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Fabrication and Characterisation of Polyvinylidene Fluoride Co-Hexafluoropropylene Polymer Inclusion Membranes for Reactive Orange 16 Dye Removal

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Abstract. By implementing green technology, polymer inclusion membranes (PIMs) were used as an extractant for the removal of Reactive Orange 16 (RO16) dye as it is an easy and effective way. The extraction process is used because it is found to be more economical and effective compared to other dye removal methods. The PIMs consists of Polyvinylidene Fluoride Co-HFP (PVDF-Co-HFP) as a base polymer, Aliquat 336 as a carrier; dissolved in tetrahydrofuran (THF). The formulation of the components was varied to determine the optimum composition of PIMs with the effective extraction ability. The PIMs was characterised by Fourier Transform Infrared spectroscopy (FTIR), ion exchange capacity (IEC), water uptake, contact angle and Universal Testing Machine (UTM) methods to determine the physical, mechanical and chemical properties of the PIMs. Various parameters such as effect of carrier, initial dye concentration and pH were investigated. The optimum extraction of RO16 dye at 99.62% were obtained at PIMs were 9 % of carrier,10 mg/L initial dye concentration, pH 2 and agitation speed of 500 rpm at room temperature for 4 hrs. This proven that the fabricated PIMs has potential in removing dye.

1. Introduction

Dyes can be categorised as a chemical compound which releases colour on the surface which it binds. The execution of huge amounts of wastewater which contain industrial textile colouring agents can affect the water quality and cause eutrophication which lead to a serious threat to health of public [1]. The release of small amount of dyes which is below 1 ppm into the waterways can lead to severe pollution as dye contain carcinogenic substances [2]. Reactive orange 16 (RO16) can be categorised under the group of azo reactive dye. It has its own benefits such as high water solubility, covalent bonding with both synthetic and natural textile fiber and excellent colouring properties [3]. Reactive azo dye is one of the dyes which is frequently produce and widely used. It can pollute the environment due to highly toxic and mutagenic properties. This dye can easily absorbed into organism's body through inhalation or swallowed which cause irritation in digestive tract to mammalian cells, eyes and skins due to its water soluble properties [4]. Thus, the contamination of dye in water must be treated prior to discharged in order to avoid severe water pollution. Removal of dye from wastewater can be accomplished through various treatment methods including adsorption, coagulation, hypochlorite treatment, ion exchange and membrane separation [5]. Nowadays, membrane technology has become an attractive alternative choice for the water purification and industrial wastewater treatment. Membrane technology is an effectual technique used for various treatment of water. It is cost effective, highly productive, no additional chemical additives, simple in operation, high removal capacity and easy for scaling up. This technology plays a major role in production of clean water by contributing up to 53% of total world processes [6]. Polymer inclusion membranes (PIMs) initially proposed by [7] is a type of liquid membrane that has been successfully used for removal and recovery of metal ions and organic solutes. PIMs is a more preferable compared to solvent extraction method because it doesn't involve large amount of organic solvent and is more environmentally friendly. Besides, the operation of PIMs is more convenient where the extraction and stripping processes occur simultaneously with high selectivity of transport ion [8]. So far, polyvinyl chloride (PVC) and cellulose triacetate (CTA) are commonly used as based polymer in PIMs. However, there are variety of other polymers such as PVDF that are able to provide mechanical strength and flexible thin film. According to [9], PVDF-Co-HFP is the type of polymer which is mostly applied in the fabrication of nanofiltration (NF), microfiltration (MF) and ultrafiltration (UF). The polymer has a higher chemical resistance, good thermal and mechanical stability compared to another base polymer. Therefore, this research was intended to prepare PIMs using PVDF-Co-HFP as a base polymer and Aliquat 336 as a carrier. The main focus of this study is to discover efficient methods of PVDF-Co-HFP PIMs in removing RO16 dye from aqueous solution. Parameters such as the effect of carrier, initial dye concentration and pH were investigated to determine the optimum parameters for the removal of RO16 dye. The PVDF-Co-HFP PIMs were also characterised to determine its physical and chemical properties.

