

THESIS OF THE PH.D. DISSERTATION

**ATR-FTIR Study of the Interaction of CO₂ with
Bacterial cellulose-Based Membranes**

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INTRODUCTION

Carbon dioxide (CO₂) is an acidic gas and a typical component of natural gas streams. CO₂ affects the heating value of the natural gas and causes detrimental effects on pipelines. Besides the natural gas process problems, CO₂ is also a major greenhouse gas contributing to Earth's global warming. Removal or transformation of carbon dioxide into environmentally safer products is an essentially important process. Membrane technology plays important role in all of these endeavors. In comparison to the other techniques for CO₂ capture, a membrane technology has multiple advantages that include price, safety, easy manipulation and light weight.

Here we propose to use bacterial cellulose (BC) obtained by fermentation of coconut juice, induced by the bacterium *Acetobacter xylinum*. The big advantages of the cellulose based membranes are their reusability, low price, as well as their safe disposal when they reach their end-of-life because of their biodegradability. The overall purpose of this research was to optimize the processing conditions for the fabrication of BC-based membranes via normal casting evaporation drying technique, additionally, to examine CO₂ adsorption study. The BC-based membrane was further modified with silk fibroin protein and ZnO nanoparticles in order to increase their affinity towards CO₂. The interaction of the CO₂ with the membranes was investigated by means of ATR-FTIR spectroscopy. The obtained spectra were determined the changes after the interaction of CO₂ with the active membranes in variation of exposure time (8h, 16h and 24h) by examining two regions of the spectra: 740-610 cm⁻¹ (bending vibrational mode of CO₂) and 2400-2300 cm⁻¹ (asymmetric stretching vibrational mode of CO₂). The active sites within the membrane, including, OH groups, CONH groups and ZnO surfaces, were expected to be favorable for CO₂ attachment. Furthermore, CO₂ permeation experiment was also executed for the permeability of our BC-based membranes.

MATERIALS AND METHODS

Purification of Raw Nata de coco and Preparation of Dried Bacterial Cellulose Films

For our research, approximately 300-400 g of *Nata de coco* was firstly cut and soaked in water for almost 1 week and then cut again into small pieces (around 1x1x0.5 cm) and boiled in distilled water until pH~7. To further improve the purity (remove non-cellulosic materials), *Nata de coco* was treated in 0.01M NaOH solution at 80°C under continuous stirring. After the alkaline treatment, the color of *Nata de coco* changed from pale yellow into white and, eventually, transparent gel was formed. The clear gel was subsequently boiled in distilled water several times under continuous stirring until the pH became neutral. Finally, the purified *Nata de coco* was blended by a laboratory blender and dried into silicone trays in an oven to obtain dried bacterial cellulose films. The dried films of 0.048 mm thickness and 40-50 mm in diameter were further used for preparation of microfibrillated and nanocrystalline cellulose suspensions.

Preparation of Microfibrillated Bacterial Cellulose Suspension

In order to prepare microfibrillated bacterial cellulose suspension, the 0.1 %w/V of the dried bacterial cellulose films were cut into small pieces and immersed in 80 ml distilled water. Then, sonication was applied at frequency of 20 kHz with a maximum power 20 W/cm² using an 18 mm tip diameter of horn (Tesla 150 WS) to obtain dispersed microfibrils of bacterial cellulose suspension. Sonication is useful for isolation of cellulose fibrils and fabrication homogeneous films.

Preparation of Nanocrystalline Bacterial Cellulose Suspension

The dried bacterial cellulose films (from the section 2.2.1) were kept for 5 days in a desiccator above 37% HCl fuming solution. During this process, the degradation of cellulose occurred and the nanocrystalline bacterial cellulose was obtained. After hydrolysis by HCl, nanocrystalline BC was immersed in 80 ml distilled water to get a 0.1%w/V suspension and sonicated until it was translucent.

Preparation of ZnO Nanoparticles Suspension

0.008g of ZnO nano-powder (10-30 nm in size) was dissolved in 80 ml distilled water to get a 0.01% w/V suspension and sonicated until a translucent ZnO nanoparticles suspension was obtained.

