

Utilisation of Banana Peel for Preparation of Bacterial Cellulose-based Ion Exchange Membrane

Bambang Piluharto^{1*}, Zulfikar¹, Maya ulfa Endah Sari¹, Istiqomah Rahmawati² and Harry Prasetyo³

¹*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Jember, Jl. Kalimantan 37, Kampus Tegalboto, Jember, Indonesia*

²*Department of Chemical Engineering, Faculty of Engineering, Universitas Jember, Jl. Kalimantan 37, Kampus Tegalboto, Jember, Indonesia*

³*PT Vanadia Utama, Komplek Sentra Industri Terpadu, Pantai Indah Kapuk, Jakarta Utara, Indonesia*

Bacterial Cellulose (BC)-based Ion exchange membrane has been successfully made by UV-photografting method. Bacterial cellulose was produced by *Acetobacter xylinum* s.p using banana peel as starting material. The effect of acrylic acid concentration on the ion exchange membrane properties was investigated. The functional group analysis by FTIR exhibit that acrylic acid was grafted on the BC membrane. The morphology analysis exhibits a significance surface change of BC membranes as result of UV-photografting treatment. The Ion Exchange Capacity (IEC) of membrane increases with increasing acrylic acid concentration until concentration of 20%, the further concentration of acrylic acid decrease IEC of membrane. The maximum IEC is 0.34 meq/g obtained acrylic acid of 20%. At this concentration, the Degree of Grafting (DG) and water absorption capacity is 4.78 and 51.22 %, respectively.

Keywords: banana peel; bacterial cellulose; UV-photografting; ion exchange capacity

I. INTRODUCTION

Banana is one of the most popular fruits in Indonesia. It has produced 50% of bananas in Asia. The fresh banana contain 35-40% of peel banana of the whole fruit weight (Aboul-Enein *et. al.*, 2016; Muhsinin *et. al.*, 2017; Vu *et. al.*, 2018; Agama-Acevedo *et. al.*, 2016; Devatkal *et. al.*, 2014; Ji & Srzednicki, 2015). The banana peel contains for about 18% of carbohydrates and it is potential to utilisation to be added value materials. Nata de banana peel is one of the food products of bacterial cellulose-based that produced using banana peel as starting material (Pereira & Maraschin, 2015; Rattanavichai & Cheng, 2015; Hang *et. al.*, 2018 ; Anjum *et. al.*, 2014; Kalemelawa *et al.*, 2012).

Bacterial cellulose is cellulose that produced by microbe e.g. *Acetobacter xylinum* s.p. Compared by cellulose from plants, BC have higher in crystallinity, water holding capacity, and mechanical stability. Based on its advanced properties, BC

have wide range of applications such as food matrix (nata de coco), filter and filler/reinforcement (Keshk, 2014; Lee *et. al.*, 2011; Basu *et. al.*, 2018; Foresti *et. al.*, 2017; De Oliveira Barud, 2016; Florea, 2016; Basu *et al.*, 2013). Modification of BC has been carried out to get the new functional properties of cellulose. One of the modifications is cellulose grafting for ion exchange membrane preparation (Choi *et. al.*, 2004; Roy *et al.*, 2009). As described by Choi et.al. that study effect of time radiation on ion exchange membrane properties. Confirmed by FTIR, ion exchange membrane has been successfully prepared. The electrochemical properties show that the prepared membrane were comparable with the commercial membrane (Choi *et al.*, 2004).

In this research, we report the result of preparation and characterisation of BC-based ion exchange membrane. Here, the BC was produced by *Acetobacter xylinum* s.p using banana peel as starting material. Ion exchange membrane has been prepared by UV-photografting with different

*Corresponding author's e-mail: bampito.fmipa@unej.ac.id

concentration of grafting agent. Characterisation of ion exchange membrane includes functional group analysis by FTIR, IEC by titrimetric method, water absorption by gravimetric method, and morphology by SEM.

II. MATERIALS AND METHOD

A. Materials

Kepok banana peel, sucrose, ammonium sulfate fertiliser were obtained from traditional market, *Acetobacter xylinum* was obtained from local industry, benzophenone, acrylic acid, NaOH, H₂SO₄, HCl, NaOH, H₂C₂O₄, phenolphthalein indicator were obtained from Merck.

B. BC Preparation

BC was prepared according to Purwanto (2012) with slight modification. Banana peel (500 g) was added into 100 mL water, then crushed using hand blender until uniform paste was obtained. Filtration was carried out to separate residue and filtrate in the paste. Filtrate was boiled, then sucrose and ammonium sulfate were added. After cooled, *Acetobacter Xylinum* starter as much as 10% (v/v) of filtrate was incubated into filtrate for days (Purwanto, 2012).

