Physical characteristics of chitosan-silica composite of rice husk ash

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Abstract. Some previous studies showed that the characteristics of chitosan membranes have a very rigid and non-porous structure so that its utilization is not maximized, particularly in the filtration process. Hence, it needs modification to improve the quality of the chitosan membranes. Adding the silica into the chitosan membranes is one of the offered solutions to overcome the problems of physical and mechanical properties of chitosan. This study aims to investigate the effect of variations in the silica composition to the physical characteristics of the chitosan-silica membranes of rice husk ash that were synthesized. The chitosan used is derived from the chitin of Vannamei shrimps’ shell with 82% degree of de-acetylation, while the silica was synthesized from rice husk ash with rendering of silica (SiO₂) by 51% and the results of XRD analysis showed an amorphous phase. Membrane synthesis was performed using the phase inversion method with chitosan-silica mass ratios of rice husk ash, which were 1:0.0; 1:0.5; 1:1.0; 1:1.5 and 1:2.0. The results showed that the addition of silica increases the swelling index and the membrane permeability. The results of the analysis, FTIR spectra, obtained a new functional group after the addition of silica, they are Si-OH, Si-O-Si, and CO-NH₂. The morphology test using CCD Microscope MS-804 results in the very tight chitosan membranes without the silica surface, it has no pores, smooth and homogeneous, while the chitosan-silica composite membrane of rice husk ash obviously has cracks and small cavities that seemed to spread out.

1. Introduction

As a maritime country, Indonesia produces massive fishery products such as crabs, shrimps, and scallops. The waste of crab, shrimp, and scallop shells poorly optimized; therefore, it would cause environmental pollution. The general society does not know that in the crab, shrimp and scallop shells waste contains chitin which could be processed into chitosan that is able to be used for various purposes.

Chitosan is a derivative component from chitin that is called (2-amino-2-deoxy-β (1.4)-D-glucopyranose) in the poly structure. Chitosan is a polysaccharide polymer amine unit composed of glucosamine and N-acetyl glucosamine which is a non-toxic, antibacterial, biocompatible and biodegradable hydrophilic polymer [16]. Chitosan has good chemical reactivity as it has a number of
hydroxyls (-OH) groups and amine (-NH$_2$) groups on its chain. Both of these groups allow modifications to the chitosan to produce physical and chemical properties desired [31].

At the moment, chitosan has a lot of uses, among others are in the area of health, water treatments, membranes, hydrogels, adhesives, antioxidants, and food packaging. Chitosan is insoluble in water but soluble in organic acid solvents under pH 6 include fomic acid, acetic acid, and lactic acid. As one of the organic polymer materials which can be used as a membrane, chitosan serves as a thin barrier to separate the two phases, which can release certain components and hold the other components of a fluid flow. Some researchers suggest that chitosan membrane can be used as an adsorbent of heavy metal ions [2, 18], the adsorbent of the urea [19, 11] edible film [21] and can be used as supporting material to produce alternative energy called fuel cell [31, 28].

Chitosan membrane will have pores when added additives or pore-formers (porogen). The pore size of the chitosan membrane can be formed in accordance with the needs of the application. Modifications are done towards the hydroxyl (-OH) group and amine (-NH$_2$) groups on the glucosamine unit of chitosan.

Some researchers have carried out some modifications to the chitosan membrane. Some of the modifications is done by adding materials or polymers that can form crosslinks with chitosan molecules, such as the addition of glutaraldehyde or genipin [13], the establishment of tissue between the chitosan molecules with other polymer molecules such as (ethylene oxide) (PEO) poly [13], and coating the surface of the chitosan membrane with alkane steam plasma (petroleum ether). Chitosan membrane modification is expected to produce membranes with better characters such as increased stability of the membrane [13], reduced size of the membrane pores to make the separation of molecules or macromolecules rejection of a solution by the membrane more effective. The cross-linked of chitosan is a proposed solution to overcome the problems of the mechanical properties of chitosan to increase the adsorption of metal [8, 2, 25] conducted a synthesis of the chitosan-zeolite composite membrane. Zeolite composite chitosan is based on morphological analysis including non-pore membrane. FTIR analysis result does not show the formation of new functional groups which means that the composite is the result of physically mixing [34] conducted a synthesis of chitosan-silica composite membrane of tetra ethoxy ortosilan (TEOS) to determine the effect of chitosan concentration on the properties of chitosan-silica composite membranes for fuel cells.

