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UNDERSTANDING THE INFLUENCE OF DIFFERENT POLYMERIC PHASES IN THE PREPARATION OF SPOROPOLLENIN-FUNCTIONALIZED METHYLIMIDAZOLIUM-BASED MIXED MATRIX MEMBRANE.

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ABSTRACT: Mixed matrix membrane (MMM) is the new age hybrid membrane that combines two different phases and brings out the best of both in the final product. Essentially, MMM comprises a continuous polymer phase, which serves as the base platform and a particle phase that is embedded and dispersed onto the polymer phase. Conventional polymeric membranes constantly face issues in the form of low permeability, low selectivity, low mechanical strength, high fouling and in some cases low chemical resistance. The hybridization of the polymer phase with a particle phase, or sometimes referred to as fillers, has been reported to overcome these hurdles. For this study, the MMM was prepared with sporopollenin-functionalized methylimidazolium (SpMIM) as the particle phase. Two different polymer phases were explored, namely polymethyl methacrylate (PMMA) and cellulose triacetate (CTA). The morphology was analyzed using a field-emission scanning electron microscope (FESEM) while particle phase dispersion was observed with optical microscope imaging. Chromatographic analysis was accomplished using high-performance liquid chromatography equipped with a diode array detector (HPLC-DAD). The prepared MMM was subjected to batch adsorption analysis of selected substituted phenol analytes. FESEM surface analysis of the MMM notably displays clearly defined embedment of SpMIM in CTA, whilst it is less discernible in PMMA. Optical imaging also notes that the dispersion of SpMIM is both dense and compacted in CTA compared to PMMA. Both the PMMA and CTA based MMM were able to successfully adsorb the substituted phenol analytes. However, batch adsorption analysis of selected substituted phenol analytes reveals that PMMA records a moderately better adsorptive interaction with the selected substituted phenol analytes. This phenomenon is attributed to the strong π-π interaction between the aromatic groups in PMMA and the analytes.

KEYWORDS: *mixed matrix membrane, cellulose triacetate, polymethyl methacrylate, sporopollenin supported methylimidazolium, substituted phenols*

1. INTRODUCTION

Separation using selective polymeric membranes might as well be termed as the millennial sustainable alternative for an energy-efficient and cost-effective technology in water treatment and many other applications involving aqueous solutions [1]. A membrane is a thin permeable

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barrier that allows the separation of contaminants or targeted molecules from bulk phases. Conventional polymeric membranes, however, constantly face issues in the form of low permeability, low selectivity, low mechanical strength, high fouling and in some cases low chemical resistance [2]. This led to the introduction of mixed matrix membranes, which offer enhanced improvements in terms of performance, fouling, permeate quality and longevity.

Mixed matrix membrane is the new age hybrid membrane that combines two different phases, comprising a continuous polymer phase, which serves as the base platform and a particle phase that is embedded and dispersed onto the polymer phase [2]. The hybridization of the polymer phase with a particle phase or fillers has been reported to overcome the common hurdles, such as fouling resistance [4, 3]. The polymeric phase functions as the continuous phase that holds the membrane together, providing permeability, homogenous structure and stability [2, 4]. The particle phase consists of either porous or non-porous dispersed particles, which promotes physicochemical stability, such as thermal, mechanical and chemical, as well as potential increased selectivity [2].

The exploration of mixed matrix membrane in the separation of organic compounds is still relatively new. Most reported works on mixed matrix membranes focus on the separation of gas phases. However, there has been an increasing interest in the exploration of sustainable development applications for water purification and pollutant removal. In this study, sporopollenin supported methylimidazolium (SpMIM) particle phase is partenered with two different polymer phases, polymethyl methacrylate (PMMA) and cellulose triacetate (CTA), respectively. PMMA is a synthetic polymer based on methyl methacrylate monomer, while CTA is derived from cellulose. Both polymeric materials exhibit promising applications in molecular separation due to their low cost, compatibility, ease of modification, and processability [5-8].

The surface and cross-section of both the prepared MMM were analysed using FESEM to study the embedding of SpMIM. SpMIM dispersion on the polymer phase was observed using optical microscope imaging. Both MMM were then applied for batch adsorption studies of nitro and chloro-substituted phenols using high-performance liquid chromatography equipped with a diode array detector (HPLC-DAD).

