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Characterization of Mussel Inspired Surface Modified and Metal Chelated Polymer Membrane

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Abstract*: Modification of a membrane surface is critical to help further functional protein binding on the membrane. Mussel inspired modification and metal chelating agent grafting on the polyvinylidene fluoride (PVDF) is proposed to increase the hydrophilicity, stability, and functionality of the membrane. This study carried out a four steps modification including polymerization of dopamine, grafting with poly (ethyleneimine) (PEI) and metal chelating agent and finally metal (ZnO) coupling. Characterization of the modified membrane was carried out using contact angle observation, permeate flux analysis, FT-IR spectrum and FESEM analysis. The results show a successful PDA and PEI deposition on PVDF membrane with significant improvement of the membrane hydrophilicity and wettability. Permeate flux analysis showed blockage on membrane surface due to the successful coating. Absorption peak increased slightly showing the deposition of PDA/PEI. Successful Zn2+ ion coupling can be seen clearly from the FESEM analysis

***Keywords* : Membrane Characterization, Metal Chelation, Polymer Membrane, Surface Modification**

I. INTRODUCTION

Massive growth of industrial activities such as petrochemical and food industries are actually causing fresh water supply depletion rapidly. The industries use large amount of fresh water while consequently producing a large volume wastewater. Authorities are trying hard to handle this situation by increasing the environmental regulations worldwide. This situation motivates many efforts to look for a highly efficient and cost-effective method to purify contaminated wastewater [1]

With high separation efficiency, using low energy, simplicity and ease of operation; polymer membrane has been rapidly studied to be use in wastewater treatment technology [2][3]. However, membranes are limited in term of severe fouling by contaminants that is causing rapid flux decline and making the process not economically feasible [4].

Polymer membrane, polyvinylidene fluoride (PVDF) for example; is strongly hydrophobic that will lead to low water flux and biofouling that will eventually results in a sharp decline of performance [2][5][6].

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Membranes from cellulose derivatives on the other hand; are unstable because it could swell easily by water during the treatment process [7][8].

In order to minimize fouling, we need the membrane to be favorable to water compared to other components. Therefore; researchers are looking for modifying method of the membrane surface in order to increase the hydrophilicity [2][3]. Apart from that, modification of membrane surface increase and verifies the membrane's potential. Membrane surface modification using polydopamine (PDA), a component in the glue-like biologically produced by marine mussel has recently becoming an interest. This is basically because of the many advantages of this method such as simple to execute, serve many purpose, stable coating, easy to manage, and causing very low damage to the membrane compared to other methods [9][10]. Preparation of the membrane using dopamine solution will cause it to self-polymerizes yielding polydopamine (PDA) on the membrane surface. PDA, containing both catechol and amine groups, was discovered to be a simple surface coating method in 2007 [11]. Polymerization process happened because of the oxidation of DA at basic pH and crosslinking between the catechol groups, thus giving a structural stability to the coating. Once ready, the formed PDA coating can now form covalent and non-covalent bonds with the membrane based on the type of the membrane used [5].

With the prepared active PDA surface membrane, an amino-rich polymer, polyethyleneimine (PEI), can simply be immobilized onto the membrane. Further modification with PEI will increase the membrane hydrophilicity and eventually increase permeability of water [12]. PEI also reacts with PDA molecules forming covalent bonds that help to accelerate the polymerization process and increase the coating stability.

Preparing polymer membrane with PDA and PEI help the process of metal chelating to the membrane surface. Chelation is a metal sorption mechanism on complex formation. Modified commercial membrane has been reported to enhance adsorption of metal ions [13]. As interest on using enzymes to help in wastewater management growing, this strategy could be used to bond enzymes with the metal-binding residues of histidine, lysine and glutamic acid on proteins and the metal ions (such as Zn^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+} and Co^{2+}) [14]. Mussel-inspired surface functionalization metal chelated membrane is being studied due to its excellent hydrophilic properties, and high potential to become a platform for protein affinity binding, which could prepare a good microenvironment for the enzymes.