2. Methodology

2.1 Materials

PVDF-Co-HFP, Aliquat 336, Tetrahydrofuran (THF) and RO16 dye were obtained from Sigma-Aldrich (USA). Ethanol, Acetone, Hydrochloric acid (HCl), Sodium hydroxide (NaOH) and Nitric acid (HNO_3) were obtained from Merck, Malaysia.

2.2 Fabrication of PVDF-Co-HFP PIMs

The PIMs was prepared using the similar procedure described by [10]. 18 wt.% of PVDF-Co-HFP were dissolved in 79 wt.% of THF. Then, 3 wt.% of Aliquat 336 was added into the solution. The solution was stirred for 4 hours until it becomes homogenous. Next, 25 mL of the polymer solution was poured onto a glass plate and spread evenly using casting machine. The polymer solution on the glass plate was left overnight inside the fume hood to let the THF evaporate. To study on the effect of carrier, different composition of PIM was prepared as tabulated in Table 1.

Table 1. Composition of casting solutions.

Membrane	PVDF-Co-HFP (wt.%)	Aliquat 336 (wt.%)	THF (wt.%)
M0	**18**	**0**	**82**
M1	**18**	**3**	**79**
M2	**18**	**6**	**76**
M3	**18**	**9**	**73**
M4	**18**	**18**	**64**

2.3 Membrane Characterisation
Characterisation of membrane was separated into two categories that were chemical and physical properties. Fourier Transform Infrared Spectroscopy (ATR-FTIR)-8400S was used under the range 600- 4000 cm^{-1} with 4 cm^{-1} resolution and 80 scans to identify the surface chemistry and functional group of the fabricated membrane surface [11]. Furthermore, titration method was carried out to calculate the ion exchange capacity (IEC). For the physical characterisation, water uptake of the membrane was determined through its dry-wet weight. To evaluate the hydrophobicity of the membrane, the contact angle between water and the membrane surface was used. CA evaluation was conducted by using contact angle measuring system (Rame-Hart 25-FI, USA) [12]. Moreover, to determine the mechanical properties of the PIMs, Universal Testing Machine was used to analyse by using the elongation break and Young's modulus theory.

2.4 Transport Studies of PVDF-Co-HFP PIMs for RO16 Dye Removal
Figure 1 shows the set-up of the H-cell device with the performance studies of the PIMs for RO16 dye removal. The batch cell consists of two phases which were feeding and receiving phases. The feeding solution used was RO16 dye while receiving solution was nitric acid. According to the procedure of [10], the experiment was carried out by using different parameters such as effect of carrier composition, effect of initial dye concentration and effect of pH.

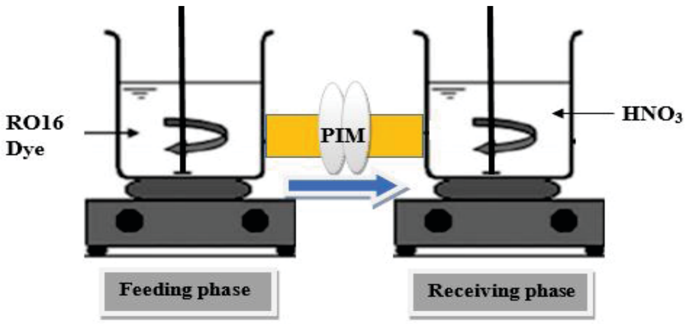

Figure 1. Schematic diagram of PIMs system.