Silica can be synthesized from a wide variety of natural resource-rich silica. One source of silica which has so far not fully utilized is rice husk. As an agricultural country, Indonesia is a rice producing country. Rice milling process produces rice husks which are usually discarded and become waste that cause environmental pollution or burned away in the rice milling area. In the process of burning rice husk, some compounds such as hemicellulose {xylose-β (1,4) - mannose-β (1,4) - Glucose-α (1,3) -Galactose}, cellulose (β-1,4-poly glucose) and others will be converted to CO$_2$ and H$_2$O. The ash obtained from the combustion of rice husk is about 13.1% - 29.04% in dry weight [14]. This rice husk ash can be used as a source of silica (SiO$_2$). The research conducted by [10] shows the content of silica (SiO$_2$) in rice husk ash is 94-96%. Silica (SiO$_2$) that is inert, hydrophobic, and transparent has a mechanical strength and high thermal stability. It does not swell in organic solvents.

Silica (SiO$_2$) is as one of the ingredients to form a solid membrane which can be used for metal ion absorption of manganese (Mn$^{2+}$), cadmium (Cd$^{2+}$) and nickel (Ni$^{2+}$) in waste water. The use of rice husk ash silica alone in membrane synthesis will produce fragile membranes because inorganic membranes have the disadvantage of limited application and are fragile [33] as well as have low selectivity level [4]. The addition of silica into the polymer matrix can increase the mechanical strength such as water resistance, strong stretching and tensile strength [30]. Modification of chitosan and silica can be used as raw materials for the synthesis of silica-based material for decolorization dye process and the reduction of heavy metal ions by filtration [31, 22].

Referring to the characteristics of chitosan and silica, and then both of the materials have the potential to be combined in an effort to get a filtration membrane with several improved characteristics. As has been done by [35] in his study, the chitosan-silica membrane is prepared by phase inversion technique.
Based on the explanation above, it has carried out research aimed 1) to synthesize silica from rice husk ash, 2) to synthesize chitosan from Vannamei shrimp shells, 3) to synthesize composite silica membrane of chitosan-rice husk ash, and 4) to characterize the result of the synthesized chitosan-silica membrane. As for the physical characterization of chitosan-silica, composite membranes of rice husk ash include swelling index, permeability, group function and morphology of the membrane. The expected benefits of this research are 1) Improving the economic value of rice husks and shells waste; 2) Providing information about the physical properties of chitosan-silica composite membranes of rice husk ash; 3) Producing a qualified composite membrane product which is environmentally friendly.

2. Method

2.1. Rice Husk Silica Manufacturing
Silica (SiO$_2$) of rice husk obtained through the charcoal using process and incineration with high temperature. The ashing process is carried out in the furnace at a temperature of 600 degree Celsius for an hour. The result of this process is white rice husk ash [23]. To determine the composition of the rice husk ash, X-Ray fluorescence (XRF) is used [26]. The ash obtained from the ashing process is then purified with acid. This aims to eliminate the metal and non-metal content from the rice husk ash. The result of the purification is the brown rice husk ash. The ash that has been through acidification is reheated by 600 degree Celsius for 1 hour [8]. Synthesized silica is then characterized by using a Shimadzu XRD-7000 X-ray Diffractometer to obtain its crystalline results.

2.2. The manufacturing of sodium silicate solution as the silica source
To make a solution of sodium silicate, rice husk ash is reacted with NaOH 4M solution. By heating and stirring the solution, the brownish viscous mixture is obtained. After the half-dried product, it is put in the furnace with 600 degree Celsius for 30 minutes to obtain solid sodium silicate with greenish white color. Solid sodium silicate is then dissolved in demineralized water. This process takes overnight until its color becomes brownish-yellow.