By maintaining the enzyme on the membrane; the enzymatic membrane reactor can reuse enzymes continuously, secure enzyme stability, and extract the product to relieve the product inhibition effect [15].

II. MATERIALS AND METHOD

A. Materials

Commercial Polyvinylidene Fluoride (PVDF) membrane obtained from Synder filtration, US, 90% ethanol, deionized (DI) water, Ultrapure Water, Dopamine Hydrochloride purchased from Synder filtration, US , tris-HCl buffer made up from fuming 37% Hydrochloric Acid purchased from R&M chemical and Trizma® Base purchased from SIGMA Life Science, Polyethyleneimine (PEI) with 50% Water Solution purchased from Solarbio Life Science, Chloroacetic acid sodium 98% salt purchased from ACROS ORGANICS , Sodium Hydroxide (NAOH) and Zinc Oxide (99%) from Systerm.

B. Membrane Preparation

The PVDF membrane was sized according to the Amicon cell holder. The approximate area of the membrane use in this experiment is 13.4 cm^2.All 5 prepared membranes were cleaned according to manufacturer's instruction. After that, all membrane was soaked in 50% ethanol for 30-40 min and then, in deionized (DI) water. The clean membrane than was assembled in the Amicon cell and the membrane skin layer was placed facing the feed.

C. Grafting with PEI

10 ml PEI solution (2 g/L) was prepared and then stirred in the cell at 100 rotation per minute (rpm) for 5 hours with the cell closed at 60°C. The membrane is then rinsed again after that.

D. Grafting with Metal Chelating Agent and Metal Coupling

The modified membrane was then soaked in 4 g/L sodium chloroacetate in ultrapure water, pH 12 at 60°C, for 12 hours and 120 rpm, to form IDA groups. After that, metal ions (Zn^{+2}) coupling will be carried out by soaking the membrane in a 0.4 M of Zinc Oxide (ZnO) in ultrapure water at room temperature for 8 hours at 120 rpm.

E. Characterization of Surface Modified Membrane

The colour changes observation was carried out after each modification step to see the effect of modification to the membrane. The modified membranes were then surface characterized using a few methods to proof the success of modification.

- *Surface wettability.* Surface wettability of membranes with water was determined using a static contact angle measuring system (DSA 30E, Krüss, Hamburg, Germany) and the sessile drop method with a distilled water.
- *Permeation Properties.* The pure water flux test was carried out for the measurement of water permeation. The experiment runs at room temperature and pressure of 1.0 bar. The permeate through the membrane was gathered for every 3 min until 15 min. The permeate water flux (PWF) was estimated by using equation:

$$F = \frac{V}{S.t} \quad (1)$$

Where,

F = the water flux (L/m^2h)

V = the volume (L) of water through the device in a given period of time (h)

S = the effective area (cm^2) of the membrane

t = the penetration time (h)

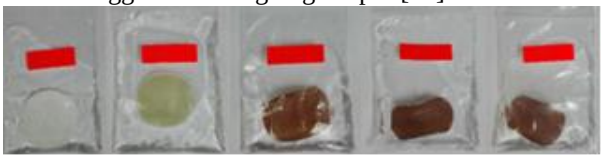
- *Chemical composition on Membrane surface.* Fourier transform IR (FTIR) measurements were taken in attenuated total reflection (ATR) mode and as transmission spectra with the Vector 22 FTIR spectrometer (Bruker Corporation, Billerica), and a diamond cell (Golden Gate Specac). The spectra were recorded in the range of 4000–500 cm^{-1} at a spectral resolution of 2 cm^{-1}.
- *Membrane surface morphology analysis.* The morphology of membrane after water flux was analyzed using field emission scanning electron microscopy (FESEM, Zeiss Supra 40VP). The surface and cross-section of the membranes were observed by photographing FESEM images at 500-1000x magnification.