3. Results and Discussion
3.1 ATR-FTIR analysis
ATR-FTIR spectroscopy studies were carried out for RO16 dye and the PIMs before and after extraction. Based on the spectrum results in Figure 2, the RO16 dye powder shows a peak at 3398.10 cm^{-1} which is due to the presence of aliphatic primary amine group (N-H). The S=O band stretching can be seen at 1370.51 cm^{-1}. This shows a strong sulfonate group in the dye as RO16 dye contain two sulfonate groups. Meanwhile, the PIM made of PVDF-Co-HFP show a clear peak at 1171.95 cm^{-1} which is related to the main polar functional group of the base polymer (C-F group). The strong electron withdrawing functional group of this polymer make it highly stable. This also shows that PVDF-Co-HFP does not exist in hydrogen bonds but, only Van der Waals forces which are weaker than hydrogen bonds. Thus, the presence of carbonyl group is able to form Van der Waals bonding with the RO16 molecule. The Van der Waals forces may occur between the azo dye reactive group and the functional groups of the PVDF-Co-HFP. However, after the extraction process, the band was stretch to 1168.97 cm^{-1}. This can shows that the amino group (N-H) in the dye can form hydrogen bonds with the strong electron-withdrawing functional group (C-F) [13]. Moreover, the PIMs after the extraction show a broad and strong intensity at 2928.87 cm^{-1} which indicates the presence of O-H group. Due to this presence of functional group such as OH^- in the dye, the carrier which contain the H^+ was easily attracted after extraction.

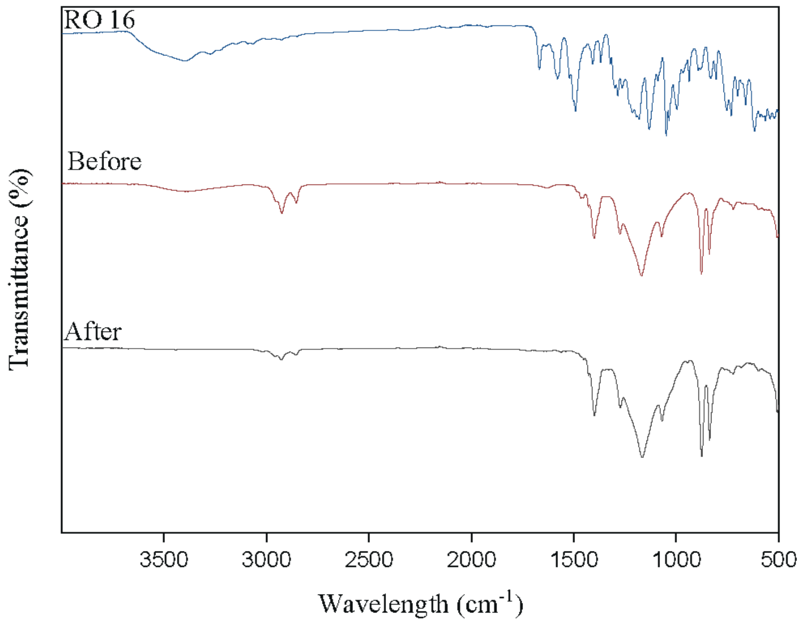

Figure 2. The spectrum of RO16 dye powder and PIMs before and after extraction.

3.2 Ion Exchange Capacity (IEC), Water Uptake and Contact Angle of PIMs

Figure 3 illustrates the composition of IEC, water uptake and contact angle of the fabricated PIMs at different composition of ionic carrier. The results showed an increasing trend in IEC value with the increasing of carrier percentage. IEC represents the ratio between the number of exchangeable ionic groups and the weight of the dry membrane [14]. The increasing of carrier content in the PIM facilitates higher ion conductivity. Proton conductivity plays an important role in the IEC. According to [11], the incorporation of carrier with a base polymer will increases the proton conductivity of the membrane. The proton will transfer under the facilitating of water and increase the acid functionalities of PIMs. This shows that 18 % highest carrier causes the highest IEC in the PIMs characterisation. This result indicate that the ionic conductivity of the PIMs is strongly dependent on the concentration of ionic carrier incorporated into the polymeric matric. Based on the results, the percentage of water uptake increase with increasing of carrier content. The mechanical stability of the membrane is measured by the water uptake of the dry membranes. The highest water uptake was 12.07 % obtained by M_4 membrane that contained 18 wt.% of the carrier. This shows that the PIM has a slightly hydrophilic character when the carrier content increase in the membrane composition. The proton conductivity in the Aliquat 336 carrier is the reasons of the water uptake increment in the PIM [15]. This is also due to the presence of quaternary ammonium groups in Aliquat 336 that is known to have high hydrophilic property induced by the positively charge quaternary amine [16]. Furthermore, the value of the contact angle of the PIMs follows the sequence of $M_0>M_1>M_2>M_3>M_4$ composition trend. As shown in Figure 3, PVDF-Co-HFP membrane (M_0) exhibit the highest contact angle due to the hydrophobic nature of the base polymer [17]. As the carrier content increase, the contact angle measurement decreased significantly. It can be concluded that Aliquat 336 can migrate and show its polar functional group which is quaternary ammonium group to the surface, thus rendering the membrane become hydrophilicity [18].

