Utilization of composite membrane polyethyleneglycol-polystyrene-cellulose acetate from pineapple leaf fibers in lowering levels of methyl orange batik waste

E V Y Delsy[1], Irmanto[1] and F N Kazanah[1]

[1]Department of Chemistry, Faculty of Mathematic and Natural Sciences, Jenderal Soedirman University, Purwokerto

Email: vaulinaeva@gmail.com

Abstract. Pineapple leaves are agricultural waste from the pineapple that the fibers can be utilized as raw material in cellulose acetate membranes. First, made pineapple leaf fibers into pulp and then converted into cellulose acetate by acetylation process in four stages consisting of activation, acetylation, hydrolysis and purification. Cellulose acetate then used as the raw material to manufacture composite membrane with addition of polystyrene and poly (ethylene glycol) as porogen. Composite membrane is made using phase inversion method with dichloromethane-acetone as a solvent. The result of FTIR analysis (Fourier transform infra-red) showed that the absorption of the carbonyl group (C=O) is at 1643.10 cm^{-1} and acetyl group (C–O) at 1227.01 cm^{-1}, with a molecular weight of 8.05 x 10^4 g/mol and the contents (rate) of acetyl is 37.31%. PS-PEG-CA composite membrane had also been characterized by measuring the water flux values and its application to decrease methyl orange content (level) in batik waste. The results showed that the water flux value is of 25.62 L/(m^2.hour), and the decrease percentage of methyl orange content in batik waste is 71.53%.

1. Introduction

Membrane is thin layer, a border between two semipermeabel phases. Membrane technology is one of separation methods that is being developed for processing wastewater, the advantages are high separation efficiency, separation can take place continuously, requires no chemical additives, and the separation is more simple. Besides, the membrane technology is clean technology because it is environmentally friendly and does not generate waste [1]. According to Wenten [2], the success of separation process with membrane depends on the quality of the membrane.

Materials used in membrane preparation is cellulose acetate. Cellulose acetate can be synthesized by acetylation. Pineapple leaves (Ananas comosus) is one of the plants contain cellulose. This plant utilization is limited to the fruit, while the leaves are relatively not used widely.

Modifications to membrane base material is increasingly diverse, one of them is the addition of polyethylene glycol. The modification is affects only the flux and membrane rejection index, but it does not affect the strength. The added PEG affects the formation of pores in the membrane. In the presence of PEG, the number pores formed is increasing and the size is more even. A mixture of

polymers that can be decomposed biologically and synthetic polymers can generate new physical properties. Besides the addition of polyethylene glycol, polystyrene can also be used as a mixture of natural polymers to increase the strength of the membrane obtained. According to Crowd [3], CA membrane with synthetic polymer addition, i.e. polystyrene (PS) have better mechanical properties compared with the CA. By adding polistyrene, the resulting membrane structure is getting tighter, and the crystallinity is getting higher, that improves the mechanical properties of the membrane. The manufacture of cellulose acetate composite membrane of pineapple leaf fibers has been made with the addition of PEG and polystyrene, as well as its application to decrease levels of the dye methyl orange on batik waste.The purpose of this research is: to determine the characteristics of the composite membrane PS-PEG-CA of pineapple leaf fibers and to determine the reduction in dye methyl orange percentage using a composite membrane PS-PEG-CA from pineapple leaf fibers.

2. Research Methods

2.1. Instruments

This study uses a set of reflux or extraction tools, analytical balance, filter paper, hot plate, shaker, measuring flask 25 mL and 100 mL, oven, one size pipette, measure pipette, Beaker glass 100 and 1000 mL, stirring rod, plastic containers, Viscometer Ostwald, filtration apparatus, desiccator, magnetic stirrer, glass plate, FTIR and UV-Vis Spectrophotometer.

2.2. Materials

This study uses materials pineapple leaves, distilled water, NaOH p.a., $Ca(OH)_2$, NaOCl, glacial acetic acid, KBr, phenolphthalein indicator, HCl, H_2SO_4 concentrated p.a., dichloromethane p.a., acetone p.a., acetic anhydride p.a., PEG (polyethylene glycol) 600, polystyrene, batik waste, dye methyl orange p.a., phosphate buffer, acetate buffer, pH indicators, pH meter, and aluminum sulfate.