Purification of Silk Cocoon (Degumming) and Preparation of Nano-Silk Fibroin Suspension

Silk fibroin was obtained by reeling from the silk cocoon. To remove gum or sericin, 20g of cocoons were boiled in 0.02 M Na₂CO₃ for 30 min and washed in water at 50 °C. This process was repeated several times. The degummed silk fibroin was then dried in an oven at 70 °C. The dried silk fibroin was placed in a desiccator for 1 night under the 37% HCl fuming condition for hydrolysis process similar to the preparation of nanocrystalline BC. In the acid system, fibroin chains are gradually degraded with time because of acid hydrolysis. In order to prepare nano-silk fibroin suspension, 0.08g of hydrolyzed silk fibroin (0.1% w/V) was immersed into 80 ml distilled water and sonicated.

Fabrication of Bacterial Cellulose-Based Membranes by Evaporation Casting

The basic BC membrane was prepared by mixing microfibrillated bacterial cellulose suspension, and nanocrystalline bacterial cellulose suspension. 50% V/V (or ~4.8% w/w) ZnO nanoparticles suspension and 10% V/V (or ~10% w/w) nano-silk fibroin suspension were added into that mixture to prepare the ZnO- and silk fibroin-modified BC membranes, respectively. Each mixture suspension (30 ml) was poured onto a Teflon membrane (used as a support) and dried by normal evaporation casting in an oven. Three types of the bacterial cellulose-based membranes on Teflon supports were obtained:

- Basic BC membrane (This membrane refers to pure BC membrane. The rest part of the thesis, “basic BC membrane” will be mentioned instead.)
- BC membrane with nano-silk fibroin and
- BC membrane with ZnO nanoparticles.

ATR-FTIR Spectroscopy Studies of the Interaction with CO₂

IR spectra were recorded using a Jasco FT/IR6300 equipped with an ATR PRO 470-H spectrometer. In order to obtain control spectra, the BC-based membranes were heated above 100°C to remove some sorbed CO₂ from normal atmosphere, following by recording the ATR-FTIR spectroscopy as the control spectra. For determining the changes of CO₂ spectra after CO₂ adsorption, the samples were measured again after keeping the membranes in a tighten reactor under CO₂ 3 bars for 8h, 16h, and 24h. During the experiment of pressurization, the reactor were tightened at the permeate side. The spectra were collected by using air as a background. A total of 30 accumulative scans were taken per sample with a resolution of 4 cm⁻¹, in the frequency range of 4000-400 cm⁻¹, in the absorbance mode. The experiment was done at room temperature, replicated three times. The spectra were analyzed and calculated the integrated absorption bands via OriginPro 8 software (OriginLab Corporation) and resolved into particular peaks using PeakFit (v4.12) software.

CO₂ Permeation Study

The experiments were performed at room temperature and feed pressure of 480 Pa using the permeation unit. Permeating CO₂ was emitted to the atmospheric condition. The area of the membrane in contact with the gas was 17.35 cm². The dynamic pressure was measured during the experiment until the steady-state using THERM TYP 2295-2B by Pitot tube. The obtained data were used to calculate the flow rate (Eq. 1) and then gas permeability (Eq. 2) by the following equations:

$$Q = Av, \quad (1)$$

where $v = \sqrt{\frac{P_{dynamic}}{\frac{1}{2}\rho}}$; v = velocity (m/s), ρ = density of gas (kg/m³) (In this case, CO₂ density is 1.842 kg/m³ at 20°C and 1 atm), $P_{dynamic}$ = dynamic pressure (Pa), Q = flow rate (m³/s) and A = area of the pipe (m²);

$$\left(\frac{P}{\delta}\right)_i = \frac{Q_i \times 10^6}{A \times (\Delta P)} \quad (2)$$

Where $\left(\frac{P}{\delta}\right)_i$ = permeance of gas “i” (GPU) (1 GPU = 10⁻⁶ cm³ (STP)/cm² s cm Hg),

P = permeability of gas ‘i’ (10⁻¹⁰ cm³ (STP) cm/cm² s cm Hg)

(1 Barrer = 10⁻¹⁰ cm³ (STP) cm/cm² s cm Hg = 7.5×10⁻¹⁸ m² s⁻¹ Pa⁻¹),

δ = thickness of membrane (μm),

Q_i = volumetric flow rate of gas 'i' (cm^3/sec),

A = membrane area (cm^2) and

ΔP = pressure difference between the feed side and the permeating side (cm Hg).

CHARACTERIZATIONS

ATR-FTIR Spectroscopy

Infrared spectra of BC-based membranes were characterized by a Jasco FT/IR6300 instrument equipped with an ATR PRO 470-H spectrometer. The spectra were collected over the range of $4000\text{-}400\text{ cm}^{-1}$ with an accumulation of 30 scans, resolution of 4 cm^{-1} , in the absorbance mode.

