

MINISTRY OF EDUCATION AND TRAINING  
QUY NHON UNIVERSITY

*DANG THI TO NU*

**PREPARATION AND CHARACTERIZATION OF  
NATURAL RESOURCES-BASED MATERIALS,  
AIMING AT CONVERTING FLOOD WATER  
INTO DRINKING/POTABLE WATER**

Speciality: Physical and Theoretical Chemistry

Code: 9 44 01 19

ABSTRACT OF DISSERTATION

BINH DINH - 2021

The research was carried out at Quy Nhon University

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## INTRODUCTION

### 1. Motivation

Sustainable development has draw widespread attention in recent years. Environmentally friendly and biodegradable materials as well as renewable sources are prioritized for use and are the target of national and international scientists. Membrane technology offers various advantages such as low energy consumption, simple process, stable water quality, low maintenance cost, and scalability. Moreover, this technology allows to recover substances with small content in the input stream materials without a significant energy consumption. Particularly, this technology is considering as a clean or environmentally friendly technology because it utilizes abundant and non-toxic materials. Therefore, it is widely used to treat wastewater, remove impurities in drinking water to produce clean and ultra-clean water, remove organic contaminants and heavy metals, soften water, separate dyes, etc.

Lignocellulose biomass is an abundant natural source of cellulose. In particular, sugarcane bagasse is a common waste in tropical and subtropical regions. Cellulose is a very important biological polymer in nature, which is the main structural component of plant cell walls. The conversion of natural cellulose into its derivatives having high economic value has attracted considerable attention in the field of green and sustainable chemistry, and has stimulated the development of environmentally friendly technologies. Among the cellulose derivatives, cellulose acetate is the most important one due to its biodegradability, non-toxicity, low cost and being a renewable source. Hence, cellulose acetate is widely

used in the production of membranes, thin films, fibers, paints, plastics, cigarette filters, jackets and biomedical gadgets.

Cellulose acetate was one of the first polymeric membrane materials used for the water treatment. Hydrophilic cellulose acetate membranes have good fouling resistance and the utilization of these membranes is cost-effective and environmentally friendly. Some publications have reported that the synthesis of cellulose acetate from sugarcane bagasse cellulose is applied to fabricate membranes for desalination, gas separation or drug separation. However, the solvents such as chloroform and dichloromethane used to make membranes from sugarcane bagasse cellulose are mostly toxic to human health and the environment. Thus, it is highly desirable to replace toxic solvents commonly used in polymer preparations such as dimethylacetamide (DMAc), N-dimethylformamide (DMF), chloroform and dichloromethane with greener solvents. Like the common solvents used in the membrane synthesis, DMSO (dimethyl sulfoxide) is a polar organic solvent which is extracted from lignin, a plant binder, or is prepared by the oxidation of dimethyl sulfide. DMSO has very low toxicity to human and animal health, and is also biodegradable, yielding non-toxic products. Therefore, DMSO is considered as a greener alternative for the membrane synthesis from cellulose acetate polymers.

Coagulation is the most widely used and successful physicochemical pretreatment process due to its low cost and relatively easy operation. Coagulation combined with ultrafiltration (UF) is a promising process for the removal of contaminants [244], maintaining high filtration membrane performance and preventing

the formation of post-disinfection byproducts. Up to now, flocculants and coagulants such as aluminum salts and synthetic polymers have been widely used in water treatment systems. However, many recent studies have mentioned some problems with applying these chemicals, such as Alzheimer's disease in the elderly linked to aluminum residues in drinking water. And many harmful synthetic polymers have been banned in Japan and Switzerland. Besides, in rural areas of Viet Nam, the cost of water treatment when using aluminum salt is still significant high for many households, which is the main reason why clean water does not reach everyone. Viet Nam is located in the tropical monsoon climate, one of the five hurricanes of the Asia-Pacific region, and frequently faces various natural disasters. In particular, the central region of Vietnam is the region that often bears the heaviest consequences. One of the issues of significant concern after floods and storms is that the water environment is heavily polluted due to the destruction of wastewater treatment works of industrial zones, and industrial wastewater drainage systems. Therefore, the untreated or incompletely treated wastewater, and feces, garbage is directly overflowed into the environment. Pollution of surface water in flood areas is mainly caused by suspended sediments, organic compounds, heavy metals, and pathogenic microorganisms. According to the "Guideline for water treatment and environmental sanitation in the stormy season" and the "Manual for handling cholera outbreaks" issued by the Ministry of Health, the most commonly used disinfectant is chlorine compounds such as chloramine B (in powder or tablet form), Aquatab<sup>67</sup> tablets, in addition, less commonly used calcium

hypochlorite powder and sodium hypochlorite solution. However, the substances mentioned are all imported products. Sometimes, they are not available when needed. According to these documents, using chloramine B with a content of 0.5% to treat environmental pollution requires very high costs. Moreover, chloramine B contains benzene - should not be used to disinfect food or used in high concentrations for drinking water - due to chemical residues that are not beneficial to human health. Nowadays, using alum and chloramine B to purify and disinfect contaminated water is widely used. However, the treated water is not safe for drinking in daily life. Heavy metals are thoroughly unremoved out of treated water. In addition, the use of chlorine to disinfect contaminated water causes discomfort for drinkers. Due to the treated water exists a lot of residual chlorines, long-term exposure users are likely to experience clinical respiratory symptoms such as cough, shortness of breath, chest pain, pulmonary edema, etc. Therefore, the choice of environmentally friendly coagulants for purifying and disinfecting the polluted water, and especially unaffacting human health, is interested in many scientists. Natural coagulants are of great interest to researchers because of their effectiveness. The main advantages of plant-based flocculants in water treatment are easy implementation, low cost, no need for pH adjustment of pre-treatment water, and no change in pH of treated water, easy biodegradable sediment. Some effective natural coagulants include *Moringa Oleifera* seed, okra, legume, corn, etc. Among all the natural coagulants, the *Moringa oleifera* seed is particularly interested in water treatment because of its role as both a coagulant and an antibacterial agent.

