

An Integral Membrane from A Blend of Quaternized Polyvinyl Alcohol/Chitosan/Polysulfone

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KEYWORDS	ABSTRACT
Quaternized PVA Scratch Integral membrane Modified quaternization process Heavy metal Wastewater treatment	Polyvinyl Alcohol (PVA) is a polymer that can be created through the hydrolysis process of polyvinyl acetate. PVA can be applied in various industries such as medical and paper production industries as well as in membrane fabrication for wastewater treatment due to its properties such as good biocompatibility and hydrophilicity and low protein absorption. However, higher performance of PVA is being sought in order to increase the effectiveness of using PVA in the industries. Quaternization technique was introduced to enhance the performance of PVA in term of enhancing the water perm-selectivity, hydrophilicity, and the ionic conductivity of the PVA. This paper demonstrated the production process of quaternized PVA that was then subsequently formulated as integral membrane with a blend with polysulfone and chitosan, and crosslinked with tetraethylorthosilicate. Based on the FTIR analysis and visual observation on the fabricated membrane, it was proven that the quaternized PVA was successfully produced through the modified process. The fabricated membrane has potential to be used in various applications such as wastewater treatment and heavy metal separation. Further research and study on the characterization and performance testing of the integral membrane must be conducted.

1.0 INTRODUCTION

Recent development in technologies all over the world have brought upon advancement in the multiple industries particularly the food industries such as the development of the production of Kappaphycus (seaweed) in Philippines (Hurtado et al., 2015), the development of fish farming through the probiotics application (Benerjee & Ray, 2017), the advancement in the non-conventional food sterilization (Li & Farid, 2016) as well as the food production method through high hydrostatic pressure method (Yamamoto, 2017). Other than the food industries, the chemical manufacturing industries that includes the organic electrosynthesis, the efficient

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electrochemical processing (Orella et al., 2018), the development of carbon nanotube transparent conductive films (Yu et al., 2016) and the development of alternative fuels that can be utilized in the cement manufacturing process (Rahman et al., 2015) are also positively influenced. These developments undeniably brought multiple benefits, but it has drawbacks such as the production of large amount of waste. The wastewater produced from these industries commonly contains high content of fat, biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), nitrogen, phosphorus and also various types of pathogens (Damasceno et al., 2018; Su et al., 2015; Varela & Manaia, 2013; Yaakob et al., 2018). In addition to that, the wastewater also contains metals such as iron, nickel, lithium, magnesium and zinc (Ugulu et al., 2019; Tunc & Sahin, 2017).

The ever-increasing amount of wastewater has demanded water treatment processes to be ran effectively to avoid numerous health issues such as diarrhoea, intense vomiting, stomach cramps and liver infections. Few wastewater treatments are currently being utilized in the industries to treat the effluents namely solvent extraction, adsorption using activated carbon, biosorption, membrane separation, electrochemical treatment as well as nanofiltration (Crini & Lichtfouse, 2019). However, there are some limitations that preventing from implementations of these methods that are high capital cost, ineffective removal of certain metals, high chemical consumption, high energy and maintenance cost as well as slow and sluggish processes nanofiltration (Crini & Lichtfouse, 2019). In contrast to that, membrane separation method is capable in treating various sources of wastewater through tailoring made of the membrane's properties by incorporating suitable additives during the fabrication of membrane (Ahmad et al., 2018).

Furthermore, membrane separation process is a mild process and requires no addition of a solvent that make it environmentally friendly process. From the classes of membrane filtration, nanofiltration membrane is widely used for heavy metal removal due to its suitable pore size, distinctive surface electric charges and their ability to separate monovalent and divalent/multivalent ions (Li et al., 2019). However, for efficient separation of multi valent cations such as Mg^{2+} and Ca^{2+} , positive charged membrane is preferred since the separation occurs according to Donnan exclusion (Li et al., 2015). Among the organic polymers polyvinyl alcohol (PVA) are widely utilized in the fabrication of membrane respectively owing to its biodegradability, chemically resistance as well as having exceptional physical properties (Voronova et al., 2015). Additionally, polyvinyl alcohol also has high water solubility, high optical transmission, stable thermal nature as well as noncorrosive nature that can be applied in various applications including heavy metal removal (Aslam et al., 2018).