III. RESULTS AND DISCUSSION

A. Colour Observation

The surface colour of the membranes was observed in order to see the changes between clean PVDF and surface modified PVDF with PDA, PDA/PEI, IDA and Zinc Oxide (ZnO). Based on Fig. 1 (a) and Fig. 1 (b), the colour surface of membrane change from white to light brown/yellow after clean PVDF membrane deposited in black and opaque dopamine solution for 30 minutes. The colour surface of membrane further changed to brown/dark brown after membrane surfaces decorated with PDA deposited in transparent PEI solution for 5 hours. This can be seen in Fig. 1 (c). In Fig. 1 (d), the colour of membrane surface further went darker showing a successfully decorated membrane forming IDA group after 12 hours soaking [2][12].

After that, the modified membrane soaked in ZnO for 8 hours and showed no significant change colour after metal ion (Zn^{+2}) coupling with modified membrane based on Fig. 1 (e). As the colour changes darker, the reaction on the membrane surface is suggested to be going deeper [16].



(a) (b) (c) (d) (e)

Fig. 1. Colour Observation for (a) Clean PVDF, (b) PDA, (c) PDA/PEI, (d) PDA/PEI/IDA, and (e) PDA/PEI/IDA/ZnO decorated membrane

B. Surface Wettability

Surface wettability was determined through water contact angle (WCA) readings. The surface wettability indicates membrane hydrophilicity where it is a crucial factor in the purpose of surface modifying the membrane. The trend in WCA of various PVDF membranes modification are shown in Fig. 2. WCA of clean PVDF membrane is seen to be larger than PVDF membrane after modification with PDA, PDA/PEI, IDA and ZnO. This indicates that surface coating endows the membranes with higher hydrophilicity compared to the clean PVDF membrane which without the surface coating [5][17]. WCA angle of clean PVDF membrane at 68.70° ± 0.1° is reduced after coating by PDA to 60.70°± 0.2° showing the improvement of membrane surface hydrophilicity [18].

After incorporating PEI on the membrane, the surface hydrophilicity of the modified membranes further improved showing a static contact angle reduced to an average of 53.60°[19]. High amount of amino groups in PEI improves the hydrophilicity significantly, and the crosslinking reaction between PDA and PEI speed up the deposition process. It also encourages the diffusion of PDA/PEI components into the membrane pores. Because of the deposition process of PDA mainly depend on the oxygen diffusion in the dopamine solution, the deposition process is quite time consuming without PEI incorporation [18]. After modified membrane was further soaked in sodium chloroacetate to form IDA group and ZnO metal coupling, WCA first reduced further to 33.65°± 0.25° and then raised a little to an average of 38.80° respectively. Metal coupling on membrane surface reduced the WCA significantly as shown in the Fig. 2 [20].

C. Permeation Properties

Based on Fig. 3, the clean PVDF membrane flux was 134.33 L/m^2 h, while the water fluxes of PDA decorated membrane and PDA/PEI membranes were 95.95 L/m^2 h and 67 L/m^2 h, respectively. Water flux is mainly affected by the surface hydrophilicity. Membrane holes blockage by the coating compound was causing the decrease of water flux through the membrane. The reaction between dopamine and PEI enhances the stability of the coating of membrane surface, which signifies the success of PDA/PEI coating on the surface of PVDF membrane [19].

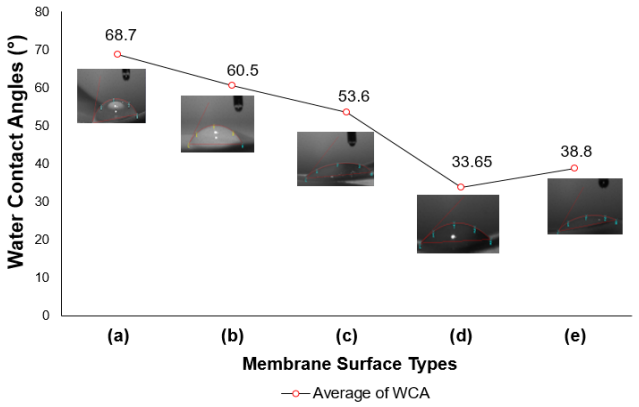


Fig. 2. WCA for a) Clean PVDF membrane, (b) ,PDA (c) PDA/PEI, (d) PDA/PEI/IDA, and (e)PDA/PEI/IDA/ZnO decorated membrane