Chromium compounds have been widely used in the chemical industry, leather tanning, metallurgy, plating, mineral engineering, and many other manufacturing fields. However, improper discharge or disposal of Cr(VI)-containing wastes from such production facilities can lead to significant contamination of surface water, groundwater, and soil. This has fatal consequences on the environment, animals, and plants as it exerts carcinogenic, mutagenic, teratogenic effects and causes tissue damage. Chromium pollution is one of the top 10 most toxic pollution problems. Pb(II) is known as another common heavy metal ion with carcinogenic potential that is discharged into water sources from industrial wastewater. Therefore, the removal of Cr(VI) and Pb(II) from water sources for drinking water and domestic use is essential.

Therefore, we conducted the dissertation "**Preparation and characterization of natural resources-based materials, aiming at converting flood water into drinking/potable water**".

## 2. Research aim and objects

### 2.1. Research aim

To fabricate ultrafiltration/nanofiltration membranes via the phase inversion method using sugarcane bagasse (SB) as the starting material.

To modify prepared membranes by  $\text{MnO}_2$ , dopamine, and  $\text{Ag/MnO}_2$  for enhancing the separation performance.

To evaluate the efficiency of using *Moringa oleifera* seed as an ecological coagulant in the coagulation/flocculation/sedimentation followed by membrane filtration to obtain drinking/potable water.

### 2.2. Research objects

- Sugarcane bagasse, *Moringa Oleifera* seed
- Cellulose acetate; MnO<sub>2</sub>, Ag/MnO<sub>2</sub>, dopamine
- Water permeability, antifouling and antibacterial properties, the separation of ultrafiltration and loose nanofiltration membranes
- Optimal coagulation/flocculation/sedimentation conditions
- Turbidity, Cr(VI), Pb(II), *E. Coli* and *Coliforms*

### 3. Methodology

#### 3.1. Methods used for characterization of obtained materials:

XRD, FT-IR, SEM, TEM, HR-TEM, SEAD, BET, EDX, XPS, AFM and Contact angle.

#### 3.2. Methods used for qualitative and quantitative analyses: UV-Vis, ICP-OES.

### 4. Research Content

- Extraction of cellulose from sugarcane bagasse using the agents NaOH 5%, H<sub>2</sub>O<sub>2</sub> 5% and 2%.
- Synthesis of cellulose acetate by esterification method, and 2D nano  $\delta$ -MnO<sub>2</sub> by solid-phase calcination method. Loading Ag nanoparticle onto MnO<sub>2</sub>. Preparation of CAD, CADA, CA/MnO<sub>2</sub> ultrafiltration membranes from synthesized-cellulose acetate using DMSO solvent. Fabrication of CA/PDA, CA/PDA-Ag/MnO<sub>2</sub> membranes via polydopamine deposition and co-deposition using CuSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> as a trigger.
- Investigation of the permeability, antifouling, and surface properties of prepared membranes.
- Study on the adsorption isotherm, adsorption kinetics and the Pb(II), Cr(VI) removal performance in aqueous solution and floodwater samples of fabricated membranes;
- Research the optimal conditions for the coagulation process



according to the factors: time and speed stirring, and *Moringa Oleifera* extract.

- Study on the treatment efficiency of turbidity, COD, BOD, heavy metals, *E. Coli*, and *Coliforms* in flood water by the process of combining coagulation/flocculation/sedimentation of *Moringa oleifera* seed extract and prepared membranes.

#### 5. The new contributions of the dissertation

- Successfully prepared two-dimensional- $\delta$ - $\text{MnO}_2$  nanomaterials by solid-phase calcination method from the precursors  $\text{KMnO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  at 550 °C.

- This is the first time in Viet Nam, researching the preparation of asymmetric ultrafiltration membrane from sugarcane bagasse source in Binh Dinh with DMSO-environmentally friendly solvent by the non-solvent induced phase separation. The molecular weight cut-off (MWCO) of prepared membranes are less than 200 kDa. The permeation flux of prepared membranes significantly elevated while maintaining high protein (bovine serum albumin) retention.

- The CA/PDA-Ag/ $\text{MnO}_2$  loose nanofiltration membrane (MWCO: 1632 Da) was successfully prepared via the surface modification of cellulose acetate ultrafiltration membrane by the co-deposition of polydopamine and nano-Ag/ $\text{MnO}_2$  with  $\text{CuSO}_4/\text{H}_2\text{O}_2$  trigger. The modified membrane exhibits a high heavy metals rejection, good antifouling (FRR > 94%), and completely inhibits *E.Coli* and *Coliforms*.