2. MATERIALS AND METHOD

Preparation of sporopollenin supported methylimidazolium (SpMIM) was prepared as described by Kumuthini, C., et al. (2021) [9] while the fabrication of cellulose triacetate-SpMIM mixed matrix membrane (CTA-MMM) was prepared as mentioned by Kumuthini, C., et al. (2022) [10].

The surface and cross-section morphology was studied with field emission scanning electron microscope coupled with energy dispersive x-ray (FESEM-EDX) by Hitachi SU8220 (Japan). Particle phase distribution in the mixed matrix membrane was analysed using inverted optical microscope Eclipse TS100 by Nikon, Japan. Chromatographic analysis was completed using high performance liquid chromatography – diode array (HPLC-DAD) unit by Shimadzu (Japan) fitted with a LC-20AT pump, SPD-M20A diode array detector, SIL-20A HT autosampler and CTO-10AS VP column oven. The HPLC-DAD system was equipped with a Shim-pack GIST C-18 reverse phase column (250 × 4.6 mm), particle size (5 µm) from Shimadzu (Japan).

https://doi.org/10.31436/iiumecp.v1i1.4419

2.1 Preparation of polymethyl methacrylate-sporopollenin supported methylimidazolium based mixed matrix membrane (PMMA-MMM).

PMMA-MMM was prepared with reference to the doping method reported by Isha, A., et al. (2006) [11]. 0.21 g SpMIM and 0.7 g of PMMA powder (30 % w/w) were mixed with 210 µL tributyl phosphate (TBP) in 10 mL tetrahydrofuran (THF). The mixture was continuously stirred for 5 hours at room temperature. Once the PMMA fully dissolved, the mixture was poured into a petri dish with a diameter of 10 cm. The mixture was then left to dry overnight at room temperature to form an even membrane. The dried and firm MMM was cut into 1 cm^2 square pieces prior to use. Figure 1 depicts the preparation of PMMA-MMM.

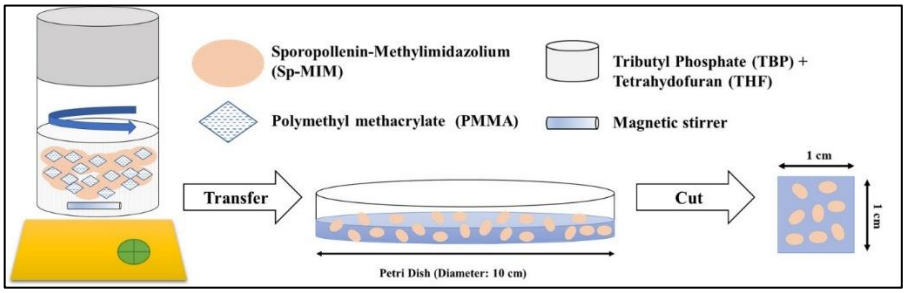

Fig 1. Preparation of polymethyl methacrylate-sporopollenin methylimidazolium based mixed matrix membrane (PMMA-MMM).

3. RESULTS AND DISCUSSION

FESEM morphology analysis was used to observe the dispersion of SpMIM in PMMA-MMM and CTA-MMM. Fig 2 depicts FESEM surface and cross-section imaging of blank PMMA and CTA, and their respective MMM. It can be observed that both blank PMMA (Fig 2a) and CTA (Fig 2b) form dense and neat membranes with a well-ordered outlook.

Top surface analysis of the MMM notably displays clearly defined embedment of SpMIM in CTA-MMM (Fig 2d), whilst it is less discernible in PMMA-MMM (Fig 2c). Cross-section of CTA-MMM (Figure 2f) reveals the SpMIM particles to be dispersed throughout the CTA polymer phase. PMMA polymer phase, on the other hand (Fig 2e) reveals that the dispersion of SpMIM is more focused on the upper brink of the membrane, while in the lower base, it is purely PMMA polymer. FESEM observations in general indicate more thorough and less confined dispersion of SpMIM in the CTA membrane.