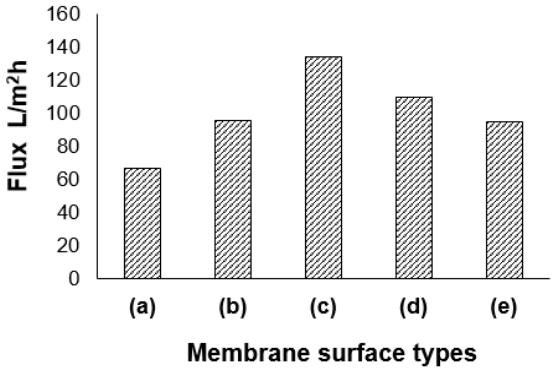


Fig. 3. Permeated flux for a) Clean PVDF membrane, (b) PDA, (c) PDA/PEI, (d) PDA/PEI/IDA, and (e)PDA/PEI/IDA/ZnO decorated membrane

D. Chemical Composition

From Fig. 4 (a), the bare PVDF membrane bands at 876.00 cm^{-1} involving C-C group that show the actual structure of PVDF membrane [21]. Absorption peaks around 1600.00 cm^{-1} and 1650.00 cm^{-1} assigned to C=C resonance vibrations in the aromatic rings can be seen after PDA modification on the membrane surface [Fig. 4(b)-(e)]. N–H bending were identified after being decorated with PDA as seen in Fig. 4 (b). This indicate significant amount of polydopamine was coated on PVDF membrane surface [17][18]. The adhesiveness of polydopamine is due to various functional groups such as amino, hydroxyl and catechol [11]. Apart from that, broad peak observed were observed between 3000.00 and 3600.00 cm^{-1} on the PDA/PEI decorated membrane surface. It is showing the N-H stretching that is abundance in PEI, and O-H stretching in the amine and hydroxyl-functional groups as they are coated on the membrane surface [12]. Finally in Fig. 4 (e), the peaks at 1652.00 cm^{-1} is showing the Zn-O stretching after the modification [22].

