Influence of Polyvinyl Alcohol (PVA) Addition on Silica Membrane Performance Prepared from Rice Straw

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Abstract. The utilization and modification of silica from rice straw as the main ingredient of adsorbent has been studied. The aim of this study was to determine the optimum composition of PVA (polyvinyl alcohol): silica to produce adsorbents with excellent pore characteristics, optimum adsorption efficiency and optimum pH for methyl yellow adsorptions. X-Ray Fluorescence (XRF) analysis results showed that straw ash contains 82.12 % of silica (SiO₂). SAA (Surface Area Analyzer) analysis showed optimum composition ratio 5:5 of PVA: silica with surface area of 1.503 m²/g. Besides, based on the pore size distribution of PVA: silica (5:5) showed the narrow pore size distribution with the largest pore cumulative volume of 2.8 x 10⁻³ cc/g. The optimum pH for Methanyl Yellow adsorption is pH 2 with adsorption capacity = 72.1346%.

1. Introduction
The development of science and technology in Indonesia directly encourages the growth of the industry. The environmental pollution problem such as industrial waste waters into river has been more serious problem of this decade. Liquid waste as a product of industrial activity often creates problems of the environment [1]. Liquid wastes containing hazardous and toxic materials could disrupt the biological processes that occur to municipal environment. Water pollution from several heavy metals and organic wastes originated by industries such as metallurgy, tannery, and textile industries [2]. The textile industry produced large amount of liquid waste such as dyestuffs, suspended solids, oils and fats that need to be treated before the wastes were released into the river [3]. The amount of dye waste in the textile industry would cause environmental pollution, while the environment has a limited ability to degrade the dye, so further research is needed to overcome these problems. Liquid waste treatment was intended to eliminate levels from pollutants that were contained in liquid waste to be disposed directly to the environment.

Several studies of the dye and organic waste removal compounds present in batik industrial have been widely studied, not only by chemical treatment such as, color degradation with oxidation reactions, anaerobic reactions and photocatalysis reactions [4], but also by physical treatment like coagulation, sedimentation, adsorption using activated carbon, silica and biomaterials [5]. The coagulation and sedimentation technique has noted by the good efficiency for waste treatment but generate new waste, such as floc or coagulant. Not only the use of activated carbon still lack of requirement of high enough cost because the price of activated carbon is relatively expensive, but also the use of photocatalyst...
reactions requires a high cost because the price of photocatalysis reagents such as TiO$_2$ was quite expensive. Liquid waste waters process by biological method was also widely applied to reduce the organic compound of liquid waste textile industry. However, the efficiency of color removal through this biological process was not really satisfactory, since the dye has the resistance to biological degradation (recalcitrance). To solve that problem, a new alternative is needed to treat the textile industries effective and efficient liquid waste for reducing organic pollutants and dyestuffs [6].

Based on El-Maghraby [7] study about utilized rice hulls for Methylene blue absorption, the hidroxyl group in rice hulls increasing with the increases of pH. Increases the number of negatively charge sites could enlarge the attraction between dye and adsorbent surface. The research of Mahatmanti et al in 2016 [8], the utilization of rice hulls as the source of silica in the making of chitosan based membrane with the supporting material Poly Ethylene Glycol (PEG) has been done. Silica/Chitosan/PEG membrane was used to reduce the content of heavy metals such as Ca, Cd, Zn, and Mg in solution. The source of silica on the membrane was obtained from rice straw. The selection of rice straw due to straw has 75% content of silica in one kilogram [9]. The manufacture of silica membranes used a mixture of rice straw silica, Poly Vinyl Alcohol (PVA), and Poly Ethylene Glycol (PEG).

2. Experimental
2.1. Chemicals
Rice straw obtained from local industry (Pacitan, East Java, Indonesia), Polyvinyl alcohol (PVA) (Merck, Indonesia), Polyethylene glycol (PEG) (Merck, Indonesia), Nitric acid (Merck, Indonesia), and Hydrochloric acid (HCl) (Merck, Indonesia) were used in the production of PVA/Silica membrane. Whereas the Methanyl Yellow used in this study is a local material and Fe$^{3+}$ solution is from Merck, Indonesia.

2.2. Process of rice straw ashes and Activation of Rice Straw Ash
The main ingredient of rice straw from Pacitan which is then nested with heating in a cauldron placed on the stove. This process was done until the gray rice straw is gray, and further characterization using STA and chemical group analysis using FT-IR. Furthermore, rice straw charcoal was burned at 800 ° C for 3 hours resulting in rice straw ash. The resulting rice straw ash is reddish-gray, and then analyzed its chemical content using FT-IR.