#### 6. Scientific and practical significance of the dissertation

The results of the dissertation are of high scientific:

- The application of biomass and natural materials to treat pollutants, especially heavy metals in water for daily life is a current issue that has

drawn widespread attention of many scientists in the country and around the world in the field of green and sustainable chemistry, while stimulating the development of environmentally friendly technologies.

- Dimethyl Sulfoxide was used as a green solvent for the asymmetric membrane fabrication from synthesized - sugarcane bagasse cellulose acetate to replace the traditional highly toxic solvents.

- The quick, easy and effective co-deposition method introduced in this dissertation opens up the ability to keep nanomaterials stable with specific functional groups on the membrane surface for the purpose of separation.

Practical significance: It is possible to apply the method and materials to treat water contaminated with heavy metals, high turbidity water as well as floodwater to clean water for people's daily life.

## **Chapter I. LITERATURE REVIEW**

## **Chapter II- EXPERIMENTAL**

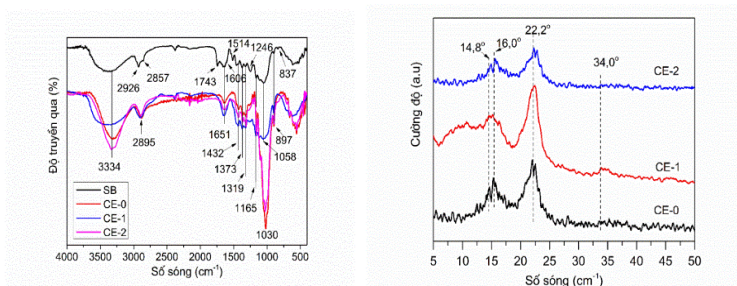
## **Chapter II. RESULTS AND DISCUSSION**

### **3.1. Characterization of sugarcane bagasse and cellulose**

**Table 3.1.** Chemical composition of sugarcane bagasse and cellulose

| Sample | Cellulose (%) | Hemicellulose (%) | Lignin (%)   | yield <sup>a</sup> (%) |
|--------|---------------|-------------------|--------------|------------------------|
| SB     | 48.58 ± 0.34  | 23.69 ± 0.26      | 24.12 ± 0.22 | -                      |
| CE-0   | 89.06 ± 0.42  | 7.11 ± 0.52       | 3.05 ± 0.43  | 64.58                  |
| CE-1   | 83.05 ± 0.31  | 8.25 ± 0.41       | 7.94 ± 0.38  | 60.21                  |
| CE-2   | 89.09 ± 0.37  | 7.11 ± 0.29       | 3.07 ± 0.44  | 66.09                  |

<sup>a</sup> Calculated by cellulose content (% wt)



**Figure 3.1.** FT-IR and XRD patterns of SB, CE-0, CE-1, and CE-2

**Table 3.2.** The crystallinity index of the cellulose samples

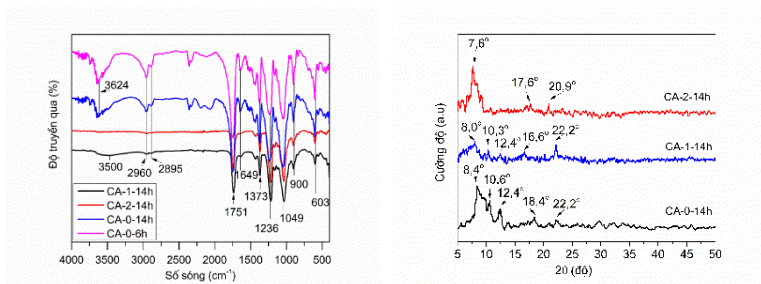
| Sample | $I_{200}$ (a.u) | $I_{am}$ (a.u) | CrI (%) |
|--------|-----------------|----------------|---------|
| CE-0   | 245.44          | 104.28         | 57.51   |
| CE-1   | 376.28          | 168.31         | 55.27   |
| CE-2   | 144.79          | 59.69          | 58.77   |

The above results show that the extracted celluloses have relatively high purity, almost completely removing the lignin component. The extracted celluloses have high crystallinity, guided by the one index (CrI) values obtained in Table 3.2. These are also consistent with the as-analyzed chemical composition results of these samples. Sample CE-2 has the highest crystallinity of the three samples. These results indicate the efficiency of the selected extraction process.

### 3.2. Cellulose acetate characterization

**Table 3.3.** The values of peak integration in  $^1\text{H}$ -NMR spectrum and DS

| Sample   | $I_{\text{acetyl}}$ (1.9 -2.2 ppm) | $I_{\text{H,AGU}}$ (3.5 – 5.2 ppm) | DS   |
|----------|------------------------------------|------------------------------------|------|
| CA-0-14h | 8.17                               | 7.33                               | 2.60 |
| CA-1-14h | 8.00                               | 6.99                               | 2.67 |
| CA-2-14h | 8.88                               | 7.37                               | 2.81 |