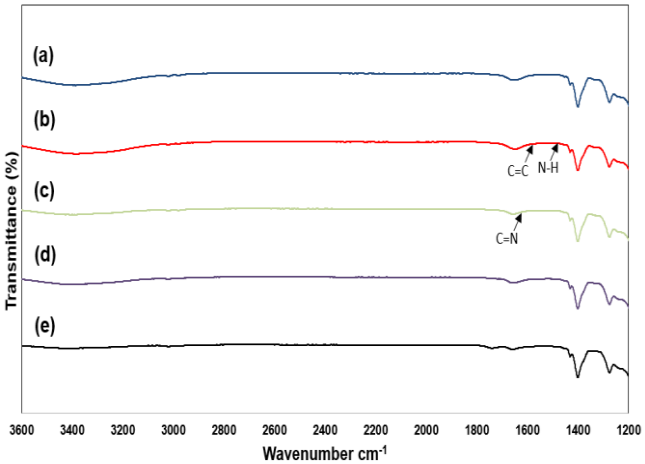
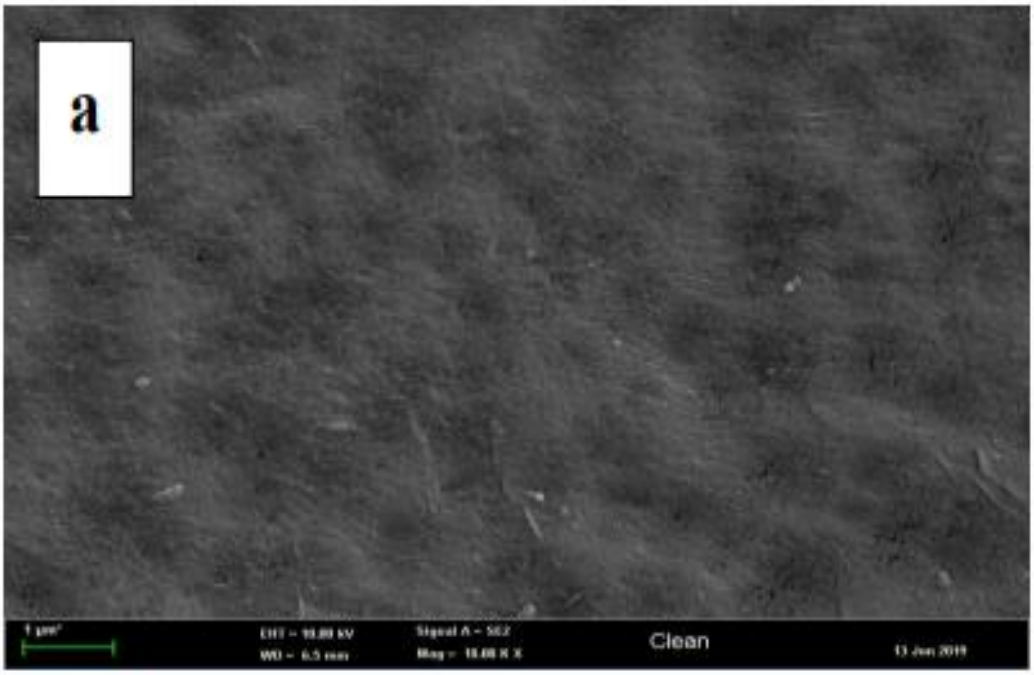


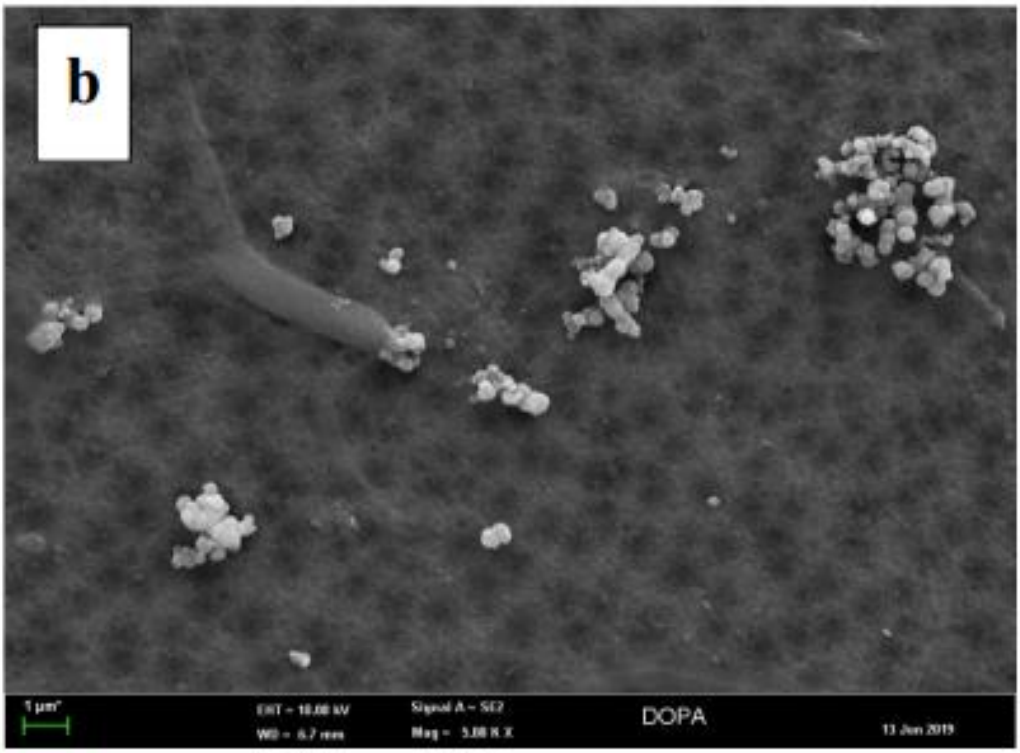
Fig. 4. FTIR reading for (a) Clean PVDF, (b) PDA, (c) PDA/PEI, (d) PDA/PEI/IDA, and (e) PDA/PEI/IDA/ZnO decorated membrane