X-Ray Diffraction Analysis

X-ray diffraction measurement were performed on a benchtop X-Ray diffractometer, Equinox 100, at 40 kV and 0.9 mA ($\text{CuK}\alpha$ radiation) to analyze crystalline structure of samples. Scans were collected in the range of $10^\circ\text{-}40^\circ$ (2θ) in steps of 0.05° . In our work, crystallinity index (or apparent crystallinity (%)) was calculated from the ratio of the area of all crystalline peaks to the total area including non-crystalline fraction using the following equation (Eq. 3):

$$\text{Crystallinity index} = \frac{I_{1\bar{1}0} + I_{110} + I_{200}}{I_{1\bar{1}0} + I_{110} + I_{200} + I_{\text{am}}} \times 100 \quad (3)$$

where $I_{1\bar{1}0}$, I_{110} and I_{200} are the crystalline peak areas of the $(1\bar{1}0)$, (110) and (200) planes, and I_{am} is the amorphous peak areas. The degree of crystallinity can be measured by several methods from an X-ray diffractogram, in our work, deconvolution method (curve fitting) was performed to find individual peak regions. PeakFit v4.12 software AutoFit Peaks II Deconvolution (Baseline Linear D2) were applied to calculate the areas under the considered XRD diffraction peaks. Gaussian peak profiles were used for our studies as Park et al. (2010) did. Gaussian functions are commonly used for deconvolution of XRD spectra.

Morphological Analysis of BC-Based Membranes by FESEM Microscopy

The morphologies of the samples were studied using TESCAN MAIA3 UHR FE-SEM in Beam Deceleration Mode at 500 V and 1.0 kV, and In-Beam SE detector at 2.0 kV

for ultra-high resolution and maximum surface sensitivity. Prior to analysis, the samples were coated with a thin layer (5 nm) of Pt.

SUMMARY OF THE RESEARCH

The BC-based membranes are in the form of thin films on the Teflon supports after normal evaporation casting drying. The thickness of a whole membrane is about 265 μm ; BC-based film is around 20 μm , and 5 cm in diameter. Macroscopically, the modified BC membranes were very similar to the basic BC membranes. Structural (FT-IR and XRD) and morphological (FE-SEM) measurements justified that all BC-based membranes were formed a fine nanofibrils entangled network structure with porous in nano-size and have very high crystallinity signifying high mechanical strength.

From XRD analysis, the diffractogram of our samples reveals three distinct diffraction peaks, where at $2\theta \approx 17^\circ$, 20° and 22° corresponding to (110), (102) and (200) crystallographic planes of cellulose. The crystallinity index was calculated by Eq. 3. We noticed that the addition of silk fibroin or ZnO nanoparticles does not affect to the crystallinity of the BC matrix. The basic BC membrane presents 89.10%, silk fibroin- and ZnO nanoparticles-modified BC membranes exhibit 88.68% and 89.76%, respectively. Consequently, these membranes are suitable for using as gas separation membrane owing to the dense structure with distribution of nano-sized pores, high crystallinity (high mechanical strength) and the presence of active sites for CO_2 .

ATR-FTIR Spectroscopy Studies of the Interactions with CO_2

The consideration of spectral bands of bound CO_2 can provide the information about the interaction of CO_2 with the functional groups of the polymers. From the CO_2 bending spectra ($740\text{-}610\text{ cm}^{-1}$), the shape of the bands changes after pressurized the membranes with CO_2 indicating possible ν_2 band splitting as a result of the interaction with membrane functional groups. It was also noticed that the CO_2 absorption spectral bands of silk fibroin- and ZnO-modified BC samples seem broader than that of basic BC samples. In our studies, the resolved spectra by PeakFit of each sample are the evidence of the CO_2 trapped in the membrane materials, which under the envelope of the bending mode peak of CO_2 clearly presents the splitting phenomenon. When CO_2 takes part in the formation of an electron donor-acceptor complex, the splitting of the CO_2 bending absorption band occurs. In regard to the modes assignment from other