2.3. Procedure

2.3.1. Preparation of pineapple leaf fibers pulp.

Added Ca (OH) 2 2.5% (w / v) of 150 mL to 20 grams Pineapple leaf fibers and soaked for three days. After washed with distilled water and put in a flat-bottom flask which had previously been filled with 300 ml of 17.5% NaOH (w/v), then refluxed for 4 hours. Once cool, pineapple leaf fibers are washed until it is free from NaOH, blended and molded into a pulp sheet and the pulp is then dried in an oven at 60 °C for 1 day.

2.3.2. Acetylation of cellulose pineapple leaf fiber[4]

Added 12 mL of glacial acetic acid to 5 grams Pulp that has been smoothed and stirred for 1 hour. After 1 hour the mixture was added 0.088 mL of concentrated sulfuric acid and 20 mL of glacial acetic acid and stirred again for 45 minutes. This mixture is cooled to a temperature of 18.3 °C then added 13.5 mL of acetic anhydride which has been cooled to a temperature of 15.6 °C and the mixture was added 0.612 mL of concentrated sulfuric acid with 20 mL of glacial acetic acid. The mixture is stirred for 20 hours until a solution is formed. The next stage is added 15 mL of 67% acetic acid dropwise over 1 hour while stirring at a temperature of 37.8 °C. The solution is left to stand for 20 hours. Furthermore, water is added while stirring until a precipitate is formed and allowed to stand for 10-15 minutes. The precipitate is filtered, then washed with water until neutral. The precipitate is then dried in an oven at a temperature of 50-60 °C.

2.3.3. Determination of Relative Molecular Weight of Cellulose Acetate[5]

Dissolved 0.15 grams of cellulose acetate in 100 mL acetone (called solution C). The resulting solution C, made into solution 0.2C; 0.4C; 0.6C; and 5 mL 0.8C Aceton put in viscometer and the flow time is measured at 25 °C. The same measurements performed on 0.2C; 0.4C; 0.6C; and 0.8C solution.

2.3.4 Preparation of Composite Membrane PS-PEG-CA[5]
Manufacture of membranes made by the method of phase inversion. The first stage began with the manufacture of the polymer solution CA 18% [w/v], PS (10% [w/v]), and PEG (10% [w/v]) in dichloromethane solvent: acetone (1:1). CA and SP polymer solution are mixed with a ratio of 9:1. Added 3 mL of PEG solution to each 100 mL CA: PS.The solution is stirred with a magnetic stirrer until it is homogeneous.Then the polymer solution is poured over a glass plate (18 × 18 cm^2) which has been given the duct tape on both sides to obtain the desired thickness, and then printed out by pressing and pushing the solution to obtain a thin layer. Furthermore, the polymer that sticks to the glass plate is left for 60 seconds to evaporate the solvent. Plate glass along the polymer is then soaked in the water to remove the polymer from the glass plate and eliminate PEG matrix trapped between CA and PS. PEG loss of the matrix leaving a cavity in the form of pores. Then, the membrane is soaked in a solution of sodium azide 1 ppm. This thin polymer is then used as a membrane.

2.3.5. Characterization of Composite Membrane PS-PEG-CA Flux[6]
Membrane samples are placed in a ultrafiltration cell. 150 mL of water put into the ultrafiltration cell and closed tightly, given the pressure of 2 kgf/cm^2. Flux value is determined as a function of time until they reached steady-state. Flux is expressed by the following equation :

$$J = \frac{V}{At}$$

J = fluks volume(L/m^2.hour)
V = perm ate volume (L)
e
A = surface area (m^2)
t = time (hour)

permeation or solution across the membrane accommodated at specified intervals within 10-minute intervals and its volume is measured. Measurements are made until a time constant is obtained. The same treatment is conducted to measure the flux value of waste by replacing water with sewage.

2.3.6. Measurement of Methyl Orange Concentration.
Measurement of methyl orange concentrations in the samples is done by measuring the absorbance using a UV-Vis spectrophotometer before it is being discharged into the membrane and once flowed into the membrane. The absorbance of the sample solution is measured under the same conditions with a standard solution that is at the maximum wavelength. The calculation of methyl orange dye level in the samples is done by substituting the absorbance of the sample as "y" on a regression equation of standard solutions. The content of methyl orange is the "x" obtained.