Optical microscope imaging was used to observe the particle phase, Sp-MIM distribution onto the polymeric membrane. Typically, it is highly likely that a well-dispersed and unhindered particle phase will impact positively for the targeted selectivity of analytes. Fig 3 portrays the dispersion of SpMIM as observed under an optical microscope. SpMIM is well dispersed in both MMM, however, the dispersion is both dense and compacted in CTA compared to PMMA.

Both FESEM and optical microscope imaging propound the possibility of CTA and SpMIM sharing a better symbiotic coalition, as Sp-MIM is well dispersed throughout the MMM and is notably discernible on the surface. Nevertheless, to better identify the ideal polymer phase, a batch adsorption study for the selected nitro and chloro-substituted phenols was conducted.

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Adsorptive efficiency of both PMMA-MMM and CTA-MMM towards the selected phenols was analysed using batch adsorption concept via chromatographic separation using high-performance liquid chromatography equipped with a diode array detector (HPLC-DAD) [15]. The selected nitro and chloro-substituted phenol analytes, namely 2,4-dinitrophenol (2,4-DNP), 2-dinitrophenol (2NP), 4-dinitrophenol (4NP), 2,4-dichlorophenol (2,4-DCP), 2-dichlorophenol (2CP), and 4-dichlorophenol (4CP) are listed under the United States Environmental Protection Agency (USEPA) priority pollutants [17] and have been reported to be toxic and inflict both severe and long-lasting effects on both humans and animals [9].

