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Water hyacinth cellulose-based membrane for adsorption of liquid waste dyes and chromium

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Abstract. Water hyacinth (*Eichornia crassipes*) is a weed in aquatic area whose trunk contains a lot of cellulose. Cellulose contained can be used as dyes adsorbent in a form of composite membrane. This study aims to investigate the capacity of water hyacinth cellulose-based membrane to adsorb dye and Chromium (Cr) contained in liquid. The process of membrane fabrication begins with isolation of water hyacinth cellulose. The isolated cellulose powder was used to make the membrane by mixing it with polyvinyl alcohol-polyethylene glycol (PVA-PEG) with various compositions. The morphology of membrane surface was analyzed using CCD microscope. The analysis using Ultraviolet Visible Spectroscopy (UV-Vis) and Atomic Absorption Spectroscopy (AAS) indicate that the membrane with composition ratio of cellulose: PVA: PEG of 6.5: 2.5: 1 adsorb Cr up to 38.75%.

1. Introduction

Indigosol with IR code is one of dye used in production process in fabric manufacturer. To enhance the dye's capacity to adhere to the fabric, indigosol dyes are first activated using acid and nitrite solutions. The activation process results in Cr residue in manufacturing waste. Therefore, effort should be made to reduce the dyes and Cr from the waste before it is disposed to the environment. The common method in reducing dyes and heavy metal ions in liquid and waste water treatment is using membrane-bioreactor. However, membrane-bioreactor is expensive and requires complicated process. Various types of membranes have been investigated to give alternative solution for waste water treatment such as pressure-driven membrane [1], nanoadsorbents based on conducting polymer nanocomposites [2], composite graphene oxide membrane [3], thin film nanocomposite (TFN) membrane [4] nanofiltration [5] and hydrophilic nanoporous ion-exchange barrier membranes [6].

Other alternative for dyes removal is using organic membrane. Various organic membranes have been fabricated using pineapple leaf [7], banana stem [8], pandan duri leaves [9], and polymeric membrane cellulose-chitosan [10]. As stated in other researches mentioned above, the main material of organic membrane is cellulose. Therefore, organic material with high cellulose content is desired to be used as organic membrane. Priya et al [11] showed that water hyacinth (*Eichornia crassipes*) contain 30-50% of cellulose. Water hyacinth has been used for various application such is Carboxymethyl Cellulose (CMC) [12] and Cellulose Acetate Membrane-PVC [13]. In this work, water hyacinth was used as cellulose source for organic membrane for dyes and Cr removal application.

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2. Research Methods

The equipment used in this research are a set of extraction tools, filter paper, beaker glass, oven, petri dish, CCD balance, magnetic stirrer, 0.1 mm^2 sized filter, FTIR, UV-Vis and AAS. Meanwhile, the materials used are $NaClO_2$, NaOH, toluene, 96% alcohol, PVA, PEG, distillated water, water hyacinth sticks, and dyes liquid waste.

2.1 Delignification of Water Hyacinth

The fabrication of composite membranes begins with the fabrication of cellulose powders. First, water hyacinth was cleaned, dried and powdered with a 0.1 mm^2 sieve. To investigate the chemical composition of the powder, the cellulose powder was characterized using *Fourier Transform Infra Red* (FTIR) Spectroscopy method. The chemical compound was determined by comparing the peak of the obtained FTIR spectrum with FTIR table.

The content of wax on the water hyacinth was removed by extraction process. The extraction process uses a mixture of 96% toluene and alcohol with a volume ratio of 2:1. Lignin was removed by bleaching process using 1% $NaClO_2$ solution at temperature of 80 ℃ for one hour. Meanwhile, the hemicellulose was removed by using 17.5% w/v NaOH solution for one hour at room temperature. After hemicellulose was removed, the obtained cellulose was then washed with aquades and 96% alcohol. The obtained cellulose powder was also characterized for its chemical compound composition using FTIR.

2.2 Preparation of Composite Membrane

The membrane was fabricated by mixing the water hyacinth cellulose powder with PVA and PEG with various compositions as shown in Table 1. The mixture was put on a glass plate forming a thin layer and then dried in a room temperature for an hour. After dry, the membranes were then washed with 1% NaOH and were dried in a room temperature to remove residual moisture content.

Table 1. Variation of cellulose membrane composition

Membrane	Cellulose (%b/b)	PVA (%b/b)	PEG (%b/b)
1	5.5	3.5	1
2	6	3	1
3	6.5	2.5	1

2.2.1 Morphological Characterization of Composite Membrane

The morphological (surface) membrane structure was characterized using a CCD (Charge Coupled Device) MS-804 Microscope. CCD microscope produces a morphological image of the membrane surface. The morphology of the membrane surface shows the pore size of the membrane that has been made.

