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CHARACTERISTICS OF CELLULOSE ACETATE COMPOSITE MEMBRANES (CA/CS, CA/PVA, CA/PEG) AS CU(II) METAL ION FILTRATION MEMBRANES

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Abstract

Industrial development in Indonesia has caused increased pollution, including water pollution by heavy metals, one of which is the metal ion Cu(II). Cellulose acetate composite membranes have been widely used to overcome the problem of Cu(II) metal ion content in water, however, studies on the performance of cellulose acetate membranes with various types of chitosan, polyvinyl alcohol (PVA) and polyethylene glycol (PEG) composites have not been widely reported. This research aims to analyze the characteristics of cellulose acetate composite membranes with chitosan, PEG, and PVA using FTIR and SEM and to determine the performance of these cellulose acetate composite membranes in filtering Cu(II) metal from the resulting rejection values. The membrane was made using the phase inversion method and the composite membrane was made using the dip-coating method. The results of characterization using FTIR showed that there were no new peaks in all cellulose acetate composites, so there were only physical interactions in the composites. SEM analysis shows that the surface of the composite membrane is more irregular and the porosity increases. The performance of the composite membrane in filtering Cu(II) metal is better than the pure cellulose acetate membrane.

INTRODUCTION

The rapid development of industry in Indonesia produces many useful products and also produces waste that can cause pollution, especially water pollution [1]. One of the water pollution~~s~~ that has the potential to endanger human life is heavy metal pollution [2]. Heavy metal pollution is becoming a serious problem with the increase in industries that use metal and produce metal waste. Industries that have the potential to produce heavy metal pollutants are industries that use heavy metals in their production processes. The type of industry with the largest amount and the greatest potential for removing heavy metals is the textile and metal plating industries (78% and 5% of the total industry respectively) [3].

Arsenic (As), cadmium (Cd), chromium (Cr), Copper (Cu), lead (Pb), and nickel (Ni) are known as heavy metals that have strong carcinogenic properties because these metals can disrupt tumor suppressor genes by damaging them. oxidative [4]. Heavy metals contained in water will have a very bad impact on ecology such as plants, animals, and microorganisms, and can have a carcinogenic impact on humans [4][5][6]. Heavy metals are dangerous pollutants in water because they can cause negative effects on human physiology and also ecological systems, especially in high enough concentrations. One of them is copper metal which can accumulate in the bodies of living creatures in waters. The metalloprotein form of Cu metal can redox react to form Cu^+ from Cu^{2+}, where Cu^+ ions resulting from redox reactions can influence the structure and function of proteins in living things [7]. Heavy metals have many negative impacts on living creatures so they must be removed from the water.

One method that can be used to overcome the problem of heavy metals in water is the use of filtration membranes. The use of membranes for the filtration process of heavy metals in water is considered more profitable because it only requires low energy, is simple, and is environmentally friendly [8] [9]. Separation using a membrane depends on the quality of the membrane and the pores formed in the membrane. The membrane manufacturing process is often carried out using polymers such as cellulose, cellulose acetate, polyamide, polysulfide, and other synthetic polymers [10].

Cellulose acetate is a polymer membrane used for separating solutions and is widely used as a Reverse Osmosis membrane material. and Ultrafiltration [6]. Cellulose acetate comes from nature, is environmentally friendly, easily degraded, has good hydrophilic properties, and can maintain high mechanical strength during the manufacturing process, making cellulose acetate widely used as a raw material for membranes. However, cellulose acetate still has shortcomings, namely the lack of functional groups in the main polymer chain which function to increase membrane efficiency [12].

To produce a membrane that can carry out ideal separation, modification of the cellulose acetate membrane is very necessary. One modification that can be made is to make a cellulose acetate composite membrane by adding a selective layer on the surface of the membrane [12]. Composites that are widely used as cellulose acetate membrane composites include chitosan [13], PVA [14] and PEG [15]. The addition of chitosan, PVA, and PEG to cellulose acetate membranes can increase the hydrophilic properties of the membrane because there are additional functional groups (amino and hydroxyl groups) in the membrane [13] [14] [15]. So, the use of cellulose acetate-chitosan (CA/CS), cellulose acetate-PVA (CA/PVA), and cellulose acetate-PEG (CA/PEG) composite membranes for filtration of heavy metals in water is quite promising as a way to overcome metal levels. weight contained in water.