**Figure 3.2.** FT-IR and XRD patterns of CA-0-6h, CA-0-14h, CA-1-14h, and CA-2-14h

**Table 3.4.** Evaluation results of synthesized cellulose acetate materials

| Sample   | % AG  | (DS) <sup>b</sup> | $\eta$ (mL/g) | $M_w$ (g/mol) | Yield (%) <sup>a</sup> |
|----------|-------|-------------------|---------------|---------------|------------------------|
| CA-0-6h  | 37.20 | $2.20 \pm 0.02$   | 46.31         | 16756.4       | 33                     |
| CA-0-14h | 41.40 | $2.62 \pm 0.02$   | 102.30        | 43318.8       | 42                     |
| CA-1-14h | 41.68 | $2.65 \pm 0.01$   | 103.21        | 43760.8       | 45                     |
| CA-2-14h | 43.05 | $2.80 \pm 0.01$   | 112.81        | 48685.9       | 51                     |

<sup>a</sup> Increase weight of the sample

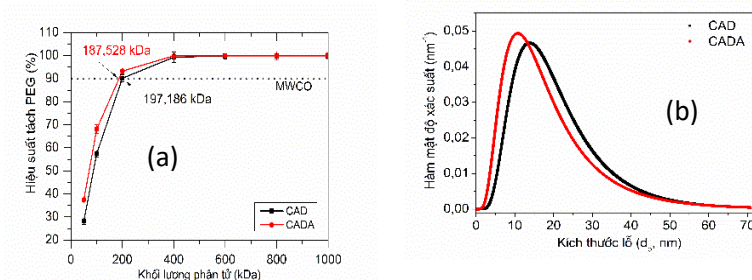
The data shown in Table 3.4 revealed that DS values determined by the titration method also consistent with ones obtained from <sup>1</sup>H-NMR.

**Conclusion:** The results of determining DS value, average molecular weight, and XRD analysis of cellulose acetate synthesized from three samples CE-0, CE-1, and CE-2, we realized that CE-0 and CE- 1

yielded cellulose acetate products with nearly similar DS values and the same crystal structure as triacetate II. In contrast, CE-2 produced triacetate I. CE-0 (89% cellulose) was obtained from hydrolysis in  $\text{H}_2\text{SO}_4$  10.0% to separate hemicellulose while CE-1 without  $\text{H}_2\text{SO}_4$ , the acetate products obtained under the same synthesis conditions are similar results which could be because the  $\text{H}_2\text{O}_2$  5% used in the bleaching step removed the guaiacyl from the CE-0 and CE-1 samples. Therefore, in the extraction process, the most critical steps for separating lignin are the alkaline treatment and bleaching with  $\text{H}_2\text{O}_2$  in the pH = 12 environment.

### 3.3. Characterization of CAD and CADA asymmetrical membranes

The fabricated membranes have been characterized by surface and cross-sectional SEM, which indicate an asymmetric structure for prepared membranes. In addition, AFM, water content, water flux, and antifouling were also conducted.



**Figure 3.3.** MWCOs (a) and pore size distribution curves (b) of CAD and CADA membrane

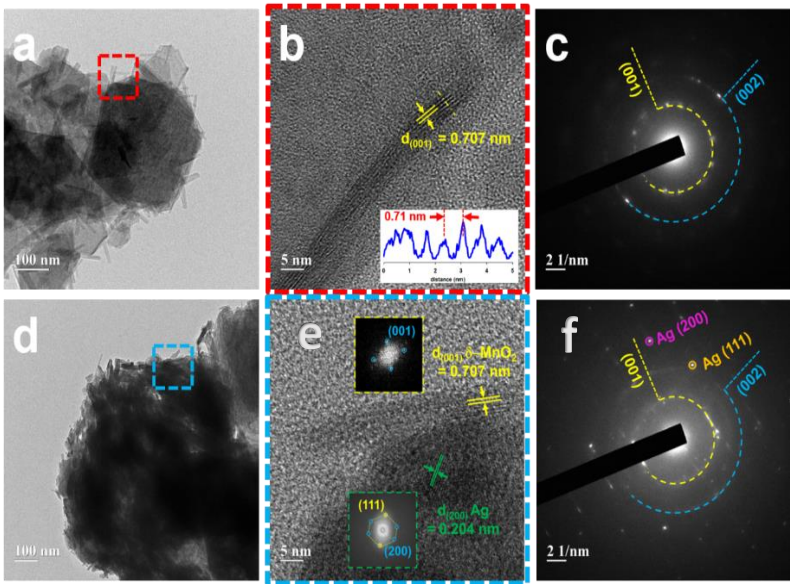
**Conclusion:** Asymmetric membranes were prepared using solvent DMSO and DMSO/Acetone, and synthesized cellulose acetate is

suitable for water treatment applications. They showed high permeability, good anti-fouling, and removal of water-soluble proteins and organic compounds with a molecular weight greater than 200 kDa.

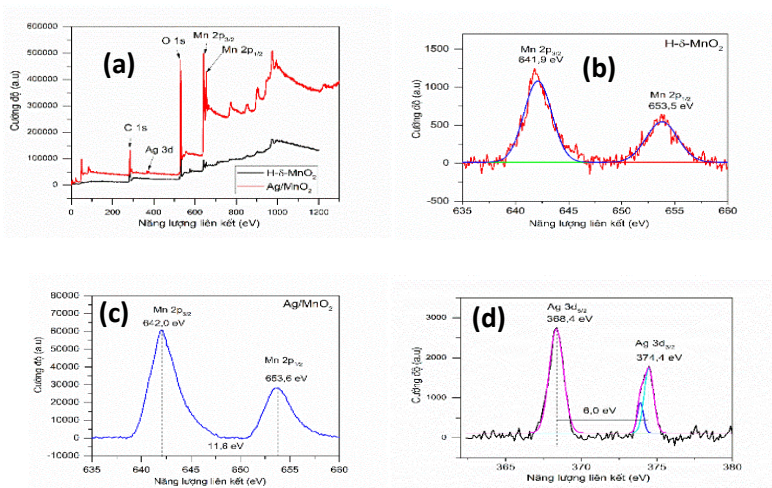
**Table 3.5.** Summary of the pure water flux, permeation BSA flux, water flux after cleaning of as- prepared membranes.