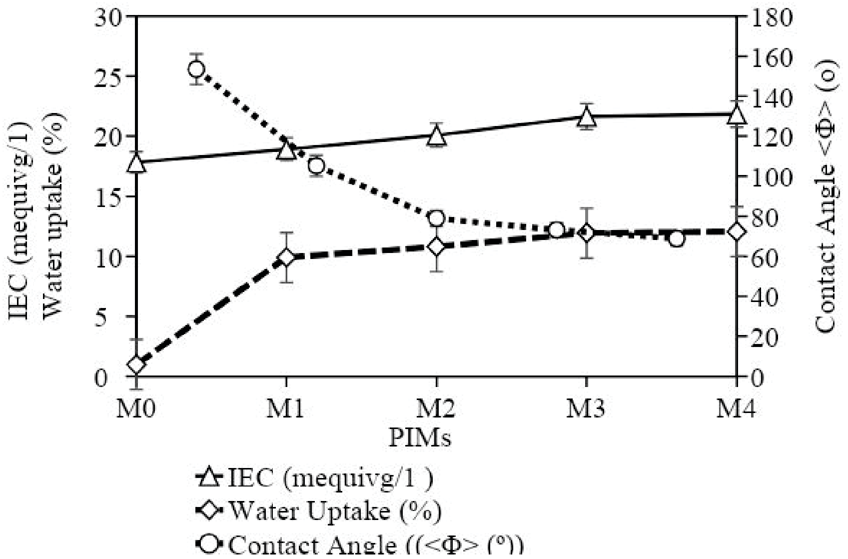

Figure 3. Characterisation of PIMs on IEC, Water Uptake and Contact Angle.

3.3. Mechanical Properties of PIMs

The tensile strength of the fabricated membranes was determined by the elongation break and Young's modulus and the results is shown in Figure 4. The elongation break shows a good result at 0 % carrier as the base polymer itself provides a good mechanical stability to the PIMs [6]. It did increase significantly at 3 wt.% carrier PIMs. This is due to the carrier in the membrane can act as a plasticiser too. Thus, it gives an additional strength to the PIMs. Unfortunately, as the amount of carrier increased above 3 wt.%, the elongation break started to drop dramatically. This shows that too much of plasticiser might lead to phase separation between the polymer and the solvent which disclose lower elongation at break because the increase of molecular weight of the plasticiser could lead to a decrease of mechanical strength [12]. Besides that, Young's modulus represents the resistance of the film to elastic deformation by determining the stiffness and strength of the film. In addition of carrier which also act as plasticiser from 0 % to 18 % caused reduction in the tensile strength and Young's modulus values. According to [12], low Young's modulus value corresponds to flexible film. This is due to the membrane lost their stiffness with the rise of the plasticiser and become more flexible [17]. This enhance that the membrane has a good mechanical stability.

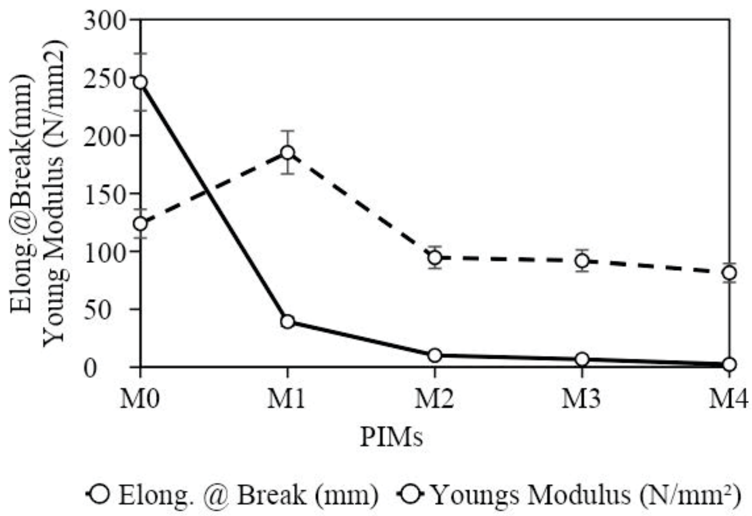

Figure 4. Characterisation of PIMs on tensile strength.