2.2.2 Characterization of Membrane Adsorption to Dyes and Cromium

The membrane adsorption characterization was done by filtering the liquid waste containing Indigosol IR code-dyes using the fabricated membrane. The filtered liquid was then investigated using UV-Vis. For comparison purposes, the un-filtered liquid was also characterized.

The decrease of Cr content in waste water was determined through AAS test. The result of initial AAS test before the adsorption process showed Cr metal content of 5.349 mg / L. This Cr content of metal will certainly pollute the environment if it is discharged directly prior to adsorption.

3. Results and Discussion

3.1 Characterization of Membrane Adsorption to Dyes and Cromium

The result of FTIR spectroscopy of the water hyacinth powder and the cellulose powder are shown in Figure 1 and Figure 2, respectively.

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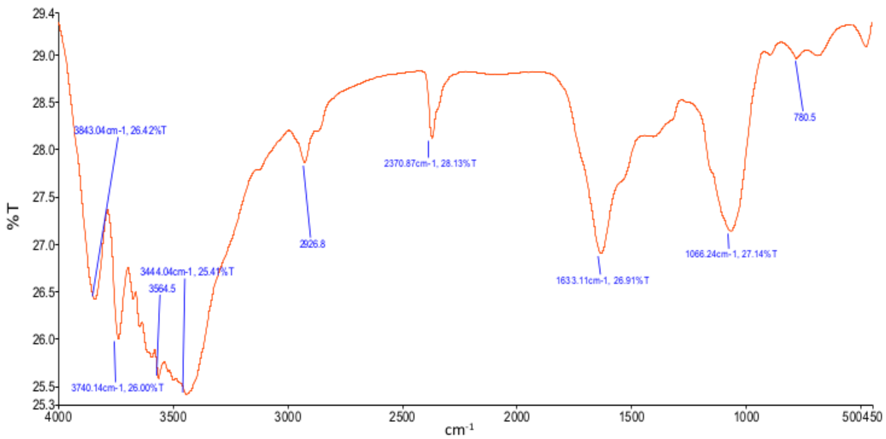


Figure 1. FTIR spectra from water hyacinth powder before the cellulose isolation process.

The main cellulose functional are represented by the bound of O-H, C-H and C-O glycosidic on a material [13]. Figure 1 shows that the peak at 2348.03 cm^{-1} is indicating the C-H, the peak at 3700 - 3800 cm^{-1} is indicating the formation of several O-H in the hydrogen bounding of hydroxyl and oxygen atoms of other hydroxyl groups on the cellulose polymer chain. The peak at 1651.79 cm^{-1} indicates of a water-absorption fiber-OH and the peak at 1064.51 cm^{-1} showing the C-O strain. Meanwhile, the peak at 806.10 cm^{-1} shows the absorption peak due to the C-H vibration. Therefore, it can be concluded that the water hyacinth powder contains cellulose as shown by the FTIR spectrum. However, there are also exist other chemical compounds which are indicated by the peaks at wave number of 4000-3500.

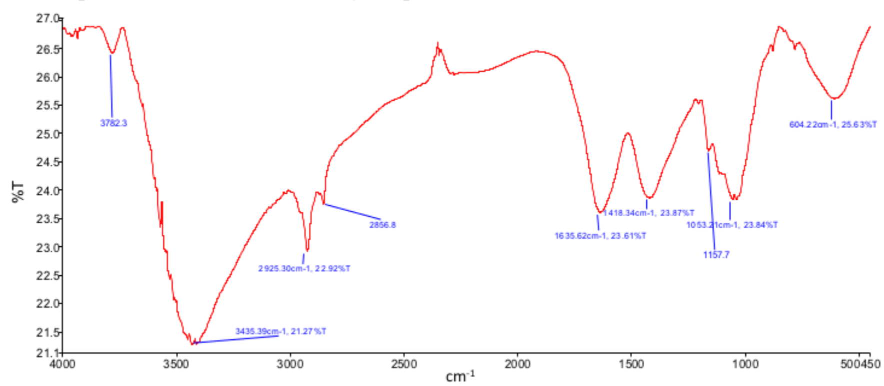
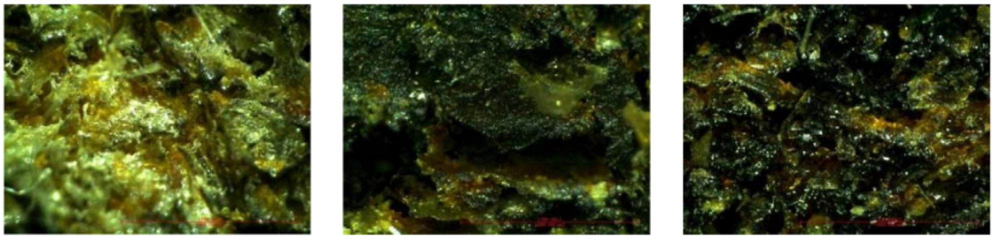