Much research has been carried out on cellulose acetate/chitosan composite membranes. In previous research, hollow fiber membranes were made using cellulose acetate and chitosan with varying concentrations, successfully producing membranes with a homogeneous structure [16]. In another study, a cellulose acetate/chitosan composite membrane was made using 15% cellulose acetate, 0.5% chitosan, and 0.25% glutaraldehyde as a cross-linking agent to produce a nanofiltration membrane which was used for filtration of copper metal [17].

PVA has a smooth coating film with good hydrophilicity and chemical stability. Apart from that, PVA also has chlorine resistance characteristics as well as high tensile strength and flexibility. To overcome this, a membrane was made that has an asymmetrical structure containing a thin layer but is still tightly supported by porous membrane material [14].

The addition of PEG can improve the mechanical properties of polymers and can influence the morphological structure and membrane performance. The addition of PEG additives can also increase the flux and hydrophilicity of the membrane. PEG was chosen because it has stable properties.

The use of CS, PVA, and PEG as composites in cellulose acetate membranes will affect the properties of the resulting membrane. No studies on this matter have been reported before. So, in this research, we identified the influence of the use of cellulose acetate composite on the properties of the synthesized membrane.

EXPERIMENT

This research was carried out for 6 months at the Chemistry Laboratory at UIN Sunan Gunung Djati Bandung. Some tests were carried out at other agencies.

Material

The tools used in this research were a 50 mL beaker, 250 mL beaker, 500 mL beaker, spatula, analytical balance, magnetic stirrer, hot plate, 250 mL Erlenmeyer flask, vacuum Erlenmeyer flask, 25 mL measuring flask, 50 mL measuring flask. mL, measuring flask 250 mL, measuring flask 1000 mL, measuring cup 10 mL, measuring cup 50 mL, measuring cup 250 mL, glass container, funnel, Buchner funnel 40 mm, dropper pipette, volumetric pipette 0.5 mL, volumetric pipette 1 mL, 2 mL volumetric pipette, 5 mL volumetric pipette, 10 mL volumetric pipette, and vacuum.

The materials used in this research were cellulose acetate (technical), PVA (technical), PEG (technical), N-methyl 2-pyrrolidone (NMP) (p.a.), chitosan (technical), acetic acid (technical), glutaraldehyde (p.a.), ethanol (technical), n-hexane (technical), $Cu(NO_3)_2$ stock solution, $CuSO_4.5H_2O$, distilled water, aqua DM, and filter paper.

Instrumentation

The instrumentation used in this research is Scanning Electron Microscope (SEM) to analyze membrane morphology, Fourier Transform Infra Red (FTIR) to analyze membrane structure, and Atomic Absorption spectrophotometer (AAS) 240FS Agilent Technologies.

Procedure

In this research, several procedural stages were carried out, namely, the manufacture of cellulose acetate membranes using the phase inversion technique, the manufacture of cellulose acetate/chitosan composite membranes, and the application of composite membranes in the Cu(II) metal ion filtration process.

Synthesis of Cellulose Acetate Composite Membranes (CA/PVA, CA/PEG, CA/CS)

The cellulose acetate (CA) solid was weighed at 15.0023 g, then added gradually into 82.5 mL of N-methyl 2-pyrrolidone (NMP) solvent which was stirred using a magnetic stirrer until all the CA solid was completely dissolved and formed a homogeneous solution. The CA dope solution that has been formed is left until all the bubbles disappear. After that, 10 mL of the CA dope solution was poured onto a glass plate that had been lined and leveled using a stir bar. The flat dope solution is then put into a coagulation bath containing aqua DM for the membrane formation coagulation process. After the coagulation process is complete, the formed CA membrane is removed and dried.