2.3. The manufacturing of Vannamei crusts shrimp Chitosan
The preparation of van named shrimp shell sample was taken from the shrimp shell waste in Tambakrejo. The amount of the shrimp shell sample used was 1 kg. Then, this shrimp shell sample was washed, boiled, and dried in an oven at 120 degree Celsius for approximately one hour. After dried, it was then milled, and it was also sieved by using a 50 mesh sieve to obtain dried shrimp shell powder. After that, the powder obtained was processed through deproteinization, demineralization, depigmentation, and deacetylation. The powder obtained was then washed by using arcades until neutral. It was also put at 60 degree Celsius until completely dry (± 8 hours). Furthermore, chitosan was characterized using FTIR to provide information about DD value, water level, and ash level. To make a chitosan solution, chitosan was dissolved in CH$_3$COOH 2% v/v, stirred using a magnetic stirrer for 1 hour until it formed a homogeneous solution [5, 19].

2.4. The manufacturing of Chitosan-silica composites membranes
Chitosan-silica composite membrane was made by mixing chitosan solution with sodium silicate solution which is the source of silica [5]. To obtain the homogeneity of the chitosan-silica solution, stirring this mixture for 1 hour will obtain a yellowish colored clear solution which has a thick texture. 100 ml of a solution of chitosan-silica mixture is poured into a mold, and make sure that the surface is even. The synthesis of membranes with the variation in composition of chitosan solution: silica 1:0; 1:0.5; 1:1; 1:1.5; 1:2. Once it is formed, the chitosan-silica solution mixture is dried at normal temperature [21]. Dried Chitosan-silica membrane is still acidic and readily soluble in water, so it needs to be neutralized with a base. According to [18], soaking the membrane in alkali solution aims to transform the amine group of cation (-NH$_3^+$) into free amine group (-NH$_2$). The membrane obtained is then washed with aquades to make it neutral. This process is done in order to facilitate the next
stage. To determine the physical characteristics of the membrane, it will undergo swelling index test, flux membrane test, and the identification of functional groups using FTIR (Fourier Transform Infra-Red) and Morphology Test of chitosan-silica composite membrane section using a CCD Microscope MS-804.

3. Results and Discussion

3.1. The results of silica manufacturing from rice husk ash
Silica (SiO$_2$) rendering of rice husk from the synthesis results are as shown in table 1.

| Rice Husk Charcoal | Rice Husk ash | Rice Husk Ash Silica |
|--------------------|---------------|----------------------|
| Mass (gram)        | Silica Mass (gram) | Level (%) |
| 180                | 90.6482       | 49.6                 |
| 250                | 122.0160      | 51.2                 |
| 250                | 119.3080      | 52.3                 |

The average levels of rice husk ash silica are 51.0%

Based on table 1, this process produced rice husk silica (SiO$_2$) up to 51.0% from 680 grams of rice husk charcoal. By using X-Ray fluorescence (XRF), the characterization result of the chemical content of the rice husk ash silica obtained SiO$_2$ = 97.24%.

Silica crystallinity of rice husk ash was characterized using XRD. This qualitative analysis was conducted with 1.54060 Å wavelength. The operating condition involved Cu radiation, with a step size of 0.0200 degrees, voltage of 40.0 kV and current of 30.0 mA. The samples were scanned from the observation area between 5.0000 to 90.0000 degrees. The data obtained were in the form of inter-field distance, intensity, and angle magnitude (2θ) which is then matched with the pattern of X-ray diffraction on JCPDS (Joint Committee on Powder Diffraction Standard) number 39-1425. Diffractogram of rice husk ash silica is presented in figure 1.

The diffractogram result of silica (SiO$_2$) obtained in Figure 1, appears a sharp peak at 2θ = 21.7200; 2θ = 20.8800; and 2θ = 22.5200, it shows the silica diffraction pattern of hydrated amorphous phase [7]. The sharp peak at 2θ = 20.8800 indicates that the silica contains the SiO$_2$ compound in the form of cristobalite mineral. According to [15], the broad peak shape with a central peak around 2θ = 22 indicates that the silica (SiO$_2$) are amorphous. Amorphous structure of the silica surface is described as random network with a low regularity degree [8, 20]. This kind of amorphous phased silica is more preferable because it is more soluble. The more soluble the silica, the better of the silica-based material making, in this case, is sodium silicate.