studies, our resolved peak positions in each IR spectrum could be assigned for the peaks at $\sim 667\text{ cm}^{-1}$, $\sim 662\text{ cm}^{-1}$, $\sim 655\text{ cm}^{-1}$ and $\sim 650\text{ cm}^{-1}$ as gas phase of CO_2 , out-of-plane bending of associated CO_2 , physically sorbed CO_2 and in-plane bending of associated CO_2 , respectively. The possibility of more pronounced spectral lines associated with these structures can be introduced depending on the number of interactions and the complex arrangements. The additional line at 681 cm^{-1} of the silk fibroin-modified sample spectrum as well as at 677 cm^{-1} of the ZnO-modified sample spectrum can be seen obviously after pressurization. This means there might be more specific structures formed between CO_2 and these membrane samples. More splitting curves referred to more existence interactions resulting in more specific structures. Hence, it can be supposed that the functional groups in the silk fibroin and also the active surfaces of ZnO nanoparticles could improve the specific sites to interact with CO_2 and then form more complex species compared to the basic BC sample. An increase of the absorbance of CO_2 bending envelope after pressurization together with the appearance of extra bands, are an evidence of CO_2 sorption to the samples. The CO_2 interaction with hydroxyl group has been described that CO_2 bonds to only oxygen atom of hydroxyl group to form the CO_2 -hydroxyl group complex by the formation of Lewis acid-base or electron donor-acceptor complex owing to the available lone pair of electrons of oxygen atom in hydroxyl group as an electron-donor site. Furthermore, CO_2 was able to bind to electron-deficient C-H bonds from bacterial cellulose/silk fibroin by a cooperative weak hydrogen bond.

Likewise, ν_3 band of CO_2 also present the peaks which are of the sorbed CO_2 by the membranes in the asymmetric stretching vibration. The spectra show that there are drastic changes of the CO_2 band in this region after incorporation of the membranes with CO_2 . The IR peak intensity enhancement of the samples after pressurization compared to that of the control sample can be clearly observed from all figures. It should be noted that an increase in the absorption band intensity reflects the amount of sorbed CO_2 increase implying the taking part of CO_2 with the membrane samples. In accordance with changes of spectral curve in the CO_2 asymmetric stretching region, this can support the CO_2 -membrane interaction suggestion.

Based on our FTIR spectra in the ν_3 region of CO_2 , the presence of several absorption bands of all BC-based membranes are responsible for a mixture of bound CO_2 with different basic sites and gaseous CO_2 . The assignment of some peak positions in this region was also described. We suggested that the peaks positioned at $\sim 2370\text{ cm}^{-1}$, ~ 2360

cm^{-1} and $\sim 2340 \text{ cm}^{-1}$, $\sim 2350 \text{ cm}^{-1}$, $\sim 2334 \text{ cm}^{-1}$, and $\sim 2323 \text{ cm}^{-1}$ are corresponding to the combination band of ν_3 and the external vibrational mode of CO_2 against the surfaces of membrane, gas phase of CO_2 , physically sorbed CO_2 , asymmetric stretching vibration of CO_2 , and hot band, respectively.

To further justify the conclusion, determination of integrated area of IR absorption spectral bands of CO_2 are useful for the quantification results. It should be noted that this method is simple to obtain the relative CO_2 attachment content by our membrane samples. It was clearly noticed from the results regarding the enhancement of the integrated absorption band areas from both vibrational modes indicating an increase of the amount of sorbed CO_2 on the membranes after pressurization with CO_2 . Overall, basic BC membrane, silk fibroin-modified BC membrane and ZnO nanoparticles-modified BC membrane were able to achieve the highest efficiency at 16h and 8h after CO_2 sorption, respectively. This signified that the ability to interact with CO_2 by the modified membranes was more rapid than that of the basic BC membrane. Consequently, it can be mentioned that CO_2 adsorption is facilitated by modification with silk fibroin and ZnO nanoparticles. This was expected owing to the presence of various active sites from silk fibroin and ZnO nanoparticles.

CO_2 Permeation Study

The gas permeation experiment were carried out by flowing pure CO_2 through our membranes in the permeation unit at room temperature and feed pressure of 480 Pa. The basic BC membrane, silk fibroin-modified BC membrane and ZnO nanoparticles-modified BC membrane presented the CO_2 permeability of 2.73, 2.69 and 2.66 Barrer, respectively. Our results showed that CO_2 permeation through the basic BC membrane was higher than other modified BC membranes slightly. The possible reason of the meaningful decreases of the permeability (direct related to flow rate) of the modified BC membranes was that CO_2 molecules were able to experience longer time inside these membranes due to the suggested Lewis acid-base type of interaction between the accessible sites within the membranes and CO_2 molecules as proved by the ATR-FTIR results. However, the selectivity of gas separation between CO_2 and other gases of our membranes was not executed in this work. Meanwhile, we determined the activity of our membranes by ATR-FTIR studies as demonstrated above.