CS composite membranes were made using the dip-coating method, while CA/PVA and CA/PEG composite membranes were made using the phase inversion method with composite compositions of 2.5%, 5%, and 7.5%. Then the resulting composite membrane was characterized using FTIR to determine the functional groups contained in the membrane before and after being composited. Characterization using SEM was carried out on the composition that had optimum Cu (II) filtration performance.

Performance Test of Cellulose Acetate Composite Membranes (CA/PVA, CA/PEG, CA/CS)

The Cu(II) metal ion filtration process using CA/CS, CA/PVA, and CA/PEG composite membranes is carried out by cutting the membrane according to the size of the Buchner funnel to be used. In the next process, the composite membrane is placed in a Buchner funnel, then 5 mL of 10 ppm Copper Sulphate Pentahydrate ($CuSO_4.5H_2O$) solution is passed through the membrane and the filtration process is carried out. The permeate solution from the filtration process is collected and then analysed using AAS. Next, the composite membrane that has the best performance is subjected to surface analysis using SEM.

RESULT AND DISCUSSION

FTIR Analysis

Analysis using FTIR is carried out to provide information in the form of functional groups contained in a compound. The detected functional groups will form peaks in the resulting spectrum. The spectrum of analysis results of cellulose acetate membranes and their composite membranes with chitosan, PVA, and PEG is shown in **Figure 1**.

The results of characterization using FTIR show the presence of typical cellulose acetate groups, namely the C=O group at a wave number of 1755 cm^{-1} and the C-O ester group at a wave number. 1159 cm-1, and there was the addition of N-H groups at wave numbers 3487 cm^{-1} and 1560 cm^{-1} which came from chitosan [16]. If you look at the FTIR spectrum between the pure cellulose acetate membrane spectrum and the composite, no new peaks appear indicating the existence of a bond between cellulose acetate and chitosan, PEG, and PVA, only a shift and change in the intensity of the peak at around 1755 cm^{-1} which is the peak C=O and OH peak at absorption 3570-3200 cm^{-1}. In chitosan, there is an N-H peak that has an absorption at a wave number close to OH so that it can coincide and increase the peak intensity. Thus, in composite membranes, only physical interactions occur in the form of hydrogen interactions between cellulose acetate and chitosan, PVA, and PEG [19] [20].

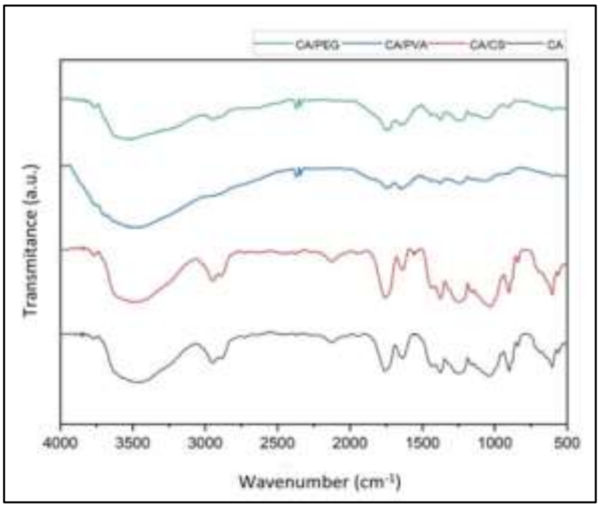

Figure 1. FTIR Spectrum.

Membrane surface morphology analysis using SEM

You can see in **Figure 2** the results of SEM analysis of the cellulose acetate membrane before and after being composited. It can be seen that the cellulose acetate membrane before being composited looks homogeneous and dense with almost no visible pores. After being composited with chitosan, the membrane surface was seen to be more irregular and had larger pores, as well as when composited with PVA and PEG.

The pores formed in the cellulose acetate membrane after being composited cause the rejection value of the membrane to be greater than that of the pure cellulose acetate membrane because the flux value increases so that the membrane's flow capacity becomes greater. It can also be seen that the pores formed in the cellulose acetate membrane composited with PVA have larger pores compared to other composite membranes, this causes the CA/PVA membrane to have a greater rejection value.