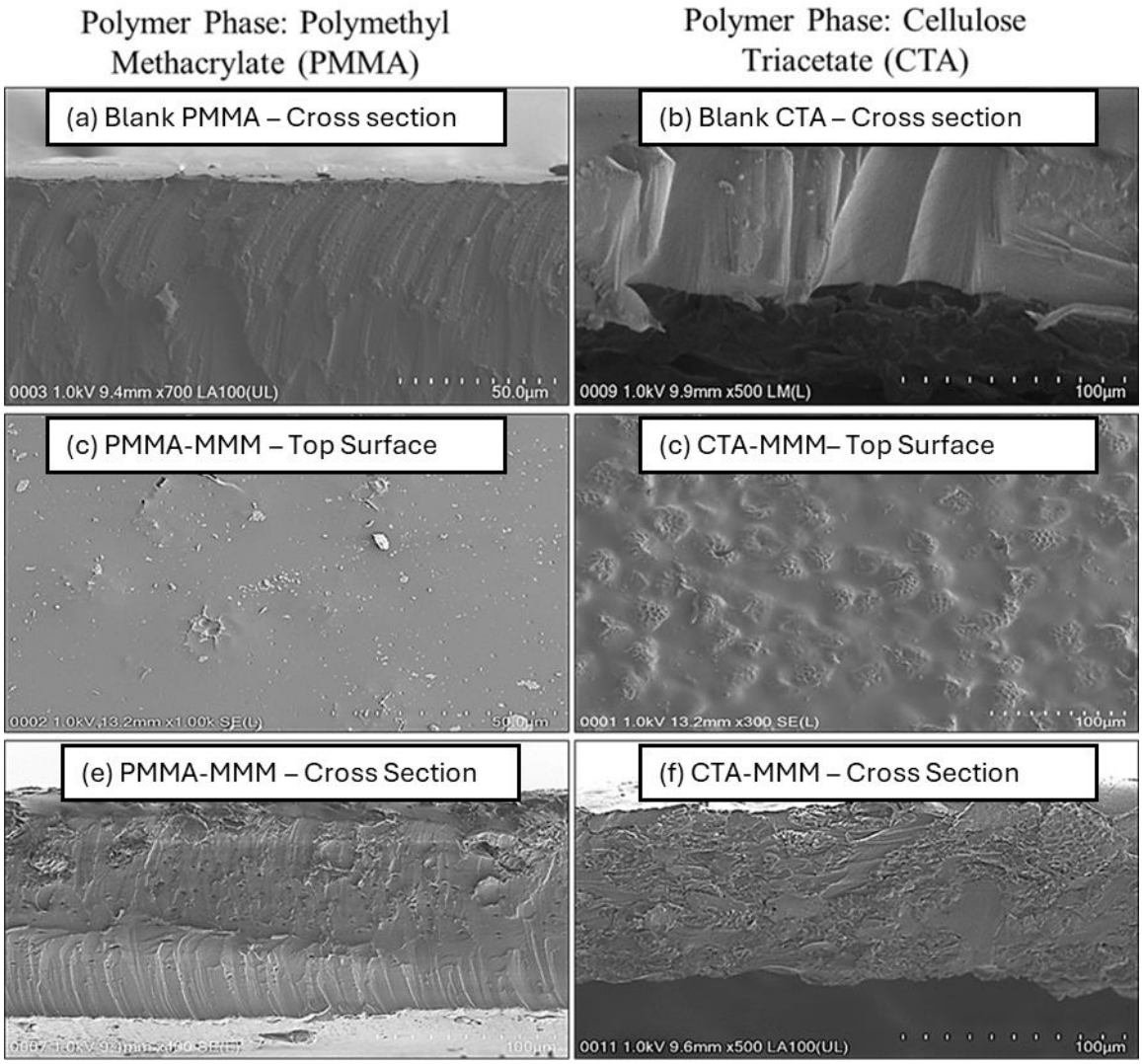

Fig 2. FESEM analysis of (a) cross section of PMMA blank membrane, (b) cross section of CTA blank membrane, (c) surface of PMMA-MMM, (d) surface of CTA-MMM, (e) cross section of PMMA-MMM, and (f) cross section of CTA-MMM.

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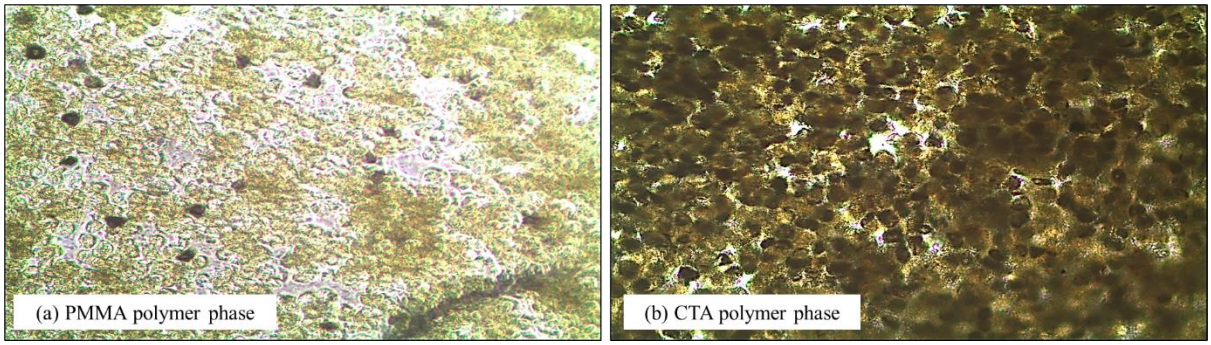

Fig 3. Optical microscope images on SpMIM dispersion in (a) PMMA-MMM and (b) CTA-MMM.

On a glance (Fig 4), PMMA-MMM records slightly enhanced adsorptive performance than CTA-MMM. It should be noted that the PMMA blank membrane itself is quite adsorptive towards the phenol analytes and contributes towards almost half of the total adsorption of PMMA-MMM. The adsorption interaction of phenol groups is largely influenced by the ionic dissociation of phenol, π-π interactions between the aromatic rings [12,13] and intermolecular interaction (van Der Waals, hydrogen bonding) [14]. As PMMA is a rich source of aromatic rings, it is highly deducible that the polymer phase PMMA itself becomes a contributory factor towards phenol adsorption. CTA-MMM, on the other hand, exhibits almost exclusive particle phase, SpMIM selectivity towards phenols, with CTA registering minimal adsorptive percentage (0-5 %).