The rice straw ash was activated by soaking the ash of rice straw on HCl 1 M for 24 hours. Then it was filtered and neutralized with water, after neutral then heated in oven for 5 hours at 110 °C. Then crushed using porcelain cup and sieved with 150 meshes sieve. Then, analysis of functional group content using FTIR and chemical content analysis using XRF.

2.3. Fabrication of Silica membrane
A total of 2, 4, 6, 8, 10 grams of PVA were mixed with 10 mL 1M HNO$_3$, and 200 mL aquades, stirred with a magnetic stirrer for 2 hours on 80 ° C heating. Then taken each 1, 2, 3, 4, 5 gram of each PVA solution that has been made, then added ash of activated rice straw as much as 5 grams and stirred until homogeneous. The silica-PVA dough of each PVA / silica composition added PEG 0.3 grams, 5 ml aquades and 4 g of Na$_2$SiO$_4$. The mixture was then stirred until homogeneous and poured onto a mold ± 20 mm in diameter and arranged with a membrane thickness of ± 4 mm, then allowed to stand for ± 30 hours.

The next stage after the process of forming the silica membrane includes drying and burning. The drying process was carried out at a temperature of about 60 °C for 1 hour. Then it was burned by raising the temperature to 800 °C. The combustion process was carried out for 5 hours, following the cool down in the furnace to room temperature. Finally we have gotten silica membrane composed by PVA:silica = 1.5; 2:5; 3:5; 4:5; 5:5, respectively.
2.4. Methanyl Yellow Adsorption Process
Silica membrane composed by PVA:silica = 1:5; 2:5; 3:5; 4:5; 5:5, respectively, was placed on a porcelain funnel, and an already prepared Methanyl Yellow solution was placed on the burette of 20 ml. Then the Yellow Methanyl solution was continuously streamed into the silica membrane. Thus, silica membrane with optimal PVA / silica ratio will be obtained to adsorb Methanyl Yellow solution. The UV-Vis spectrophotometer UV-Vis Shimadzu PC 1601 was used to calculate the maximum wavelength in the 300-600 nm range. Based on maximum wavelength have been obtained we plotted the standard curve of that dye to determined the sample concentration later.

2.5. Determination pH Optimum of Methanyl Yellow and Fe$^{3+}$ Solution
The silica membrane was used to adsorb Methanyl Yellow. However, the Metanyl Yellow solution was prepared at various pH condition from pH 1 to pH 8. The silica membrane were immersed into Fe$^{3+}$ solutions in certain pH conditions in the range 1 – 7. While, the adsorption process of Methanyl Yellow with optimum pH was carried out. In addition, the membrane was placed on a porcelain funnel, and a 20 mL solution of Methanyl Yellow was placed on the burette. Yellow Methanyl solution was continuously streamed into the silica membrane. Based on this procedure we also study the influence of Fe$^{3+}$ addition in methanyl yellow solutions and also calculate the optimum pH for Fe$^{3+}$ solution will pass to silica membrane.

3. Result and Discussion
3.1. Characteristic of Straw Ash due to Activation and combustion Process
Rice straw is one of the large amount of agricultural waste and has not been fully utilized. Rice straw when burned will produce ash as much as 10-17%, which means that any 1000 kg of rice straw burning will produce 100-170 kg of rice ash, and contain 75% silica in each kilogram [9].

From the Table. 1, it can be seen that the silica content is 82.12%, which is the dominant composition of rice straw ash used in this study. Several studies that have been done previously obtained the silica ash content of rice straw as much as 82.5% [10] and 75% [9].

Table 1. Result of Chemical Composition Content (% w/w) of Rice Straw Ash using XRF

| Composition | SiO$_2$ | K$_2$O | CaO | Al$_2$O$_3$ | P$_2$O$_5$ | Cl | Na$_2$O | Fe$_2$O$_3$ | SO$_3$ | TiO$_2$ | Rb$_2$O | ZnO | SrO |
|-------------|--------|-------|-----|------------|-----------|----|--------|------------|-------|--------|-------|-----|-----|
| Quantity (%)| 82.12  | 9.72  | 2.52| 1.00       | 0.99      | 0.98| 0.87   | 0.82       | 0.73  | 0.09   | 0.06  | 0.05| 0.01|

Base on the result (Figure 1), there is no significant difference of wave numbers in each sample, which means that in each treatment does not change the composition of the functional groups in the sample. The sharped absorption number at 1090 cm$^{-1}$-1095 cm$^{-1}$ was represented Si-O-Si (siloxane) groups. The FTIR spectras (Figure 1) shown that reduction of C content was happened in Activated Rice Straw Ash. HCl solution was able to dissolve impurities, its can be known by the loss of small peaks (very low intensity).
3.2. Characteristic of silica membrane with addition of PVA.