3.4. Effect of Parameters of the Performance of PIMs

3.4.1 Effect of Carrier Composition. Figure 5 shows the effect of carrier composition (Aliquat 336) from 0 to 18 wt.% of the removal of R016 dye. As the carrier content increase in PIM, the removal of RO16 also increased. The highest removal percentage obtained was 82.04 % at 9 wt.% of carrier content. The ion pair or complex that formed between the ion and the carrier was solubilized in the membrane and the ion was diffuse by facilitate transport across the membrane. The presence of Aliquat 336 as a carrier in the PIMs allowed the dye transportation to occur. As the dye is an anionic, it consists the negative charge existing as the OH^-. Therefore, it was readily to move towards the positive charge of Aliquat 336 to form a neutral ion pair complex (RO16-Aliquat 336). However, as the carrier content increase to 18 wt.% there is a decrease in the removal of the dye due to the high viscosity of the PIMs. The high viscosity in this PIMs will cause the limitation in the diffusion of the dye and the carrier complex into the membrane phase [19]. Thus, PIMs with 9 wt.% carrier was chosen as optimal and will further used in the study.

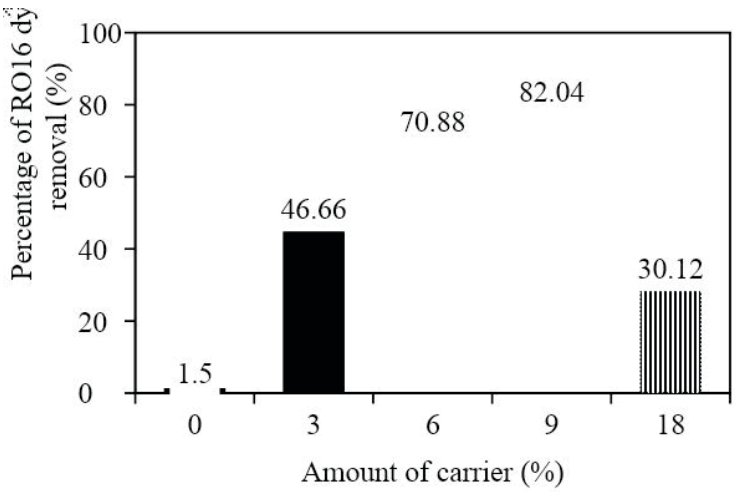

Figure 5. Effect of carrier on composition.

3.4.2 Effect of initial dye concentration. The effect of initial dye concentration to the RO16 dye removal process were investigated using 10 mg/L, 20 mg/L, 30 mg/L and 50 mg/L as shown in Figure 6. The optimized composition of PIMs, (M_3) was used as it shows the highest removal percentage in previous parameter. Based on the Figure 6, the removal percentage was the highest at the 10 mg/L of RO16 with 95.77 %. As the initial dye concentration increased from 20 to 50 mg/L, the percentage removal decreased to 94.04 %, 91.22 % and 82.04% respectively. This is due to the lower efficiency of the membrane area and membrane become saturated [20]. At higher RO16 dye concentration, the internal droplets in the peripheral region are more readily saturated with the ions and cause the ion exchange rate decrease largely due to the reduced capacity of the internal phase to strip the transported ions. Thus, the removal of the dye from the aqueous solution decreases with increasing of initial concentrations as the ions have difficulties in diffusing in the membrane.

