a basis for making chitosan. Chitosan can be used in the adsorption process because it is rich in amino and hydroxyl groups as chelating, biocompability, biodegradation and high adhesion power (Kolodynska D,. 2011; Budnyak TM, et al., 2013; Li et al., 2009; Hu et al., 2018; Li et al., 2018; Badwan et al., 2015). Chitosan without modification has low mechanical strength and low solubility in acidic medium. The amine groups in chitosan are unstable in acidic conditions and cause protonation. Therefore chitosan in original form generally does not have specific selectivity for certain types of heavy metals such as complex pollutants in water or wastewater, even though the chitosan has high content of amine and hydroxyl groups. The modification of silica surface with chitosan by sol gel method will produce silica chitosan composite adsorbent in the development of technical

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nanomaterials, due to performance benefits such as ease of synthesis, reduction in size, weight, and multifunction. The sol-gel process provides many advantages such as reaction conditions at room temperature, easy and simple, high purity and homogen, uniform and small size due to the binding process going on simultaneously (Zhao et al., 2017; Budnyak et al., 2015; Budnyak et al., 2016). The improvement effectivity of silica-organic polymer-based materials because it combines the hardness properties of silica and the functional properties of chitosan polymers (Shchipunov et al., 2004). The purpose of this research was study the effect of the use of glutaraldehyd croslinking on the formation of composite materials and their characteristics.

2 RESEARCH METHODS

2.1 Materials

The Na2SiO3 solution precursor from volcanic ash of Sinabung mount and shrimp husk were obtained on previous research. Reagents consist of HNO_3, NaOH, HCl, CH_3COOH, etanol, and glutaraldehyd 25% were Analytical Grade (AR) from E-Merck..

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2.2 Instrumentations

Equipment includes: analytic balance, mortar, 200 mesh sieve, desiccator, filter paper whatman 42, magnetic strirer, universal indicator, buchner funnel, glassware and plastic glass container. The measurements was made by using a Fourier Transform Infra Red (FTIR) Bruker spectrometer equipped with a Digitec detector (Shimadzu), Rigaku ZSX X- Ray Difraction (XRD) (Shimadzu XRD 6000).

2.3 Procedure

2.3.1 Synthesis of Precursor Na_2SiO_3 Solution

The volcanic ash as much as 20 g was soaked into 120 mL HNO_3 for 24 hours. Dried on the oven at T = 120°C for 6 hours and then weight was recorded. Subsequently, the volcanic ash was destructed with 156 mL NaOH 4M until the viscous on the furnace at T = 500 °C during 30 minutes. After that, it was added 200 mL water for 24 hours. Finally the solution was filtered as Na-Silicat (Na_2SiO_3) (Simatupang et al., 2018).

2.3.2 Synthesis of Silica-based Chitosan Composite

The Na_2SiO_3 solution as much as 20 mL put into a plastic glass containers. The other plastic glass containers were put (0.2; 0.3) g chitosan and dissolved in 10 ml of acetic acid (2%, v / v) and then stirred for 1 hour to form (2%, 3%) w/v chitosan solution. The glutaraldehyde of 5% as much as 1 mL was put into a chitosan solution (2%, 3%) and stirred vigorously for 5 minutes and in another plastic glass containers (2%, 3%) chitosan solution without glutaraldehyde. Then the mixture of chitosan and glutaraldehyde is poured into a sodium silicate solution while stirring with a magnetic stirrer. Chitosan solution without glutaraldehyde is added to the other Na_2SiO_3 solution. Gel formation is done by adding 3M HCl drops to pH 7. The gel is left overnight, filtered, washed with distilled water. The obtained gel is dried at 70° with the use of a vacuum pump. The obtained gel was sieved with a 200 mesh sieve. The end product is named as silica chitosan composite material. Silica chitosan composite are labelled based on the composition of the chitosan, successively the composites material prepared from 20 mL of Na_2SiO_3 with 2% chitosan used glutaraldehyd as crosslinking is labeled as composite S-g-ChC1, with 3% chitosan is composite S-g-ChC2. While 20 mL of Na_2SiO_3 and 2% chitosan without glutaraldehyd is labeled as SChC1, and 3% chitosan without glutaraldehyd as SChC2.

Characterizations of Silica Chitosan Composit

The methods for silica chitosan composit research are versatile. X-Ray Diffraction (XRD) data at room temperature using an X-ray diffractometer (Siemens D 500) with copper anticathode radiation ($\lambda CuK\alpha$=1.541838 Å) at 2θ from 7 to 70°. Fourier Transform Infrared (FTIR) spectra were obtained on a Vertex 70 spectrometer equipped with a digital detector, via the conventional KBr pellet method. The samples were scanned in transmission mode with 2 and 4 cm^{-1} resolution, at the range of 4000 to 400 cm^{-1}.

3 RESULTS AND DISSCUSION

The preparation of silica chitosan composite (S-g-ChC) was done by mixing 20 mL of Na_2SiO_3 and chitosan with variation (20 mL: 2%), (20 mL: 3%) using glutaraldehyde as crosslinker, and silica chitosan composite without glutaraldehyd (SChC) with variation (20 mL: 2%), (20 mL, 3%). The modification of the silica surface was done using sol

gel method. Chitosan has a high affinity to the surface due to the interaction between part of protonated amino groups of polymer and dissociated hydroxyl groups of silica.