In the manufacture of silica membrane consists of several stages. The initial stage is the manufacturing of PVA (liquid) with the addition of nitric acid as the activating agent of the hydroxyl functional group. PVA will perform a strong secondary bond with siloxane (Si-O-Si) and silanol (Si-OH) groups in rice straw ash. This is because PVA has a hydroxy group in every iteration of the polymer, therefore, there will be a three-dimensional structure between PVA and silica. According to Reed James (1988) [11], PVA will act as a binder between particles that will increase the green strength of the silica membrane.

The function of the addition of PEG as a pore-forming agent in the silica membrane. As stated by Kim & Lee (1998) [12], that PEG can be used as a pore-forming and increase membrane permeability. In addition, PEG also has a function as a plasticizer. The only adhesive-containing system is very elastic like rubber, so it takes a plasticizer that will make the dough is viscoelastic. Viscoelastic will make the dough easily formed according to desire [11].

The thermal characteristics of the PVA/silica membrane in the combustion process is performed thermal analysis which can be seen as Figure 2.
Figure 2. Termogram of silica membrane (PVA/Silica = 5/5)

From the silica membrane thermogram, at 43.6 °C there is a mass loss of 1.34 mg which means that the water content in the membrane has decreased and up to 85.8 °C has decomposition of 2.06 mg. Transition Glass (Tg) PVA occurs at a temperature of 85.8 °C. While melting temperature (Tm) of PVA occurs at a temperature of 231.9 °C.

At the temperature of 395.2 - 460.9 °C occurs endothermic, where at this temperature PVA and PEG will burn. According to Gilman (1994) [13], at 350 °C, the alcohol fraction, methylene, aliphatic carbon will be lost by ± 70 ppm, ± 45 ppm, ± 15-50 ppm from the original composition up to 776.6 °C most of the PVA and PEG are lost, where up to this temperature the total mass decomposition is 3.73 mg.

At the temperature of 460.9-776.6 °C oxidation reactions, recombination and polymerization occur within the silica membrane. According to Remmey (1994) [14], the temperature of 500 °C-800 °C is the temperature of the filtration, where the glass forming elements will melt and become hard when cooled. In this period the silica changes in volume and crystal structure so that it will expand rapidly. While at temperatures above 776.6 °C there will be recrystallization in the membrane, which takes place exothermically (releasing heat).

With the loss of PVA and PEG will result in empty spaces (pores) in the silica membrane and rearrangements of bonds within the membrane. The pore characteristics of each membrane composition can we seen in SAA result. Comparison of pore size, pore distribution, pore volume, and surface area of each PVA/silica composition can be seen in Table 2.
Table 2. Surface and Pore Analysis Result of Silica Membrane

| PVA/Silica | BJH Desorption | BET |
|------------|----------------|-----|
|            | Pore Diameter (Å) | Cumulative pore volume x10⁻³ (cc/g) | Average Diameter Pore (Å) | Pore Volume x 10⁻³ (cc/g) | Surface Area (m²/g) |
| 1/5        | 18 1.5          | 34.4747 | 1.472 | 0.854 |
| 2/5        | 19 1.6          | 27.7030 | 1.555 | 1.122 |
| 3/5        | 28 0.9          | 64.2095 | 1.159 | 0.361 |
| 4/5        | 18 2.5          | 53.7122 | 2.515 | 0.937 |
| 5/5        | 18 2.8          | 37.1623 | 2.793 | 1.503 |

The cumulative volume of pore is the volume (cc) of each pore diameter in each 1 gram of sample. From Table 2, it can be seen that in the silica membrane composed from PVA: silica = 1:5; 2:5; 4:5; and 5:5 had the largest pore size distribution on micropore (< 20 Å), whereas in the silica membrane composed from PVA:silica = 3:5, the highest pore size distribution was obtained at mesoporous (20 Å - 50 Å).

From the micropore diameter, it can be seen that the composition of the 5:5 silica membrane has the highest cumulative volume of the micropore. The more micropores in the sample, the greater the total pore volume and total surface area in the sample are known by the BET method. Where BET (Brunau-Emmett-Teller) is a method used to determine the total surface area and pore structure of a solid (Haber et al, 1995) [15].