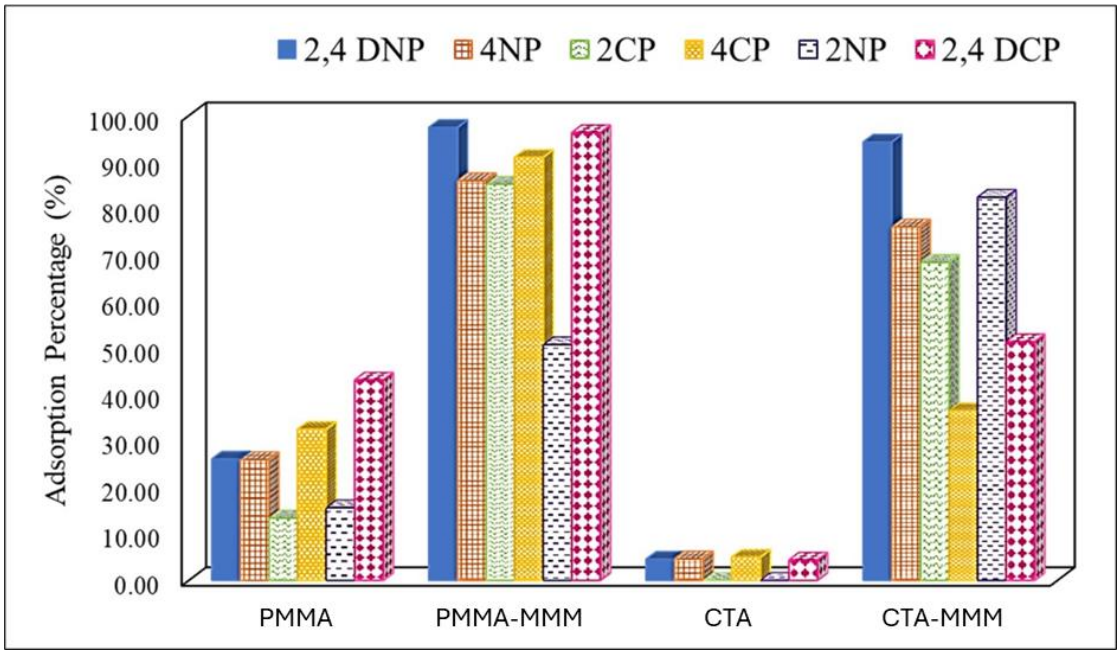

Fig 4. Batch adsorption of selected nitro and chloro-substituted phenols, 2,4-dinitrophenol (2,4-DNP), 2-dinitrophenol (2NP), 4-dinitrophenol (4NP), 2,4-dichlorophenol (2,4-DCP), 2-dichlorophenol (2CP), and 4-dichlorophenol (4CP) analytes by PMMA-MMM and CTA-MMM.

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Table 1. Evaluating key parameters of PMMA-MMM and CTA-MMM.

Parameter	PMMA-MMM	CTA-MMM
Polymer phase	Commercially available	Commercially available
Preparation Time	5 hours	5 minutes
Membrane formation	Overnight	2-3 hours
Membrane quality	Sturdy, Pliable	Sturdy, Pliable
SpMIM particle phase dispersion	Less densely dispersed with focused dispersion on the brink of the membrane surface	Densely and well-dispersed throughout the membrane
Phenol analyte selectivity	Highly influenced by PMMA	The particle phase SpMIM displays exclusive selectivity

Both membranes are sturdy and pliable, they could be cut into the desired shape with ease. Their respective preparation time and steps, however, vary significantly. The preparation of CTA-MMM is more facile and requires the use of only dichloromethane. PMMA-MMM on the other hand, requires 5 hours of stirring and overnight drying together with tributyl phosphate and tetrahydrofuran. Table 1 compares the relevant parameters that evaluate both the MMM.

4. CONCLUSION

The fabrication methodology of mixed matrix membrane (MMM) using sporopollenin supported methylimidazolium (SpMIM) depends on the choice of the polymer phase. In the case of polymethyl methacrylate (PMMA) and cellulose triacetate (CTA), CTA requires shorter preparation time and fewer reagents. However, in terms of adsorption of the selected nitro and chloro-substituted phenols, namely 2,4-dinitrophenol (2,4-DNP), 2-dinitrophenol (2NP), 4-dinitrophenol (4NP), 2,4-dichlorophenol (2,4-DCP), 2-dichlorophenol (2CP), and 4-dichlorophenol (4CP) analytes, PMMA-MMM records higher adsorption percentage influenced by the strong π-π interactions between the aromatic rings.

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