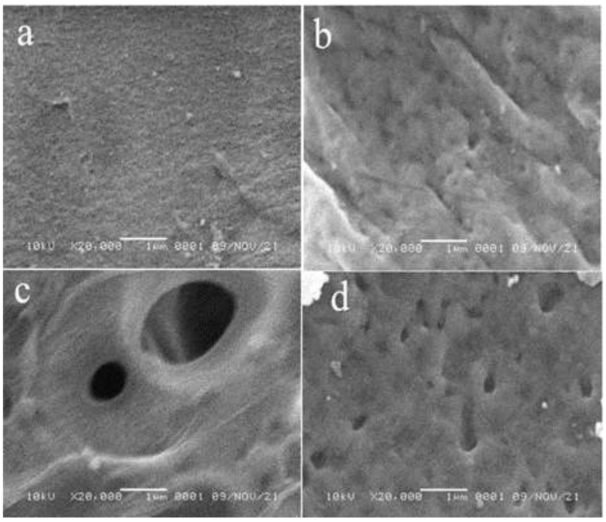

Figure 2. Membrane surface morphology (a) CA membrane (b) CA/CS membrane (d)CA/PEG membrane.

Composite Membrane Performance

The rejection value of each membrane is shown in **Table 1**. From the results of Cu(II) metal filtration, it is known that chitosan, PVA, and PEG affect the rejection value of the membrane. The addition of chitosan, PVA, and PEG in cellulose acetate membranes can increase the membrane rejection value. This occurs because the addition of chitosan, PVA, and PEG forms a layer with more pores on the membrane surface [20]. The size of the Cu^{2+} metal ion is 87 pm, and the size of the metal ion is larger than the membrane pores formed so that the Cu^{2+} metal ion is retained on the membrane surface. However, the resulting rejection value is still relatively small, this is due to the non-uniform size of the membrane pores, which allows Cu^{2+} metal ions to still escape and be present in the filtrate.

The concentration of chitosan, PVA, and PEG added to the membrane can also affect the rejection value in Cu(II) metal filtration. The rejection value increased along with the added concentration of chitosan, PVA, and PEG, and decreased again after reaching the optimum limit. The rejection value of pure cellulose acetate membrane is 15.41%, the CA/CS composite membrane with 5% chitosan composition has a rejection value of 31.55%, the optimum CA/PVA composite membrane has a PVA composition of 2.5% with a rejection value of 74.10 % while the CA/PEG composite membrane is optimum at a PEG composition of 2.5% with a rejection value of 41.21%. Thus, the performance of the cellulose acetate composite membrane in filtering Cu(II) metal is better than the pure cellulose acetate membrane. This is because the surface of the composite membrane has a surface layer with more pores so that more Cu(II) metal ions are retained.

Table 1. Cellulose acetate composite membrane rejection results.

Composition	Rejection Results		
	CA/CS	CA/PVA	CA/PEG
0%	15,41%	15,41%	15,41%
2,5%	27,60%	74,10%	41,21%
5%	31,55%	62,40%	38,15%
7,5%	-	44,20%	36,53%

Based on the data in **Table 1** we can see that addition of chitosan, PVA, and PEG composites in cellulose acetate has an optimum composition limit. It’s because increasing the concentration of the composite causes the membrane to tend to be inhomogeneous so that the formation of pores becomes more irregular, resulting in a decrease in the rejection value.

CONCLUSION

Based on functional group analysis, compared to non-composited membranes, composite cellulose membranes do not form new functional groups. So the interactions that occur in the formation of composites are only physical interactions. The surface structure of the composite membrane is more irregular, but more pores are formed. This results in the performance of the cellulose acetate composite membrane in filtering Cu(II) metal ions better than the pure cellulose acetate membrane. This can be seen from the increased rejection of Cu(II) metal ions. The rejection value of pure cellulose acetate membrane is 15.41%, the CA/CS composite membrane with 5% chitosan composition has a rejection value of 31.55%, the optimum CA/PVA composite membrane has a PVA composition of 2.5% with a rejection value of 74.10 % while the CA/PEG composite membrane is optimum at a PEG composition of 2.5% with a rejection value of 41.21%.

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