3. Results and Discussion

3.1. Relative molecular weight cellulose acetate
Measurement of relative molecular weight cellulose acetate aims to determine the physical characteristics of pineapple leaf fibers' cellulose acetate which is a basic ingredient in the manufacture of cellulose acetate membranes. Membranes with a high average relative molecular mass will have a denser membrane structure and stronger chemical bonding than the membrane with a small average relative molecular mass [6]. Relative molecular weight is determined using Ostwald viscometer, where the principle of this method is the measurement of viscosity by comparing the flow time of a polymer solution with various concentrations and pure solvent flows through two boundary markers capillary tube at the viscometer [7].Measurements were performed by comparing the viscosity of the pure solvent with cellulose acetate solution at various concentrations, namely 0.03; 0.06; 0.09; and 0.12 g / dL. Pure solvent used is acetone because it can dissolve cellulose acetate well at room temperature

[8].The higher the concentration of the solution of cellulose acetate then the longer the flow time of the solution in the viscometer. Relative molecular weight cellulose acetate based on the results of the study was 8.05 x 10^4 g / mol. where relative molecular weight to commercial cellulose acetate are 7.5 x 10^4 g / mol [9]. The amount of the molecular weight of the cellulose acetate fibers is affected by the length of the cellulose material used as a basis for making membranes.

3.2. Composite membrane PS-PEG-CA Pineapple leaf Fibers

Composite means a blend of two or more materials to produce new materials with characteristics that more than origin. Manufacture of composite membrane PS-PEG-CA is done by phase inversion method. Phase inversion is a process of changing the form of the polymer from a liquid into a solid phase under controlled conditions. Cellulose acetate used in this study is the result of the synthesis of pineapple leaf fibers with acetyl level of 37.31%, soluble in acetone. The amount of the solvent effect on the acetyl content that will be used in the production of membrane [10].

3.3. Flux Membran

Flux measurements performed by flowing water into the filtration cells of dead-end system pressure 2 kgf/cm^2. Before measuring the flux values then firstly be compacted by passing distilled water on a membrane for 30 minutes. Compacting is done for conditioning the membrane so that the pores is equilibrium and constant flux data obtained. Compaction [1] is a mechanical change in the structure of the polymer membrane that occurs due to the thrust (pressure). This causes the cellulose acetate structure becomes more compact, and the membrane pores docked so it impacts the value of flux.

Flux measurements is done at 10 minute intervals until it reaches a constant permeate volume. Water flux value comparison chart on the membrane CA and membrane PS-PEG-CA can be seen in Figure 1