To enhance on heavy metal removal, PVA was blended with chitosan as it contains large number of $-NH_2$ and $-OH$ groups as excellent biosorbent for heavy metal ions (Liu et al., 2013). The blend was then cross-linked with inorganic material such as tetraethylorthosilicate (TEOS) by sol-gel method to stabilize the polymer blend from degradation and improve its chemical resistance and mechanical properties (Kumar et al., 2009) The hydrophilic polymers could not stand alone as the membrane and it must be blended with other polymers such as polysulfone. Polysulfone is widely used due to its good physico-chemical, mechanical and hydraulic stability. The blend of polysulfone with hydrophilic polymers could also overcome issue of high fouling and low permeability towards water due to its hydrophobic nature, which has given an impact on its service life (Leo et al., 2012). Despite its good properties, for a wider application of polyvinyl alcohol, quaternization process is performed as this process can improve water perm-selectivity, conductivity values, resistance towards chemicals and also provides modification on the surface charge of the material (Lin et al., 2017; Liao et al., 2015). The degree of quaternization of the polyvinyl alcohol (PVA) (Lin et al., 2017) might affect the surface charge of the membrane which make it more positively charged that may influence its application in the industries.

1.1 Polyvinyl Alcohol (PVA)

Polyvinyl Alcohol is a polymer that was introduced by both Hermann and Haehnel in year 1924 through the saponification process of polyvinyl ester in the sodium hydroxide solution (Muppalaneni, 2013). Polyvinyl alcohol is one type of organic polymers which is cream and whitish, odourless as well as nontoxic (Xu et al., 2020). The abundant of hydroxyl group that presence in the polymer structure causes the PVA to be biodegradable and possesses hydrophilic property to make it highly water-soluble (Gaaz et al., 2015).

The production of PVA commonly through the polymerization of vinyl acetate to polyvinyl acetate which is then followed by the hydrolysis process to produce polyvinyl alcohol (Zhang & Van Le, 2020; Thong et al., 2016). The percentage hydrolysis during this process together with the molecular weight of the PVA can affect the properties of the PVA itself. The molecular weight of PVA usually range between 20,000 g/mol to 400,000 g/mol with different properties that includes but not limited to viscosity, water resistance and tensile strength for different value of molecular weight (Leo et al., 2012; Thong et al., 2016). Other than that, the hydrolysis of PVA also may differ where the percentage of hydrolysis can be categorized into three, partially hydrolysed, moderately hydrolysed and completely hydrolysed with hydrolysis percentage of 84.2% to 89%, 92.2% to 96.5% and 98% to 99% respectively (Leo et al., 2012). Different percentage of hydrolysis affects the flexibility and water sensitivity of the material. Figure 1 shows the structural formula of both partially hydrolysed PVA and fully hydrolysed PVA which shows significant different between the two PVA.

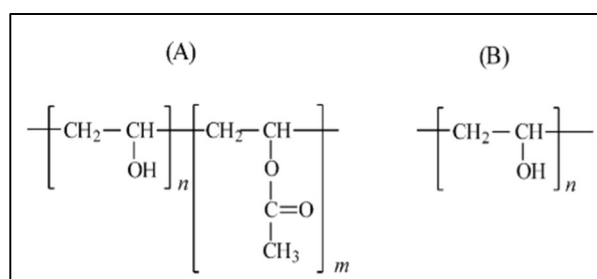


Figure 1: The Structural Formula for Both Partially Hydrolysed PVA (A) and Fully Hydrolysed PVA (B) life (Demerlis & Schneker, 2003)

1.2 Quaternized Polyvinyl Alcohol (QPVA)

The establishment of the quaternary ammonium group in the quaternized polyvinyl alcohol makes the material possess enhanced water perm-selectivity and hydrophilicity, which makes it more versatile and adaptable to be utilized in various applications (Lin et al., 2017; Liao et al., 2015). In addition, the conductivity values of QPVA have been proven to be higher compared to the conductivity of PVA due to the introduction of the ammonium functional group (Liao et al., 2015). Figure 2 shows the chemical structure of the quaternized polyvinyl alcohol.

Quaternized polyvinyl alcohol (QPVA) can be utilized as an alternative polymer membrane that is able to be applied in the direct methanol fuels cells (DMFC) and direct ethanol fuel cells (DEFC), which are used as an alternative power generator (Zulfirdaus Zakaria & Kamarudin, 2020). Additionally, a blend of QPVA/chitosan also being applied as effective hydroxide conducting electrolyte. The electrolyte commonly being used as batteries which contain higher maximum power densities that increase the life expectancy of the batteries. This is due to the in-plane swelling ratio of the nano-composite of QPVA that can be achieved without sacrificing the alkali uptake level (Liao et al., 2015). Gopi et al. (2019) has developed anion exchange membrane from quaternized polyvinyl alcohol and chitosan respectively, then cross linked with glutaraldehyde. It was found that the mixed matrix membrane exhibits enhanced alkaline stability

until 300 hours with lesser conductivity loss. Furthermore, the quaternization process has improved the thermal stability of the membrane.