C. BC Purification

The BC gel was purified NaOH of 2% to remove non-cellulose components and bacterial residues (Indarti and Asmawati, 2011). The gel was then washed by water until pH was neutral. Finally, the gel was then hot pressed to obtain membrane and dried in oven 10 minutes at 100 °C.

D. Modification of BC

BC modification was carried out using UV-photografting technique with benzophenone as photoinitiator (Choi *et al.*, 2004). BC membrane (0.1 g) was immersed in benzophenone 5 % w/w for 3 hours then it was dried in air for 30 minutes. The membrane was then irradiated using UV light for 3 minutes. 0.2 mL of acrylic acid solution (5 %) was added and re-irradiated with UV light for 32 minutes. Modified BC was washed by methanol to remove the remaining acrylic acid and the homopolymer formed. Modified BC was dried in the oven for 5 minutes at 60 °C. Similar treatment was carried out for

the others acrylic acid concentration (10 % w/w, 15 % w/w, 20 % w/w, 30 % w/w, 40 % w/w, and 50 % w/w).

E. FTIR

FTIR measurement was carried out to confirm the UV-photografting on the membrane successful. The measurement was carried out in the range 500 cm⁻¹ to 4500 cm⁻¹ (Choi *et al.*, 2004).

F. Morphology Characterisation

Samples analysis was carried out by SEM by Zeiss EVO MA 10. Samples were subjected to an accelerated voltage 7.0 kV under high vacuum. Surface samples were coated by gold.

G. DG

The DG was indicated as weight increment of BC and calculated according to formula:

$$DG (\%) = (W_1 - W_0) / W_0 \times 100\% \quad (1)$$

W₁ is the weight of modified BC dan W₀ is unmodified BC (Kali and Sabaa, 2013).

H. Water Absorption

The water absorption capacity of modified BC was carried out by weighing the modified BC which had been dried in the oven at 60 °C for 5 minutes, then soaked in distilled water for 24 hours. After 24 hours, the modified cellulose bacteria are removed and placed on filter paper to remove residual water on the surface of modified BC, then weighed and calculated using the formula:

$$\% \text{ Water absorption} = (W_h - W_d) / W_d \times 100\% \quad (2)$$

W_h = weight of wet modified BC (gram)

W_d = weight of dry modified BC (gram) (Shahi & Vinod, 2007).

I. IEC

Ion Exchange Capacity (IEC) of modified BC is determined by acid-base titration. The membrane was immersed in 50 mL of 0.01 N NaOH for 12 hours at room temperature. Then 10 mL of the solution was taken and titrated with 0.01 N H₂SO₄ using methyl red indicator. While the membrane is taken and stored in 1 M HCl solution, excess HCl is removed using water,

then the membrane is dried. IEC (meq/g) can be calculated using the following formula:

$$\text{IEC} = (B - P \times 0.01 \times 5) / m \quad (3)$$

With, B is the amount of H_2SO_4 used for neutralising 0.01 N NaOH (as blank), P is the amount of H_2SO_4 used for neutralising the remaining NaOH cellulose grafting bath, and m is the mass of sample (gram).

III. RESULT AND DISCUSSION

A. BC Synthesised

Figure 1 (a-d) show the sequence process of the modified BC membrane preparation. Inoculated of *Acetobacter Xylinum* into filtrate media of banana peel for 9 days generated a pellicle (Figure 1(b)) and then followed hot-press treatment to obtain membrane (Figure 1(c)). By UV-photografting treatment, the modified membrane has obtained (Figure 1(d)). As shown in Figure, after modification, BC membrane turns to white and stiffer.

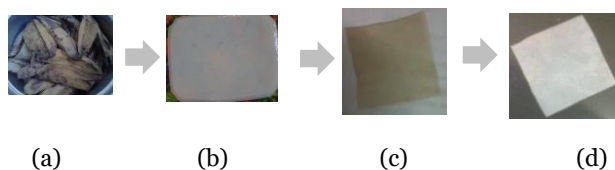


Figure 1. Sequence process of the modified BC membrane

B. Confirmation of BC Membranes Grafting by FTIR

Functional group analysis by FTIR have used to confirm that grafting have occurred on the BC membrane. Based on Figure 2, it can be seen that all of membranes have similar peaks of spectra. Some characteristic of peaks are in around $3200\text{--}3400\text{ cm}^{-1}$, $2800\text{--}3000\text{ cm}^{-1}$, $1000\text{--}1300\text{ cm}^{-1}$ corresponding to --O--H stretching, --C--H stretching and C--O stretching, respectively. However, BC membranes with UV-photografting treatment (Figure 2(b)-(f)) have a new peak at range of $1700\text{--}1750\text{ cm}^{-1}$ that do not appear in BC membrane without treatment. This is characteristic peak that correspond to --C=O stretching vibration of carboxyl group of acrylic acid.