![Figure 1. The Result of X-ray diffractogram Rice Husk Silica Synthesis.](image_url)
3.2. The result of chitosan characterization from Vannamei shrimps crust waste

Table 2 presents the results of the synthesized chitosan characterization from Vannamei shrimp shell.

| Parameter                  | Chitosan          |
|----------------------------|-------------------|
| Base material              | Vannamei shrimp crust |
| Partikel size              | Powder (50 mesh)  |
| Water level                | 5.8%              |
| Ash level (%)              | 0.12%             |
| Solubility in acetic acid 1 % | > 99%            |
| Degree of deacetylation    | 82%               |

The result shown in table 2 indicates that chitin from Vannamei shrimp shell has been converted into chitosan.

3.3. The result of rice husk ashes chitosan-silica characterization

The results of the synthesis of rice husk ash chitosan-silica composite in the form of membranes of which the shape is like a thin sheet of plastic, transparent, mushy when exposed to water, and rigid when dried. In general, the synthesized rice husk ash chitosan-silica composite membrane product has good water resistance. This is indicated by the unbroken, strong membrane. The result of swelling index test Swelling index results is presented in table 3.

| Variation chitosan: silica | Swelling index (%) |
|----------------------------|--------------------|
| 1:0                        | 45.538             |
| 1:0.5                      | 51.333             |
| 1:1                        | 53.486             |
| 1:1.5                      | 54.518             |
| 1:2                        | 54.936             |

Based on table 3, it can be seen that the chitosan-silica composite membrane will cause higher water absorption capacity than the membrane with chitosan composition only. This is based on [12]. This is possible because silica (SiO$_2$) is a compound which has a strong affinity towards water molecules. It is hygroscopic and has a broad surface area. These properties make the membrane easily absorb water on the surface, and increase the water resistance properties [9].

Another thing that also affects the swelling degree of chitosan membrane is its hydrophilic characteristic [24]. In general, the membranes with chitosan as the basis have higher hydrophilicity properties. This is possible because of the active functional group in chitosan such as a group of -OH and -NH$_3^+$ which can bond the H$_2$O molecules. Hydrophilicity properties of chitosan-silica membrane allow it to be used as the filtration media in decolorization. The membrane of which water absorption degree is more than 50% can be used for absorption or filtration [8].

The water content in the membrane is also one important part of the characterization of polymer electrolyte membrane for fuel cell application as it relates to its conductivity ability [6]. According to [8], the good membrane used for fuel cell application is ones who have a water absorption of less than 50%. If the water absorption is too high (more than 50%), the membrane will become really soft. If so, the membrane’s lifetime will be shorter. The soft membrane cannot be used in fuel cells because it cannot function as an insulator between the two electrodes. According to [29] the higher the water
uptake (percentage of water swelling), the higher the proton conductivity will be like the more water molecules in the membrane which can be the proton transfer media.

3.4. Water Vapor Permeability (WVP) of chitosan-silica membrane

In this permeability test, 0.0025 L of permeate volume with diameter membrane of 0.04 m was used, the area of the membrane was $1.256 \times 10^{-3}$ m². Table 4 shows the result of permeability test of chitosan-silica membrane in a synthesized rice husk ash.

| Membrane Variation | Flukes (L/m²·Hour) |
|--------------------|-------------------|
| 1:0                | 13.2733           |
| 1:0.5              | 16.9138           |
| 1:1                | 19.0346           |
| 1:1.5              | 20.9051           |
| 1:2                | 23.8127           |

Table 4 shows that there is an improvement of membrane permeability/ fluke value along the material addition in the chitosan membrane.

The added silica gave effect to the structure of chitosan. The silica will form some pores with intermolecular silica-oxygen bonds, so it forms a long chain of SiO$_2$ and bonds between silica and oxygen in –OH group [29]. The formed pores influences permeate to pass quickly through the membrane [3]. The result shows that chitosan-silica membrane was the appropriate membrane that was used in the filtration process because it had pores, so it was a good fluke value. However, permeability value should not more than 75 L/m²·hours. That membrane is not good to use as filtration media [8]. This is because membrane with big permeability value could not resist unwanted species.