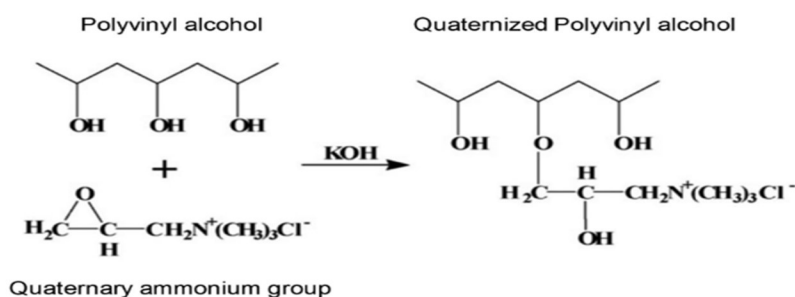


Figure 2: The Chemical Structure of the Quaternization Reaction of Polyvinyl Alcohol (Zulfirdaus Zakaria & Kamarudin, 2020)

1.3 The characteristics of membrane from quaternized PVA

1.3.1 Membrane Morphology

Based on the previous study by Liao et al. (2015), the quaternization of PVA was performed using glycidyltrimethyl ammonium chloride (GTMAC). The QPVA was then blended with chitosan and cross linked with molybdenum disulfide (MoS_2) to produce membrane. Figure 3 shows the cross-sectional image of the QPVA/Chitosan membrane obtained from the Scanning Electron Microscopy (SEM) analysis. The SEM image portrays a smooth and homogenous structure of the membrane (Liao et al., 2015).

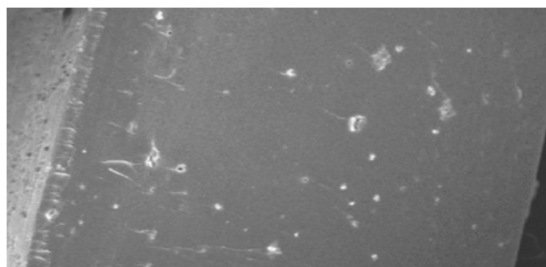


Figure 3: The SEM Images of the Cross-Section View of the QPVA/Cs Membrane (Liao et al., 2015)

In addition to the characterization of QPVA, the X-Ray Diffraction (XRD) analysis was also performed. As shown in Figure 4, the result was obtained from study conducted by Zakaria & Kamarudin (2020). Both QPVA and PVA membranes shows the peak around the same degree which is around $2\theta = 19.6$ but with different intensity where the intensity for the QPVA is lower compared to the PVA membrane. The lower intensity on the peak of the QPVA membrane shows the reduction of crystal line structures of PVA polymer matrix through the presence of quaternary ammonium functional group that aids to balance the amorphous structure which promote better properties towards the membrane. The strong interaction between the polymer is the caused for the decrease of the crystallinity of the membrane where the hydrogen bonding of the polymer could be destroyed due to the interaction which result in the reduction of crystallinity. The high crystallinity of membrane limits the mobility and the ion exchange capacity of the membrane, hence the lower crystallinity of the QPVA membrane indicates the better properties of QPVA as membrane.

This paper describes the process of preparing the quaternized polyvinyl alcohol (QPVA) that was further incorporated into the formulation of integral membrane from a blend of

QPVA/Chitosan/Polysulfone where the functional group and physical characteristic were analyzed.

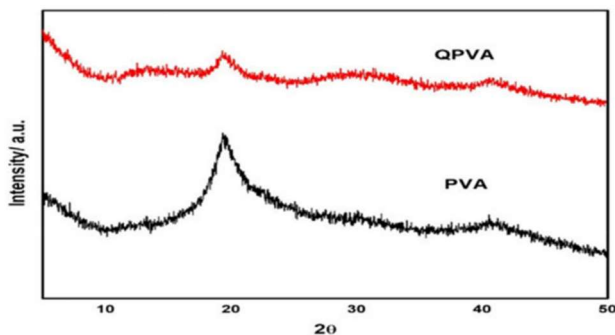


Figure 4: X-Ray Diffraction (XRD) Analysis [31]

2.0 MATERIALS AND METHODS

In this section, QPVA was produced by using the method adapted from Liao et al. (2015), Jiang et al. (2018), and Kassim Shaari et al. (2019) with some modifications.