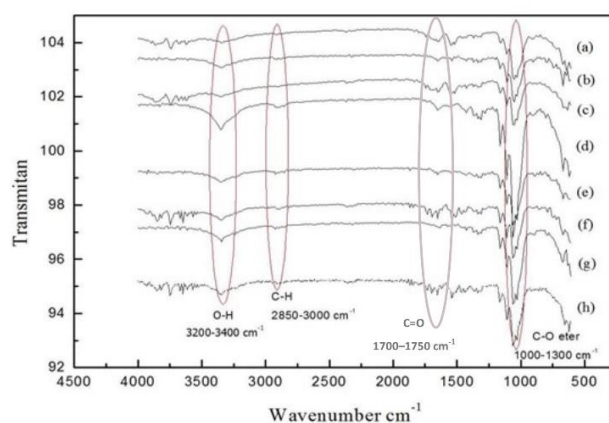


Figure 2. IR spectrum of modified BC-acrylic acid (a) 5%, (b) 10%, (c) 15%, (d) 20%, (e) 30%, (f) 40%, (g) 50%, and (h) pure BC

C. Morphology Analysis

The morphology analysis shown in Figure 3. Figure 3 evidences surface morphology of neat BC Figure 3 (a) and two graft modified membranes (20% Figure 3(b)) and 50% (Figure 3(c)). We observe that BC modified membranes (Figure 3(b) and 3(c)) have surface with thicker and whiter than pure BC (unmodified). Change of surface on the modified membranes show that grafting process was occurred on the BC membrane. The modified membrane surface becomes smoother as acrylic acid concentration increases. This due to the membrane surface is covered by acrylic acid through covalent bond which indicates that the grafting process was successful.

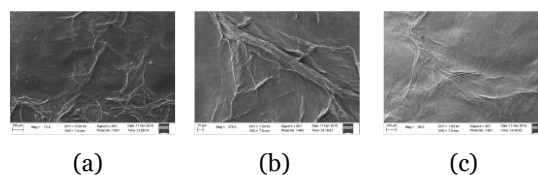


Figure 3. Surface morphology of unmodified and modified BC membrane ((a) 0% acrylic acid, (b) 20% acrylic acid, (c) 50% acrylic acid) with a 100x magnification

D. Degree of Grafting (DG)

Grafting degree is a quantity parameter refer to amount of acrylic acid was grafted onto BC membrane. Figure 4 show that DG increased with increasing of acrylic acid concentration at 5-20%. However, at the further concentration of acrylic acid, DG decrease. It can be

explained that at high concentration, UV-photografting treatment not only generate the grafted BC membrane, but also homopolymer.

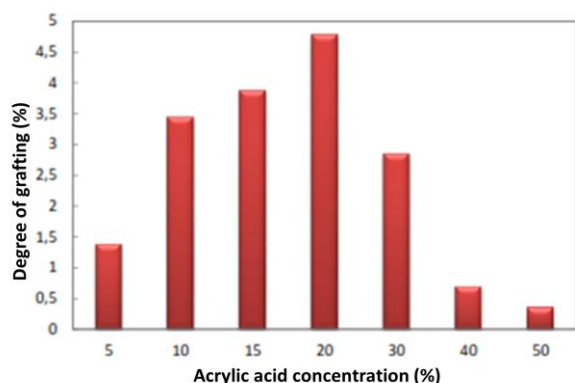


Figure 4. Effect of acrylic acid concentration on the DG

E. Water Absorption

Water Absorption shows the ability of modified BC to absorb water. The results of DSA can be seen in Figure 5. The value of water absorption is determined by the presence of hydrophilic groups from the polymer structure. In this polymer, the group that plays a role in the hydrophilicity is the -OH group of BC. The presence of heat factors accompanying the grafting process can result stronger intramolecular interactions between the -OH groups in the polymer, so that the structure of modified BC is increasingly tight (Susanto *et al.*, 2007).