Figure 2. FTIR spectra from cellulose powder after the cellulose isolation process.

Figure 2 shows that the spectrum of the cellulose powder has peaks at 1418.34 cm^{-1}, 1635.62 cm^{-1}, 2925.3 cm^{-1}, 3444.04 cm^{-1} and 3435.39 cm^{-1} which indicates –CH, C-O, C-H, OH, and –O-H, respectively. It is also shown that the peaks at wave number of 4000-3500 no longer appear. It means that the powder only consist of cellulose.

3.2 Surface Morphology of Membrane Cellulose Water Hyacinth

The surface morphology of the membranes are shown in Figure 3. It is shown that as PVA-PEG composition increases, the surface is more covered by PVA-PEG.



(a) (b) (c)

Figure 3. Membrane surface with composition variation a) membrane 1, b) membrane 2, and c) membrane 3.

3.3 Characterization of Membrane Adsorption to Dyes and Cromium

Figure 4 shows the UV-Vis results of unfiltered liquid (membrane 0), filtered liquid using membrane 1, membrane 2 and membrane 3, respectively.

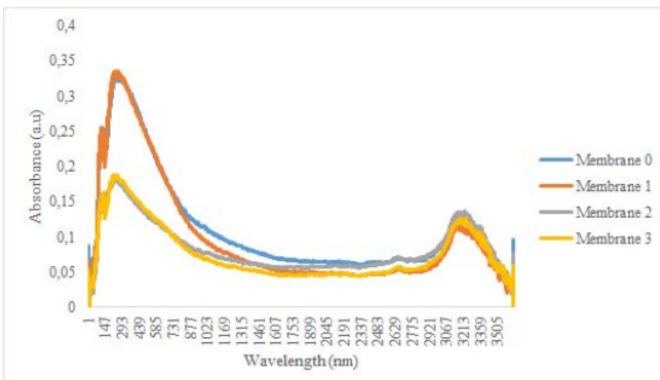


Figure 4. UV-Vis results of filtered liquid through membrane 1, 2 and 3 and unfiltered liquid.

Based on Figure 4 it can be seen that the dye concentration decrease after filtration using cellulose membrane as indicated by the decrease of the absorbance peak. The decreased of the dye levels occurs since the pores size of the membrane is lower than the indigosol dye particles size. Therefore, the dye was maintained on the surface of the membrane. It is also shown that the membrane with highest cellulose composition, which is membrane 3, has the highest adsorption capacity.

The Cr content in the filtered liquid waste was obtained from the AAS analysis as shown in Table 2. It can be seen that the Cr concentration is decreased after the liquid filtered using the membrane. It is also shown that membrane 3 has the highest capacity to reduce the Cr concentration. Compared to other composite membranes, such as polyethylene glycol-polystyrene-cellulose acetate from pineapple [7], banana stem [8] and pandan duri leaves [9], the fabricated water hyacinth membrane has lower adsorption capacity. However, the proposed water hyacinth membrane provides short fabrication time and simple fabrication process without the need for further cellulose treatment such as acetylation [7].

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Table 2. AAS results of the liquid waste before and after filtration using water hyacinth membrane

Membrane	Cr Metal Metals Before Filtration	Cr Metal Content After Filtration	Percentage of Waste Dye Decrease
Membrane 1	5.439 mg/L	3.901 mg/L	28.27%
Membrane 2	5.439 mg/L	3.610 mg/L	33.62%
Membrane 3	5.439 mg/L	3.331 mg/L	38.75%

4. Conclusion

Based on the results, it can be concluded that the water hyacinth membrane has a good adsorption to Indigosol IR and Cr. The optimum composition of the membrane is consisting of 6.5: 2.5: 1 of cellulose: PVA: PEG with Cr adsorption of 38.75%. Further improvement of Cr adsorption can be done by combining water hyacinth cellulose with cellulose from other plants such as pineapple and banana stems.

Acknowledgements

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