| Membrane | $J_{w1}$              | $J_{p1}$ | $J_{w2}$ | $J_{p2}$ | $J_{w3}$ |
|----------|-----------------------|----------|----------|----------|----------|
|          | $(l\ m^{-2}\ h^{-1})$ |          |          |          |          |
| CAD      | 314.41                | 136.24   | 288.21   | 128.38   | 248.91   |
| CADA     | 301.31                | 131.01   | 248.91   | 99.56    | 196.51   |

### 3.4. Characterization of $\delta$ -MnO<sub>2</sub> and Ag/MnO<sub>2</sub>



**Figure 3.4.** HR-TEM and SEAD of H- $\delta$ -MnO<sub>2</sub> (a, b, c) và Ag/MnO<sub>2</sub> (d, e, f)



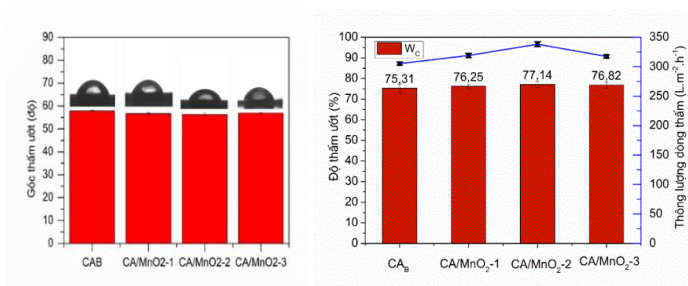
**Figure 3.5.** XPS of H- $\delta$ -MnO<sub>2</sub> and Ag/MnO<sub>2</sub> (a), Mn 2p (H- $\delta$ -MnO<sub>2</sub>) (b), Mn 2p (Ag/MnO<sub>2</sub>) (c), Ag 3d (d)

**Conclusion:** MnO<sub>2</sub> nanoparticles were successfully synthesized with the 2D layer structure and dispersed silver nanoparticles onto MnO<sub>2</sub> without changing the desired 2D structure.

### 3.5. Characterization of modified membranes of CA/MnO<sub>2</sub> and CA/PDA-Ag/MnO<sub>2</sub>

**Table 3.6.** Roughness parameter of CA<sub>B</sub> and CA/MnO<sub>2</sub> membranes

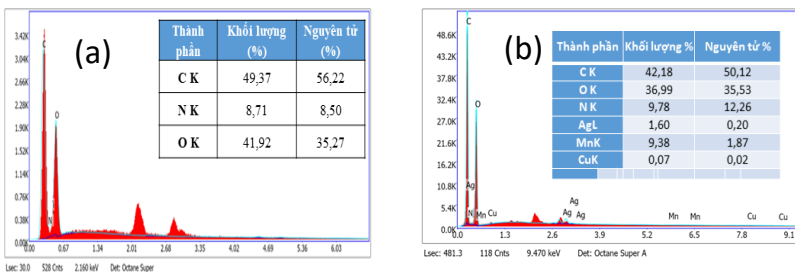
| Membrane               | R <sub>a</sub> /S <sub>a</sub> (nm) | R <sub>rms</sub> /S <sub>q</sub> (nm) |
|------------------------|-------------------------------------|---------------------------------------|
| CA <sub>B</sub>        | 3.65                                | 4.65                                  |
| CA/MnO <sub>2</sub> -1 | 3.64                                | 4.58                                  |
| CA/MnO <sub>2</sub> -2 | 2.84                                | 3.85                                  |
| CA/MnO <sub>2</sub> -3 | 3.42                                | 4.96                                  |



**Figure 3.6.** Contact angle values and the pure water permeability of membranes: CA<sub>B</sub>, CA/MnO<sub>2</sub>-1, CA/MnO<sub>2</sub>-2, CA/MnO<sub>2</sub>-3

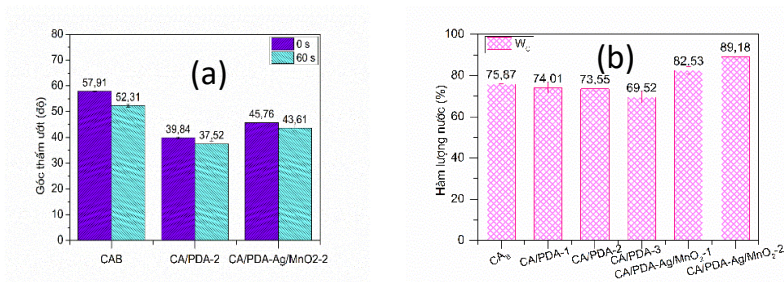
The dispersion of MnO<sub>2</sub> nanoparticles onto membranes was also studied by elemental mapping techniques on the surface and cross-section of the CA/MnO<sub>2</sub>-2 membrane. The obtained results show that the nanoparticles are very uniformly dispersed in the polymer matrix.