Main Conclusions of the Research Work

The main conclusions of this work can be summarized as follows:

1. Bacterial cellulose (BC)-based membranes were successfully fabricated via normal casting evaporation drying technique using bacterial cellulose from *Nata de coco* as membrane matrix. The addition of silk fibroin and ZnO nanoparticles into the BC matrix (the silk fibroin- and ZnO nanoparticles-modified BC membrane) was able to increase the number of specific sites for interaction with CO₂ as proved by the results from ATR-FTIR study.
2. The results from structural analysis by FTIR spectroscopy demonstrated that there were no important bands changed and no new covalent bonds for the modified BC membranes. While, the modified BC membranes spectra show only some peaks shifted and extra peaks from either silk fibroin or ZnO nanoparticles characteristics compared to the basic BC membrane.
3. The FESEM analysis shows mesh network nanofibrils structure with the distribution of pores in nano-size of all BC-based membranes. XRD analysis also proved that the crystallinity of BC did not affect by the presence of silk fibroin or ZnO nanoparticles. Also, our BC-based membranes have very high crystallinity that refers to high mechanical strength.
4. The interaction of the BC-based membranes with CO₂ was studied using ATR-FTIR spectroscopy. It has been found that an increase in the absorbance of CO₂ bending and asymmetric stretching IR envelopes after pressurization, the appearance of additional bands, and the presence of several splitting bands could confirm the CO₂ sorption to the membranes. The Lewis acid-base type of interaction was supposed to be a main interaction. However, we do not have conclusive spectroscopic evidence for which types of adsorbed carbonate species were formed since their vibrations are located in the same region as cellulose and silk fibroin characteristics.
5. It is noteworthy that the modified BC membranes provide the highest ability to capture CO₂ by displaying broader and more splitting peaks in both vibrational modes of CO₂. The general conclusion is that CO₂ interact strongly with BC-based membrane materials and that adsorption can be facilitated by the active sites from silk fibroin and ZnO nanoparticles.
6. The results of CO₂ permeation were confirmed the performance of the BC-based membranes achieving high permeability even extremely low feed pressure, temperature and relative humidity was applied.

List of my selected publications

1. Yanin Hosakun, Katalin Halász, Miklos Horváth, Levente Csóka, and Vladimir Djoković. "ATR-FTIR Study of the Interaction of CO₂ with Bacterial Cellulose-Based Membranes" (submitted).
2. Katalin Halász, Yanin Hosakun, and Levente Csóka. "Reducing Water Vapor Permeability of Poly(lactic acid) Film and Bottle through Layer-by-Layer Deposition of Green-Processed Cellulose Nanocrystals and Chitosan," *International Journal of Polymer Science*, vol. 2015, 6 pages, 2015.
3. Yanin Hosakun, Katalin Halász, Miklos Horváth, Levente Csóka, and Vladimir Djoković. "ATR-FTIR Study of the Interaction of CO₂ with Bacterial cellulose-Based Membranes" COST Action FP1205: Innovative Applications of Cellulose Fibers Regenerate Wood: Cellulosic material properties and industrial potential - Final meeting in COST FP1205. Meeting place and date: KTH Royal Institute of Technology, Stockholm, Sweden, 2017.03.07-2017.03.09. 2017, p. 22-23.
4. Yanin Hosakun. "Preparation of Bacterial Cellulose-Based Membranes for CO₂ Adsorption" PhD Conference at University of West Hungary, 2016.06.10.
5. Yanin Hosakun. "Preparation of Noble-Metal Nanoparticles Impregnated Bacterial Cellulose Membranes for CO₂/CH₄ Separation" PhD Conference at University of West Hungary, 2015.06.05, p.8.
6. Yanin Hosakun, Sujitra Wongkasemjit, and Thanyalak Chaisuwan. "Preparation of Bacterial Cellulose Membranes from Nata de coco with and without Silver Ions for CO₂/CH₄ Separation" The 5th Research Symposium on Petrochemical and Materials Technology and The 20th PPC Symposium on Petroleum, Petrochemicals and Polymers, Bangkok, Thailand, 2014.04.22.
7. Yanin Hosakun, Sujitra Wongkasemjit, and Thanyalak Chaisuwan. "Preparation of Bacterial Cellulose Membranes from Nata de coco for CO₂/CH₄ Separation" ICCEE 2014: 16th International Conference on Chemical and Environmental Engineering, Barcelona, Spain, 2014.02.27-2014.02.28, p. 1.