The FTIR spectrum of the synthesized silica chitosan composit with glutaraldehyd as crosslinking (S-g-ChC) show fig 1(A) and (B), without glutaraldehyd (SChC) show fig 1 (C) and (D) .

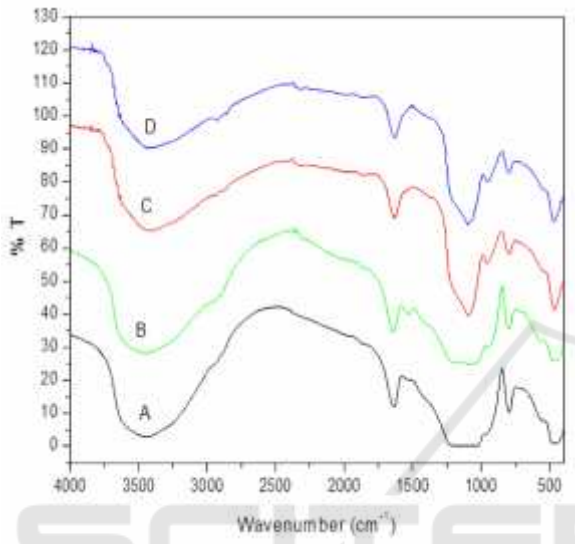

Figure 1: The FTIR spectra of: (A) S-g-ChC1 (20 mL:2%), (B) S-g-ChC2 (20 mL:3%), (C) SChC1 (20 mL:2%), and (D) SChC2 (20 mL:3%).

The formation of silica chitosan composites occurs because silanol groups on the surface of silica take hold of important role in the modification of chitosan copolymers. FTIR results show a significant difference in wave numbers between silica chitosan composites using crosslinking glutaraldehydes S-g-ChC and without crosslinking glutaraldehydes (SChC). At S-g-ChC, the wave number for O-H, C-H, and C-O group stretch vibrations appears to shift to a higher wave number compared to SChC. The wave number shift is due to the cross link formed between the chitosan polymer and silica. When silica gel is introduced into chitosan copolymers, the number of hydroxyl groups (Si-OH) increases which results in an increase in hydrogen interactions between the copolymer matrix and silica gel (Nithya et al., 2016). This cross linking causes the movement of molecules to be more limited, so that more energy is needed to conduct vibrations (Bin et al., 2013)

Table 1: Analysis of S-g-ChC and SChC function groups based on FTIR spectrum.

No	Wave number		Streaching vibration
1	S-g-ChC1	SChC1	
	3447,44	3421,72	-OH
	2928,57	2927,94	-CH
	1637.71	1631.78	-C=N
	1099.42	1095.57	-Si-O
2	S-g-ChC2	SChC2	
	3436,05	3421.72	-OH
	2927,35	2927.94	-CH
	1639,48	1631.78	-C=N
	1095,10	1091.71	-Si-O

This result was further supported by the XRD. The XRD of SChC and S-g-ChC show Fig 2.

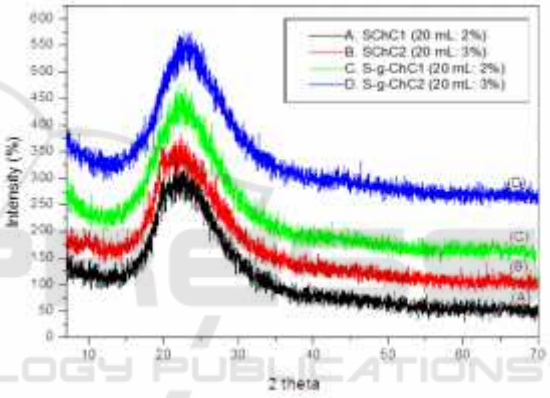

Figure 2: The XRD pattern of: (A) and (B) komposit silika chitosan without crosslinking glutaraldehyde (SChC); (C) and (D) komposit silika chitosan wih crosslinking glutaraldehyde S-g-ChC

Figure 2 that silica chitosan composites with various variations of chitosan have a peak pattern widened which represent a low degree of crystallization (amorphous). The decrease in chitosan crystallinity evidence the conjugation between chitosan and silica polymer chains so that it suppresses crystallinity to a certain extent. The silica and chitosan polymer chains are well mixed at the molecular level wherein that the peak of SChC is more lowest than S-g-ChC (Gandhi et al., 2012). There is also a 2θ difference between SChC and S-g-ChC where SChC at 2θ = 20-22 while S-g-ChC at 2θ = 22-23. This is due the silica chitosan composite S-g-ChC has greater conjugation of silica and chitosan compared to SChC. This can occur because the glutaraldehyde as cross-linker on the composit S-g-ChC will cause a higher density form so that the

chemical bond will be much stronger compared to SChC which has a lower density.

4 CONCLUSIONS

The silica chitosan composites from precursors of sodium silicate (Na_2SiO_3) from volcanic ash of Sinabung mount and chitosan from shrimp husk combined with glutaraldehyde crosslink (S-g-ChC) and without cronsslink glutaraldehyde (SChC) by sol gel method have been successfull. The results of the FTIR and XRD analysis showed differences in the characteristics of the two composites due to the glutaraldehyde crosslink effect.

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