XPS was conducted to confirm the existence of Mn in the post-blended membrane. This spectrum appears in two peaks of 641.3 eV corresponding to Mn 2p<sub>3/2</sub> and 652.9 eV corresponding to Mn 2p<sub>1/2</sub>. The energy difference of these two peaks is 11.6 eV demonstrating Mn(IV) existence in the membrane matrix.

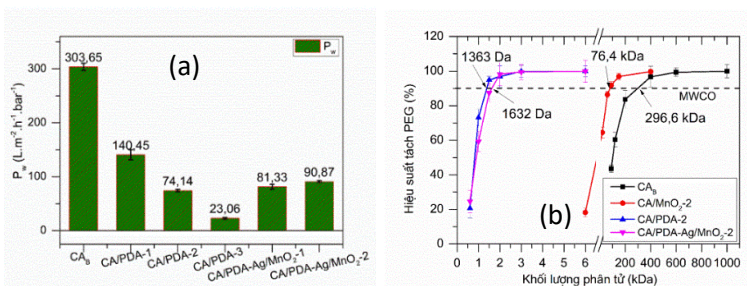


**Figure 3.7.** EDX spectrum of CA/PDA-2 (a), and CA/PDA-MnO<sub>2</sub>-2 (b) membranes





**Figure 3.8.** Contact angle (a) and water content (b) of CA, CA/PDA-2 and CA/PDA-Ag/MnO<sub>2</sub>-2 membranes

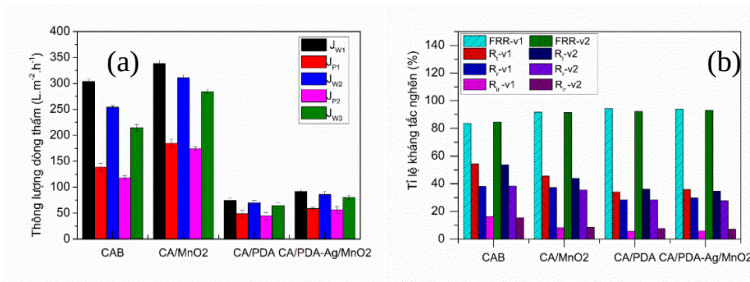


**Figure 3.9.** Average water permeability (a) and MWCO (b) of CA, CA/PDA and CA/PDA-Ag/MnO<sub>2</sub> membranes at 1-6 bar

In the DSC thermal analysis of the CA/PDA membrane, we found that PDA deposition did not significantly affect the thermal stability of the pristine CA membrane, which was demonstrated by the shape and location of exothermic peaks. On the DSC curve of the CA/MnO<sub>2</sub> membrane, at about 270 °C, an exothermic peak appeared, which is related to chemical dehydration with oxygen loss from the MnO<sub>6</sub> group corresponding to a partial reduction of Mn(IV) into Mn(III). The TGA curve of CA/MnO<sub>2</sub> membrane shows the melting

peak at 296.54 °C and decomposition peak at 348.04 °C, corresponding to the mass loss of 78.15%. The TGA curve of CA/PDA-Ag/MnO<sub>2</sub> membrane is similar to CA/MnO<sub>2</sub> membrane appeared exothermic peak at 253.81 °C also due to oxygen loss in MnO<sub>2</sub>, maximum mass loss at 352.49 °C with 62.48% due to deacetylation of cellulose acetate. In addition, the second mass loss in the range of 420 - 550 °C is the decomposition of the CA and PDA polymer chains, and the loss of O in Ag/MnO<sub>2</sub>.

### The antifouling performance of CA<sub>B</sub>, CA/MnO<sub>2</sub>-2, CA/PDA-2, and CA/PDA-Ag/MnO<sub>2</sub>-2 membranes



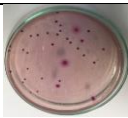
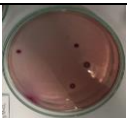
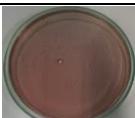
**Figure 3. 10.** Pure water and BSA 500 ppm permeability (a), flux recovery rates and resistance values (b) of CA<sub>B</sub>, CA/MnO<sub>2</sub>-2, CA/PDA-2, and CA/PDA-Ag/MnO<sub>2</sub>-2 membranes

The calculated FRR and R<sub>ir</sub> results show that the fabricated membranes exhibit excellent antifouling properties. In addition, the BSA separation efficiency of the modified membranes is more than 95%.

### Antibacterial results of membrane materials

The CA/MnO<sub>2</sub>-2, CA/PDA-2, and CA/PDA-Ag/MnO<sub>2</sub>-2 membranes were tested for antibacterial activity by the colony

counting method. The experiments were conducted with the sampled bacteria concentration at the threshold of  $10^6$  CFU/mL to  $10^7$  CFU/mL. The results obtained are shown in Figure 3.11.

|                 | Reference sample                                                                  | CA/MnO <sub>2</sub> -2                                                            | CA/PDA-2                                                                          | CA/PDA-Ag/MnO <sub>2</sub> -2                                                     |
|-----------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| <i>E.Coli</i>   |  |  |  |  |
| <i>Coliform</i> |  |  |  |  |

**Figure 3.11.** Petri dish imaging was conducted by the bacterial count method to determine the antibacterial properties of the CA/MnO<sub>2</sub>-2, CA/PDA-2, and CA/PDA-Ag/MnO<sub>2</sub>-2 membranes after 24 hours of incubation.