3.5. The function group test of Chitosan-silica membrane

Based on result analysis of group function in FTIR spectra in a combination of the membrane in figure 2, it is specifically presented in Table 5.

| Types of absorption | The number of the wavelength (cm$^{-1}$) of membrane |
|---------------------|---------------------------------------------------|
|                     | 1:0      | 1:0.5   | 1:1     | 1:1.5   | 1:2     |
| Si-OH               | -        | 902.69  | 902.69  | 902.69  | 902.69  |
| Si-O-Si stretch     | -        | 1072.42 | 1072.42 | 1072.42 | 1072.42 |
| CH$_2$ bending      | 1427.42  | 1411.89 | 1427.42 | 1419.61 | 1381.03 |
| CO-NH$_2$           | -        | 1658.78 | 1658.78 | 1635.64 | 1635.64 |
| CH stretch          | 2885.51  | 2885.51 | 2877.79 | 2885.51 | 2924.09 |
| OH stretch          | 3425.58  | 3448.72 | 3448.72 | 3417.86 | 3441.01 |
| NH$_3^+$            | 1604.77  | -       | -       | -       | -       |

From Table 5, it can be seen that there is some new absorption in Chitosan-silica membrane: Si─O─Si group, Si─OH, Si─O─Si stretch. The existence of new function group after adding the silica shows that the added silica has interacted with chitosan chemically. The existence of the Si─OH group shows hydrogen silanol groups of the silica interacts with the amide group or oxy group in chitosan [25, 27] while a combination of functional groups between the constituent components of
composite indicates physical mixing. Ionic bond happens between amino group from chitosan of silanol group, and covalent group happens because of the reaction between hydrosol groups from chitosan of the silica network [1]. The mechanism of cross binder of chitosan silica can be showed as follow in figure 3.

![Mechanism of the cross binder of Chitosan-silica](image)

**Figure 3.** Mechanism of the cross binder of Chitosan-silica[3].

Besides covalent bonding occurs, most likely the silica enter to matrix chitosan through ionic interaction. However, this interaction could not be seen in the infrared spectrum. Another interaction probably happened was showed in figure 4 [3].

In figure 4 also shows there is Vander Waals interaction between amino group and silanol group (Si-OH), and hydrogen bonding in acetamide group with silanol group that contribute power to chitosan-silica membrane.

Silica interaction to Chitosan also can be seen from the decreasing of the stretch intention of N-H in the 3270-3290 cm⁻¹ area that overlaps with the absorption of –OH. It is because of the group N-H interacted with the added silica. In Chitosan-Silica 1:0 contained NH₃⁺ absorption in 1597.06 cm⁻¹ area, and it was not found –NH₂ absorption. It was because, in chitosan-silica membrane, there is no coagulation that change NH₃⁺ to be a –NH₂ group, while in the membrane with the adding silica has passed the coagulation process with NaOH solution in making natrium silicate as Silica source.
Figure 4. Chitosan Silica Interactions[3].

The absorption in the form of bending in 900-1000 cm\(^{-1}\) indicates symmetry stretch vibration of –Si-OH [17]. From the data obtained comes another absorption long wavelength 594.08; 594.08; 563.21 cm\(^{-1}\). This absorption identifies the symmetry stretch vibration to Si-O from –Si-O-C. Wide absorption in 500-700 cm\(^{-1}\) area with special characteristic on it's not too sharp bending was the absorption that indicated symmetry stretch vibration of –Si-O from –Si-O-C [8]. From the absorption of –Si-O-C, it can be identified that the added silica has interacted with chitosan. The interaction occurs between Silica and Chitosan affected the opening of the cavities or cracks that make the synthesized membrane with pores.

4. Conclusion
Based on the test results of the physical characteristics of the composite membrane of chitosan-silica of rice husk ash which is synthesized, it can be concluded that the silica has properties as porogen to provide the pores on chitosan membrane so as to increase the capacity of water absorption, permeability, and increase the active sites of chitosan membrane. Thus, the chitosan-silica composite membranes of rice husk ash that are synthesized are very high potential to be used as a filter to reduce metal ions and dye textiles.

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