2.1 Materials

Materials involved in the process include Polyvinyl Alcohol (PVA) with hydrolysis degree of 87%-89% (MW: 85000 – 124000) pellets, Polysulfone resin pellets (MW: 44000 – 53000), commercial Chitosan (deacetylation degree $84.4 \pm 12\%$), Tetraethylorthosilicate (TEOS) with 99% purity, Chloro Hydroxypropyl Trimethylammonium Chloride (CHTAC), Potassium Hydroxide (KOH), Hydrochloric Acid (HCl) with 37% purity as catalyst. All the chemicals are purchased from Merck Malaysia.

2.2 Methods

2.2.1 Preparation of quaternized PVA

10 g of PVA was dissolved in 90 mL of Dimethyl Sulfoxide (DMSO) with heating at 90°C under continuous stirring at 400 rpm for 4 hours until the solution mixture become homogenous with a viscous and transparent appearance. The solution was cooled to 65°C, and then 15 g of CHTAC with 15 g of KOH was added to the solution. It was followed with heating at 90°C and stirring at 400 rpm for 4 hours.

2.2.2 Preparation of hybrid membrane solution

The produced QPVA was mixed with chitosan to form the hybrid membrane solution. For the chitosan solution, 2wt% of acetic acid was used to dissolve 0.02 g of chitosan under vigorous stirring at 400 rpm at 90°C. The QPVA solution was then mixed with the chitosan solution to create a blend mixture. Subsequently, 0.5 wt% of TEOS that acts as a cross linker was added to the mixture. 1 mL of hydrochloric acid with 37 wt% concentration as catalyst was added into the solution. Then, the solution was heated to 40°C under constant stirring at 400 rpm for 7 hours. The above procedures were repeated for another concentration of QPVA which was 25 g and without the addition of TEOS.

2.2.3 Preparation of integral membrane

The integral membrane was prepared by mixing the polysulfone solution with the hybrid QPVA. The polysulfone solution was prepared through the mixing of 13 g of polysulfone, 5g of polyethylene glycol and 82 g of N-methylpyrrolidone with continuous heating at 80°C and stirring at 750 rpm for 3 hours. Then, 50 g of the solution was mixed with 1 g of QPVA membrane solution

prepared in Section 2.2.2. The mixture was heated at 80°C and stirred continuously at 600 rpm for 3 hours. The mixture was then left at room temperature. The mixture was poured on the glass plate, spread homogeneously using a film applicator before the film and plate were soaked into a large amount of water. The membrane film was then removed from the water after 1 day. Figure 4 shows the resulted membrane.

2.2.4 Characterization of membrane

The Fourier Transform Infrared Spectroscopy (FTIR) was performed by using the (Perkin – Elmer Spectrum 2000). The instrument was used to identify the functional groups structure of the membrane. The wavelength between the range of 400 cm^{-1} to 4000 cm^{-1} was used to evaluate the membrane sample.

3.0 RESULTS AND DISCUSSION

As shown in Figure 5, based on visual observation, a defect free membrane was produced from the modified quaternization process.

The FTIR spectra for the fabricated integral membrane was shown in Figure 6. Based on the figure, there are several peaks were observed. These results can be compared with the one reported by Zakaria & Kamarudin (2020) on the formulation of quaternized PVA as shown in Figure 7 and Jiang et al. (2018) on the formulation of membrane from the blend of QPVA/Chitosan/Molybdenum Dilsulfide (MoS_2) as shown in Figure 8 respectively. The pattern shown is similar to the pattern of FTIR analysis of PVA where there are common peaks at 1245 cm^{-1} and 1150 cm^{-1} due to strong absorption peak of C-O of the spectra as shown in Figure 7. Based on the figure, besides the common peak of PVA at 3399 cm^{-1} and 1643 cm^{-1} , the QPVA exhibits an additional peak bending at wavelength of 968 cm^{-1} which indicates the presence of ammonium quaternary group. The FTIR analysis also shows the deforms of aliphatic bending of backbone chain of the PVA at 686 cm^{-1} which was due to the interaction of grafting process between the polymer backbone and the quaternary ammonium functional group (Gopi et al., 2019). As for the spectra from the fabricated integral membrane in Figure 6, there is a peak at 914 cm^{-1} , which represents C-N group of the QPVA, which is similar with the spectra shown in Figure 8. This finding has proven that the PVA has successfully been quaternized through the modified process (Jiang et al., 2018). From Figure 6, peak at 2969 cm^{-1} was assigned to amine band from chitosan. The cross-linking process from TEOS by formation of Si-O-C bond was portrayed at 1105 cm^{-1} . Overall, similar trend of the spectra was shown by the fabricated integral membrane with that in Figure 8 that uses the same type of polymer blend, which further proven the quaternization process was managed to be conducted through the modified process.