CA/PDA-Ag/MnO<sub>2</sub>-2 membrane exhibits the best antibacterial ability among the three studied membranes, completely inhibiting *E.Coli* and *Coliform* bacteria (100%). CA/PDA-2 membrane also presents high antimicrobial capacity against *E.Coli* and *Coliforms*, respectively 98.80 and 96.88%. The existence of copper ions formed by PDA deposition with CuSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> trigger increased the antibacterial activity of CA/PDA and CA/PDA-Ag/MnO<sub>2</sub>-2 membranes. CA/PDA-Ag/MnO<sub>2</sub>-2 membrane completely inhibits bacteria due to the existence of both nano copper and nano silver. CA/MnO<sub>2</sub> membrane also showed good antibacterial property

(*E.Coli*: 98.10%, *Coliforms*: 84.38%). The bactericidal mechanism is based on the toxicity of the nanoparticles and their reactive oxygen species.

### **3.6. Pb(II) and Cr(VI) separation performances of CA and modified membranes**

The adsorption isotherm of prepared membranes was fitted better with the Langmuir isotherm model than the Freundlich model. Therefore, the single-layer adsorption is suggested for the adsorption process and exhibits the heterogeneous nature of adsorptive sites on the surface of membranes. The pseudo-first-order and pseudo-second-order adsorption kinetic models were employed to fit the experimental data. As a result, the correlation coefficients  $R^2$  in the linear kinetic equations for the adsorption of Cr (VI) and Pb (II) on the as-prepared membranes are pretty significant ( $R^2 > 0.84$ ). Moreover, all adsorption processes of CA<sub>B</sub>, CA/MnO<sub>2</sub>, CA/PDA, and CA/PDA-Ag/MnO<sub>2</sub> membranes could be better fitted using second-order kinetic model than first-order kinetic due to exhibited more significant correlation coefficient ( $R^2 > 0.99$ ).

### **3.7. Results of the pollutant and bacteria treatment in floodwater via the combination of pretreatment with *Moringa oleifera* seed extract and CA/MnO<sub>2</sub> and CA/PDA-AgMnO<sub>2</sub> membranes.**

The floodwater samples are denoted as follows: M0 is the raw flood water sample. M1 is the M0 sample after treatment with *Moringa oleifera* extract. M2 is the M1 water sample after being filtered through the as-prepared membrane (CA/PDA-Ag/MnO<sub>2</sub>). All

samples were conducted at Environmental Monitoring Center- Binh Dinh Department of Natural Resources and Environment, the results are shown in Table 3.7.

**Table 3.7. Analysis results at Environmental Monitoring Center - Binh Dinh Department of Natural Resources and Environment**

| NO. | Parameters                  | Test Methods/<br>Measuring Equipment | Units       | Results            |         |         |
|-----|-----------------------------|--------------------------------------|-------------|--------------------|---------|---------|
|     |                             |                                      |             | M0-04.3            | M1-04.3 | M2-04.3 |
| 1   | pH                          | HI 2211 pH/ORP Meter                 |             | 6.8                | 6.8     | 6.8     |
| 2   | Turbidity                   | Orbeco-Hellige 975MP                 | FTU         | 253                | 1.94    | 0.00    |
| 3   | BOD <sub>5</sub><br>(20 °C) | SMEWW 5210D:2012                     | mg/L        | 27                 | 12      | ND      |
| 4   | COD                         | SMEWW 5220.C:2012                    | mg/L        | 40                 | 20      | ND      |
| 5   | <i>Coliform</i>             | TCVN 6187-2: 1996                    | MPN /100 mL | 21.10 <sup>2</sup> | 900     | ND      |
| 6   | <i>E. Coli</i>              |                                      |             | 43                 | 23      | ND      |
| 7   | Cr(VI)                      | UV-Vis                               | mg/L        | ND                 | ND      | ND      |
| 8   | Pb(II)                      | SMEWW 3500:2005                      |             | 0.008              | ND      | ND      |

Coagulation/flocculation pretreatment with *Moringa oleifera* extract presented the following yield: turbidity (99.23%), BOD<sub>5</sub> (55.56%), COD (50%), *E.coli* (46.51%), *Coliforms* (57.14%). In this stage treatment, only turbidity index reaches the permissible threshold of drinking water quality standards, *Coliforms* reaches the permissible threshold of surface water quality standards, and other criteria such as BOD<sub>5</sub>, COD, *E.coli* have not reached the permissible threshold of drinking water quality standards. Thus, *Moringa oleifera* extract - coagulant has reduced nearly half of bacteria, BOD<sub>5</sub>, and COD.

M1 sample was obtained from the separation of CA/PDA-Ag/MnO<sub>2</sub>-2 membrane. The operating pressure adjusted to 3.5 bar with a flow rate of 58.389 (L/m<sup>2</sup>.h). The M2 sample obtained exhibits indicators reaching 100%.

## **CONCLUSIONS AND RECOMMENDATION**

### **Conclusions**

1. Cellulose was extracted from bagasse with high purity (83-89%). From bagasse cellulose, cellulose acetate (CA) material was synthesized with degree of substitution DS = 2.62 ÷ 2.81, average molecular weight according to viscosity over 43000 g/mol.