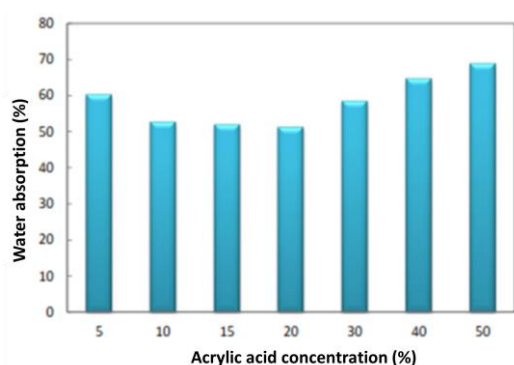


Figure 5. Effect of acrylic acid concentration on water absorption

The high density of the modified BC structure (20%) produced the lowest water absorption capacity (51.22%). This shows that more acrylic acid is grafted on BC, the ability of modified cellulose bacteria to absorb water decreases.

F. Determination of IEC

The results of IEC determination can be seen in Figure 6. The IEC value increases with increasing of acrylic acid concentration. The IEC value increases with the addition of 5-20% acrylic acid, however at a concentration of 30-50% there is a decrease in the IEC value. The highest IEC is 0.34 meq/g obtained by grafted BC membrane with acrylic acid concentration of 20%. IEC show good agreement with DG which at high concentration of acrylic acid (30-50%) both of IEC and DG decreased.

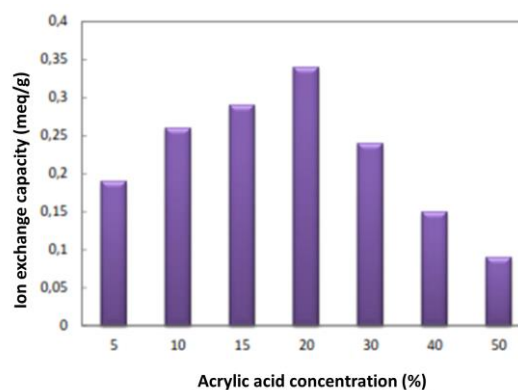


Figure 6. Effect of acrylic acid concentration on IEC

IV. CONCLUSION

BC-based Ion exchange membrane have prepared successfully by UV-photografting technique. Functional group by FTIR and morphology analysis confirmed that BC membrane have grafted by acrylic acid. The effect of acrylic acid concentration on BC membrane properties show that acrylic acid concentration of 20% has highest value for both IEC and DG, however lowest for water absorbancy.

V. ACKNOWLEDGEMENT

This work was supported by Ministry of Research, Technology and Higher Education of the Republic of Indonesia through a fundamental research grant.