E. Surface Morphology

The top surface morphology of the modified membrane and unmodified membrane was shown in Fig. 5. Fig. 5 (a) below shows the surface and cross- sectional structure of clean PVDF membrane surface that is smooth with abundant pores. In Fig. 5 (b), the membrane pores showed reduction due to coated the surface with polydopamine (PDA) which blocked the membrane pores. The deposition of dopamine (DA) formed agglomerates on the PVDF membrane surface and cause the surface roughness of PVDF membrane to increase [9].

Finally, in Fig. 5 (c) which is the modified PVDF membrane grafted with ZnO shows present of many smaller particles with rod shape [22]. It concludes the success of metal ion coupling (Zn^{+2}) on membrane surface. Successful grafting is important for further protein binding on membrane and the potential of the membrane is now high.





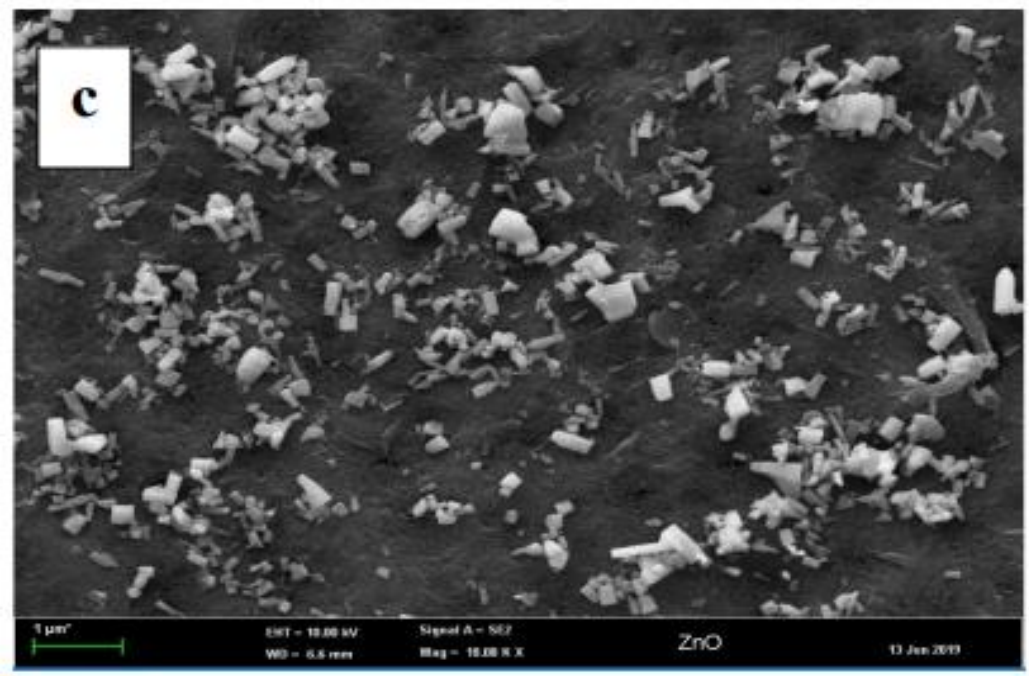


Fig. 5. FESEM Image of (a) Clean PVDF, (b) PDA, and (c) PDA/PEI/IDA/ZnO decorated membrane

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