2. The 2-dimensional nanomaterial-MnO<sub>2</sub> has been successfully prepared by the solid phase calcination method at 550 °C from the precursor KMnO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub> C<sub>2</sub>O<sub>4</sub> (molar ratio 1: 1.2).

3. Asymmetric cellulose acetate membranes have been successfully fabricated by phase inversion, using sugarcane bagasse as the starting material.

- Ultrafiltration membrane materials CAD, CADA, CA<sub>B</sub>, and

CA/MnO<sub>2</sub> blended membrane have been successfully fabricated by the phase inversion method using eco-friendly DMSO solvent with asymmetric membrane structure, high water permeability, good antifouling (FRR> 80%), and molecular weight cut-off (MWCO) from 76 to 300 kDa.

- The surface-modified membranes of CA/PDA and CA/PDA-Ag/MnO<sub>2</sub> were successfully prepared by dopamine deposition and co-deposition method using CuSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> trigger. The as-prepared membranes have a more uniform and hydrophilic surface, high permeability (74.14 and 90.87 (L.m<sup>-2</sup>.h<sup>-1</sup>.bar<sup>-1</sup>, respectively)), and better antifouling (FRR> 94%). The MWCOs of these membranes are 1363 and 1632 Da corresponds to loose nanofiltration membranes. The removal of heavy metals and *E. Coli* and *Coliforms* are more efficient pristine membrane.

4. The max adsorption capacity of CA/PDA-Ag/MnO<sub>2</sub> membrane with Cr(VI) is the highest ( $q_{\max}$  = 61.12 mg/g), followed by CA/MnO<sub>2</sub> membrane ( $q_{\max}$  = 52.52 mg/g and CA/PDA membrane ( $q_{\max}$  = 36.24 mg/g). The max adsorption capacity of CA/MnO<sub>2</sub> membrane with Pb(II) is the highest ( $q_{\max}$  = 103.41 mg/g), followed by CA/PDA-Ag/MnO<sub>2</sub> ( $q_{\max}$  = 83.47 mg/g) and CA/PDA membrane ( $q_{\max}$  = 82.44 mg/g). The adsorption kinetic of these membrane is consistent with pseudo second order kinetic model.

5. Optimal conditions for the coagulation/flocculation of *Moringa Oleifera* seed extract with floodwater samples were established: extract concentration 5 mL per 1000 mL of turbid water (<450 FTU), rapid stirring speed 150 rpm for 3 minutes and maintenance 20 minutes at 15 rpm, settling time 120 minutes.

6. It has been successful in combining pretreatment with *Moringa Oleifera* seed extract and filtration membrane to convert floodwater into drinking/potable water, ensuring the standards of domestic water.

### **Recommendation for further research**

In view of the experiments and conclusions obtained in this dissertation, some recommendations for further research are given below.

- The effect of temperature on the adsorption process of the prepared membranes should be deeply investigated.
- The dye and antibiotic separation of membranes should be continuously studied.
- Studying the effect of anions in aqueous solution on heavy metal ion treatment through filtration membrane separation.
- Furthermore, nanoporous materials (MOF, zeolite, porous graphene) with intrinsic controllable pore apertures and functionalities can lead to ideal molecular sieving membranes for remarkable separation properties. Therefore, two-dimensional materials with an ultrathin thickness and well-defined nanopores are considered a class of promising materials for constructing highly permeable NF membranes.



## LIST OF PUBLICATIONS

1. **Dang Thi To Nu**, Cao Van Hoang, Nguyen Vu Thuyen, Nguyen Thi Hien, Nguyen Phi Hung, *Synthesis and characterization cellulose acetate from sugarcane bagasse*, VietNam Journal of Catalysis and Adsorption, Vol 6(4), pp.50-55, (2017) (ISSN 0866-7411).
2. **Dang Thi To Nu**, Nguyen Thi My Duyen, Cao Van Hoang, Nguyen Thi Lieu, Nguyen Phi Hung, *Synthesis, structural characterization and methylene blue adsorption of H- $\delta$ -MnO<sub>2</sub>*, VietNam Journal of Catalysis and Adsorption, Vol 7(2), pp. 80-85, (2018) (ISSN 0866-7411).
3. **Dang Thi To Nu**, Cao Van Hoang, Dang Thi Phuong Dung, Tran Van Hien, Nguyen Phi Hung, *Synthesis and characterization of CA/PDA membrane for Pb<sup>2+</sup> removal from aqueous solution*, VietNam Journal of Analytical Sciences, Vol 24(1), 50-55 (2019) (ISSN 0868-3224)
4. **Dang Thi To Nu**, Nguyen Thi My Duyen, Nguyen Thi Thuy Linh, Cao Van Hoang, Nguyen Phi Hung, *Preparation and characterization of nano  $\delta$ -MnO<sub>2</sub>-blended cellulose acetate membrane*, Vietnam J. Chem., 2019, 57(6), 741-746. DOI: vjch.2019000115.
5. **Dang Thi To Nu**, Nguyen Phi Hung, Cao Van Hoang, Bart Van der Bruggen, *Preparation of an asymmetric membrane from sugarcane bagasse using DMSO as green solvent*, Appl. Sci. 2019, 9(16), 3347, <https://doi.org/10.3390/app9163347> (ISI, Q1)