Figure 5: A defect free membrane

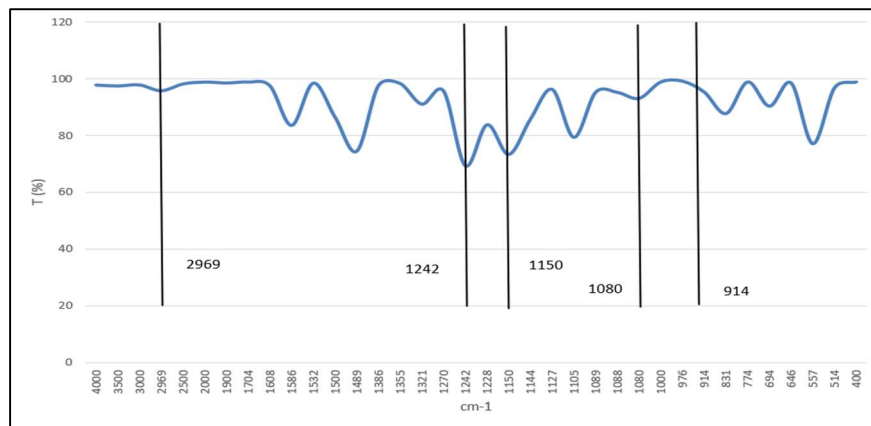


Figure 6: FTIR spectra for the integral membrane

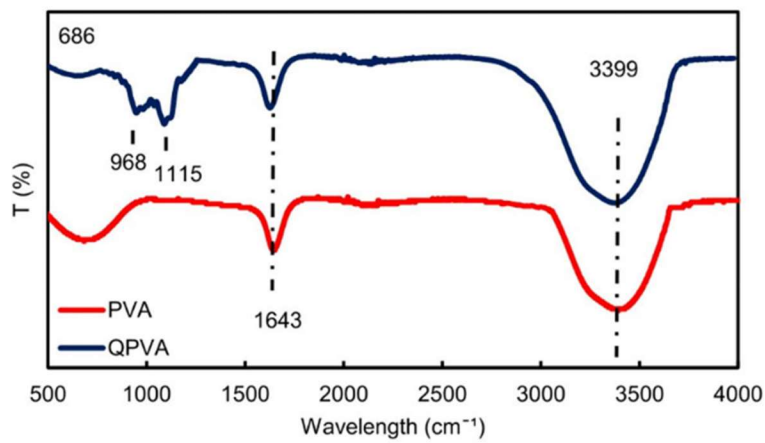


Figure 7: FTIR Analysis of PVA and QPVA ((Zulfirdaus Zakaria & Kamarudin, 2020)

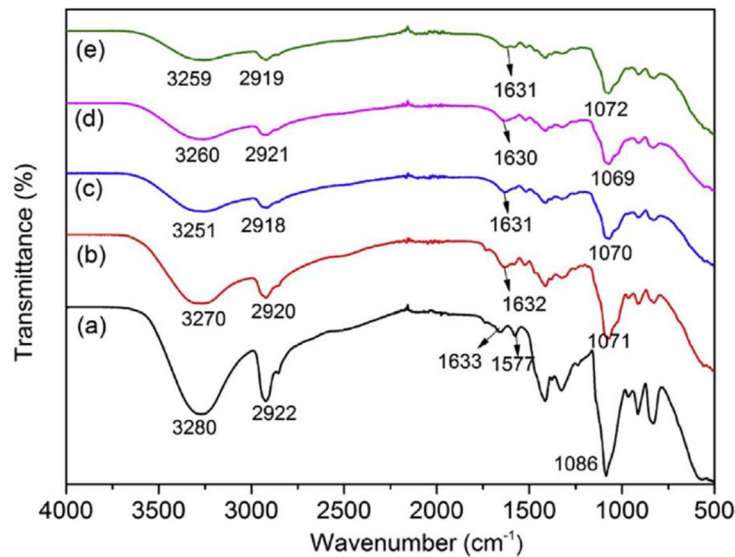


Figure 8: The FTIR Spectra of QPVA Mixtures with Different Concentration [33] (a) QPVA/CS, (b) QPVA/CS/ MoS₂-0.1, (c) QPVA/CS/ MoS₂-0.2, (d) QPVA/CS/MoS₂-0.5 and (e) QPVA/CS/ MoS₂-1.0

4.0 CONCLUSION

The modified quaternization process was successful to produce a defect free of membrane. Furthermore, the result from FTIR analysis proves that the quaternization process has taken place. Further studies and research have to be conducted to investigate the most optimum condition of usage of QPVA application as membrane as well as its limitations.

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