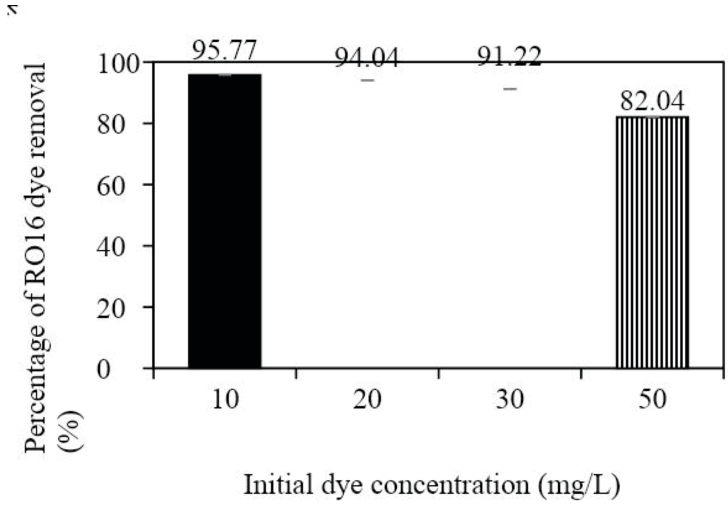

Figure 6. Effect of initial RO16 dye concentration.

3.4.3 Effect of pH. The effects of pH ranging from 2 to 12 on the removal of RO16 dye using M_3 membrane was investigated and the results are shown in Figure 7. Based on the Figure 7, increasing of pH from 2 to 12 significantly reduce the percentage removal of RO16 dye. The highest RO16 removal was observed at pH 2 with 99.62 % while the lowest was at pH 12 with 65 %. This is due to the presence of functional group such as OH^- group in the anionic dye. At a low pH, the surface becomes more positively charged whereas the number of binding sites at RO16 dye for negatively charged amine increased and thereby, the removal of RO16 increased. However, when the pH increased, the removal of dye was decreased. This is due to repulsion between the negative sulfonate groups in the dye of RO16 and the negative charged surface. The deprotonation of surface groups in higher pH range results in electrostatic repulsion between anionic dye and negatively charged sites. This results in the decrement of RO16 removal in alkaline condition [21]. Therefore, it can be concluded that, the removal percentage was the best in acidic media.

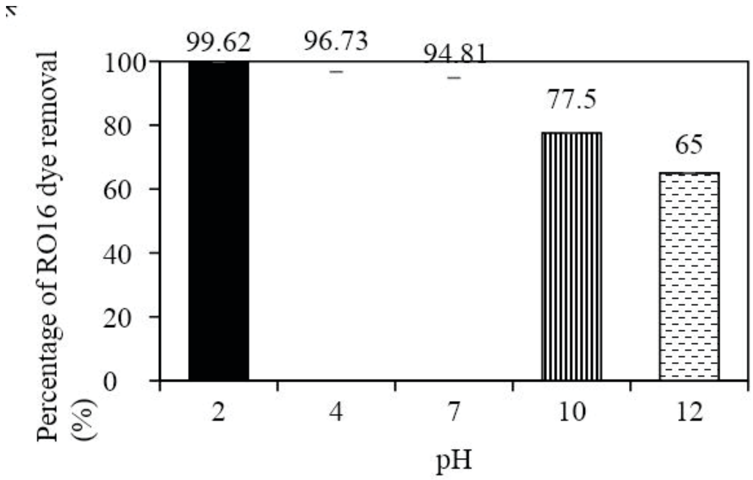

Figure 7. Effect of pH on the removal of 10 mg/L RO16.

4. Conclusion

In this study, different composition of PIMs with various carrier content (M_0, M_1, M_2, M_3 and M_4) were investigate to observe the potential of the PIMs in removing RO16 dye. The removal efficiency of RO16 onto PIMs not only depends on carrier content but also depend on initial dye concentration and pH of the solution. It can be concluded that, M_3 membrane which contain 9 wt.% of carrier shows a capability to remove 99.62 % of RO16 at pH 2 and 10 mg/L of initial dye concentration. The characterisation of PIMs was determined to identify the functional groups in the PIMs and dye used in this study. Based on the simplicity and improved hydrophilicity, the PIMs can be viewed as an alternative technology for the application of dye removal in water.

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