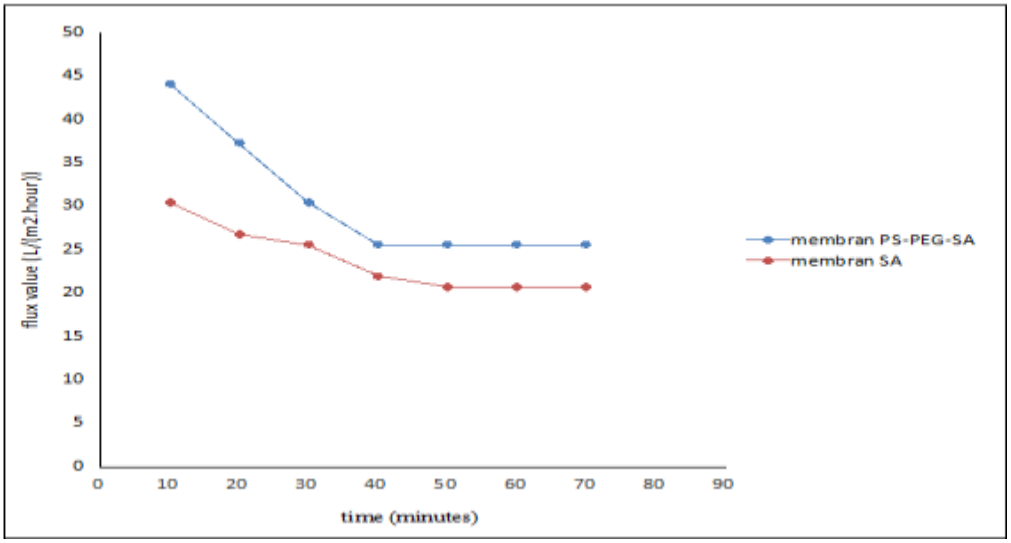

Figure 1. Curve of linkage between membrane water flux CA and PS-PEG-CA

Based on the chart above it shows that the longer membrane operation time, the flux value generated decreases. According [1], this is due to the occurrence of fouling, because the water used may still contain particles of the same size or larger than the pore size of the membrane, so that the particles will accumulate on the surface of the membrane. These conditions resulted in inhibition of the feed flow rate, so that the membrane's ability to parse the feed reduce. Based on the results of measurements using CA membrane and composite membrane PS-PEG-CA water flux values obtained successively at 20.74 L/(m^2.hour) and 25.62 L/(m^2.hour) Membrane water flux value PS-PEG-CA acquired is higher than the value of the water flux membranes CA. This is due to the addition of PEG. PEG is capable of forming pores in cellulose acetate membrane. The number of pores formed becomes

more and more uniform in size, thereby increasing the value of water flux as it flows permeate will be easier with the increasing number of pores in the membrane.

3.5. Methyl Orange Level

Composite membrane PS-PEG-CA from pineapple leaf fibers is used to lower the levels of methyl orange dye in batik waste. Batik waste to be used previously undertaken the process of coagulation-flocculation. Coagulation-flocculation occurs at the fast and slow mixer unit. These coagulation-flocculation process through three phases, the addition of a coagulant, and then stirring rapidly during 5 min with a speed of 1500 rpm and slow stirring at 1000 rpm for 15 minutes. Rapid stirring serves to disperse the coagulant material in the water, resulting in sufficient contact between the coagulant with the particles suspended and will form a small flocs. Slow stirring serves to help establish a larger flocs so it will be easier to settle. The flocs formed then left to settle for 30 minutes. Coagulant used in this study is alum or $Al_2(SO_4)_3$.

Based on the results obtained by the equation y = 0,08415x + r2 of 0.0011 to 0.9998. The decreasing percentage methyl orange level of batik waste using CA membranes and membrane PS-PEG-CA from pineapple leaf fibers can be seen in Table 1.

Table 1. Decreasing Percentage of Methyl Orange levels On Batik Waste

Membrane	*Methyl Orange* Level Before Filtration	*Methyl Orange* Level After Filtration	Decreasing Percentage of *Methyl Orange* Level
Membrane CA	45.27 mg/L	17.52 mg/L	61.29 %
Membrane PS-PEG-CA	45.27 mg/L	12.885 mg/L	71.53 %

Based on Table 1 it can be seen that a decline in the concentration of methyl orange after filtration. Decreasing concentration of this methyl orange happens because methyl orange dye has a large molecular size so that when the filtration process the dye will be retained in the membrane surface and the resulting concentration of the dye will be reduced. The percentage decrease in the levels of methyl orange using CA membranes and membrane PS-PEG-CA amounted to 61.29% and 71.53%. Membrane PS-PEG-CA can degrade methyl orange dye is greater than the membrane CA. This is because the membrane PS-PEG-CA has a molecular structure that is denser than the membrane so that the macromolecules particles will be retained on the membrane [1].From the results of this study concluded that the composite membrane PS-PEG-CA from pineapple leaf fiber can degrade methyl orange dye in batik waste.

4. Conclusion

Based on the research described, it can be concluded that the composite membrane PS-PEG-CA from pineapple leaf fibers has a flux value of 25.62 L/(m^2.hour) with a relative molecular weight 8.05 x 10^4 g/mol and acetyl levels 37.31%. The concentration of methyl orange on batik waste before and after flow through the membrane PS-PEG-CA of fiber pineapple leaf is equal to 9.054 mg/L and 2.577 mg/L, so the percentage decrease in the levels of methyl orange on batik waste using a membrane PS-PEG-CA of pineapple leaf fiber is equal to 71.53%.

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