The 5:5 silica membrane provides the largest total surface area. This proves that, when burned to a temperature of 800 °C, PVA will be degraded and rearranged to form new pores. Thus, the more PVA the added surface of the silica membrane will be. However, the pore size distribution on the 5:5 silica membrane does not different significantly between micropore and mesoporous size. This gives information that on the 5:5 silica membrane, the micropore is not distributed uniformly (randomly). While the silica membrane with uniform pore size distribution can be seen on the 2:5 silica membrane, which is characterized by a significant difference between micropore and mesoporous size. Thus, the PVA:silica composition which gives a uniform pore size distribution is the PVA:silica = 2:5 composition. However, the optimum surface area was obtained on a silica membrane with a PVA:silica composition = 5:5.

3.3. Performance of Silica membrane on adsorption of Methanyl Yellow

The 10 ppm Yellow Methanyl solution was used as the starting solution which would later be adsorbed with the silica membrane. The variation of PVA/silica composition (b/w) is 1/5; 2/5; 3/5; 4/5; 5/5 adsorbed with 20 mL of Methanyl Yellow solution.
Based on data in Figure 3, it can be seen that the optimum adsorption capacity occurs when use silica membrane composed from PVA: silica = 5:5 (w/w) as 48.3077 %. Methanyl Yellow molecules will be retained more in the silica membrane as the radius (microspores) becomes smaller and the larger the surface area. In addition, Methanyl Yellow is a kind of negatively charged (anionic) textile dyestuff. Thus, the negative group of Methanyl Yellow, the SOOH functional group, will bind to the Si-O-Si group present in the silica membrane.

The determination of pH optimum of Methanyl Yellow was conducted at pH = 1, 2, 3, 4, 5, 6, 7, and 8 the pH solution have effected Methanyl Yellow adsorption process. The optimum Methanyl Yellow can be absorbed maximum in silica membran 72.1346 % at pH 2 condition. At an acidic condition, the NH and -SOOH groups will be formed as -NH\(^{3+}\) and -SOOH\(^{2-}\). The cluster will bind strongly with the negative group (-SO\(^{-}\), -SiO\(^{-}\)) on the silica membrane. In addition, the acid conditions will change the nature of Methanyl Yellow to be a hydrophobic. The hydrophobic methane particle of Methanyl Yellow will be readily accumulated on the surface of the solution [16], making it more readily adsorbed by the silica membrane. However, if it is too acidic (pH 1) the adsorption becomes less efficient because at this pH the excess H\(^{+}\) occurs, so the negative group of silica membranes can no longer bind to the amount of H\(^{+}\) (saturated), consequently there are still many free H\(^{+}\) ions in the solution causing competition between dyestuffs with free H\(^{+}\) ions to be adsorbed by the silica membrane. It is characterized by the color change of Methanyl Yellow into a dark purple.

Figure 3. Optimum Composition of Silica membrane
The determination of the optimum pH of Fe$^{3+}$ solution aims to find out how the influence of Fe$^{3+}$ on Methanyl Yellow optimum pH adsorption. The effect of pH variation of Fe$^{3+}$ solution in Methanyl Yellow adsorption is shown in Figure 4. Based on the Figure 4, the optimum pH of Fe$^{3+}$ solution in Methanyl Yellow adsorption process is pH 3 with adsorption capacity = 70.8077%. However, more OH$^{-}$ or more alkaline causes the Fe$^{3+}$ solution over the saturation point (Yellow FeCl$_3$ precipitate). With the formation of this precipitate, FeCl$_3$ covers the pores of the silica membrane. So the adsorption of methanyl Yellow is not optimal. At pH 3, the Fe$^{3+}$ solution will change to Fe(OH)$_3$ which will be bound to the pores of the silica membrane. So that will increase the amount of positive charge on the silica membrane that will bind Methanyl Yellow (anionic compound).

4. Conclusion

Silica membrane have been successfully synthesized. X-Ray Fluorescence (XRF) analysis results showed that straw ash contains 82.12 % of silica (SiO$_2$). Based on the pore surface area, a silica membrane composed from PVA: silica = 5:5 have highest surface area (1.503 m$^2$/g) with an adsorption capacity value is 48.3077 %. Besides, based on the pore size distribution of PVA: silica (5:5) showed the narrow pore size distribution with the largest pore cumulative volume of $2.8 \times 10^{-3}$ cc/g. The optimum pH for Methanyl Yellow adsorption is pH 2 with adsorption capacity = 72.1346%.

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