VI. REFERENCES

- Aboul-Enein, AM, Salama, ZA, Gaafar, AA, Aly, HF, Bou-Elella, FA & Ahmed, HA 2016, 'Identification of phenolic compounds from banana peel (*Musa paradaisica* L.) as antioxidant and antimicrobial agents', *Journal of Chemical and Pharmaceutical Research*, vol. 8, no. 4, pp. 46–55.
- Agama-Acevedo, E, Sañudo- Barajas, JA, Vélez De La Rocha, R, González-Aguilar, GA, & Bello-Peréz, LA 2016, 'Potential of plantain peels flour (*Musa paradisiaca* L.) as a source of dietary fiber and antioxidant compound', *CYTA – Journal of Food*, vol. 14, no. 1, pp. 117-123.
- Anjum, S, Sundaram, S & Rai, G 2014, 'Nutraceutical application and value addition of banana (*Musa paradisica* L. Variety, "Bhusawal Keli") peel: A review', *International Journal of Pharmacy and Pharmaceutical Sciences*, vol. 6, no. 10.
- Basu, A, Mishra, B & Jan Leong, SS 2013, 'Immobilization of polybia-MPI by allyl glycidyl ether based brush chemistry to generate a novel antimicrobial surface', *Journal of Materials Chemistry*, vol. B1, pp. 4746–4755.
- Basu, A, Vadanani, SV & Lim, S 2018, 'A novel platform for evaluating the environmental impacts on bacterial cellulose production', *Nature Scientific Reports*, vol. 8, pp. 5780.
- Choi, YJ, Ahn, Y, Kang, MS, Jun, HK, Kim, IS & Moon, SH 2004, 'Preparation and characterization of acrylic acid-treated bacterial cellulose cation-exchange membrane', *Journal of Chemical Technology and Biotechnology*, vol. 79, no. 1, pp. 79–84.
- De Oliveira Barud, HG 2016, 'A multipurpose natural and renewable polymer in medical applications: Bacterial cellulose', *Carbohydrate Polymers*, vol. 153, pp. 406–420.
- Devatkal, SK, Kumboj, R & Paul, D 2014, 'Comparative antioxidant effect of BHT and water extracts of banana and sapodilla peels in raw poultry meat', *Journal of Food Science and Technology*, vol. 51, no. 2, pp. 387–391.
- Florea, M 2016, 'Engineering control of bacterial cellulose production using a genetic toolkit and a new cellulose-producing strain', *Proceedings of the National Academy of Sciences of the United States of America*, vol. 113, pp. 3431–3440.
- Foresti, ML, Vázquez, A & Boury, B 2017, 'Applications of bacterial cellulose as precursor of carbon and composites with metal oxide, metal sulfide and metal nanoparticles: A review of recent advances', *Carbohydrate Polymers*, vol. 157, pp. 447–467.
- Hang, T, Vu, Christopher, J, Scarlett & Quan, V, Vuong 2018, 'Phenolic compounds within banana peel and their potential uses : A review', *Journal of Functional Foods*, vol. 40, pp. 238–248.
- Indarti, D & Asnawati 2011, 'Karakterisasi film nata de coco benedict secara adsorpsi untuk sensor glukosa dalam urine', *Jurnal Ilmu Dasar*, vol. 12, no. 2, pp. 200-209 (Indonesian version).
- Ji, L & Srzednicki, G 2015, 'Extraction of aromatic compounds from banana peels', *Acta Horticulturae*, vol. 1088, pp. 541–546.
- Kalemelawa, F, Nishihara, E, Endo, T, Ahmad, Z, Yeasmin, R, Tenywa, MM & Yamamoto, S 2012, 'An evaluation of aerobic and anaerobic composting of banana peels treated with different inoculums for soil nutrient replenishment', *Bioresource Technology*, vol. 126, pp. 375–382.
- Kalia, S & Sabaa, MW 2013, *Polysaccharide Based Graft Copolymers*, Berlin : Springer-Verlag.
- Keshk, SM 2014, 'Bacterial cellulose production and its industrial applications', *Journal of Bioprocessing & Biotechniques*, vol. 4, no. 2.
- Lee, KY, Quero, F, Blaker, JJ, Hill, CAS, Eichhorn, SJ & Bismarck, A 2011, 'Surface only modification of bacterial cellulose nanofibres with organic acids', *Cellulose*, vol. 18, no. 3, pp. 595–605.
- Muhsinin, S, Putri, NT, Ziska, R & Jafar, G 2017, 'Bacterial cellulose from fermented banana peels (*Musa paradisiaca*) by *Acetobacter xylinum* as matrix of biocellulose mask', *Journal of Pharmaceutical Sciences and Research*, vol. 9, no. 2, pp. 159–162.
- Pereira, A & Maraschin, M 2015, 'Banana (*Musa spp*) from peel to pulp: Ethnopharmacology, source of bioactive compounds and its relevance for human health', *Journal of Ethnopharmacology*, vol. 160, pp. 149–163.
- Purwanto, A 2012, *Produksi Nata Menggunakan Limbah Beberapa Jenis Kulit Pisang*. Madiun: Widya Warta (Indonesian version).
- Rattanavichai, W & Cheng, W 2015, 'Dietary supplement of banana (*Musa acuminata*) peels hot-water extract to enhance the growth, anti-hypothermal stress, immunity and disease resistance of the giant freshwater prawn, *Macrobrachium rosenbergii*', *Fish Shellfish Immunology*, vol. 43, no. 2, pp. 415–426.
- Roy, D, Semsarilar, M, Guthrie, JT & Perrier, S 2009,

- 'Cellulose modification by polymer grafting: A review', Chemical Society Reviews, vol. 38, no. 7, pp. 2046–2064.
- Shahi & Vinod, K 2007, 'Highly charged proton-exchange membrane: sulfonated poly(ether sulfone)-silica polyelectrolyte composite membranes for fuel cells', Solid State Ionics, vol. 177, pp. 3395-3404.
- Susanto, H, Balakrishnan, M, & Ulbricht, M 2007, 'Via surface functionalization by photograft copolymerization to low-fouling polyethersulfone-based ultrafiltration membranes', Journal of Membrane Science, vol. 288, pp. 157-167.
- Vu, HT, Scarlett, CJ & Vuong, QV 2018, 'Phenolic compounds within banana peel and their potential uses : A review', Journal of Functional Foods, vol. 40, pp. 238–248.