THE REMOVAL OF METHYLENE BLUE USING POLYVINYL ALCOHOL (PVA) POLYMER INCLUSION MEMBRANE

by

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DECLARATION

I declare that this thesis entitled "The Removal of Methylene Blue using Polyvinyl Alcohol (PVA) Polymer Inclusion Membrane" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and it is not concurrently submitted in candidature of any other degree.

Signature :_______________________________

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Date :_______________________________

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The Removal of Methylene Blue (MB) using Polyvinyl Alcohol (PVA) Polymer Inclusion Membrane (PIMs)

ABSTRACT

In this study, the removal of cationic dye (Methylene Blue; MB), which is carcinogenic and harmful to human health and environment were carried out from their aqueous solution using polymer inclusion membrane (PIMs) consisting of PVA as the based polymer, Aliquat 336 as a carrier and dimethyl formamide (DMF) as a solvent. The composition of the carrier, pH, and temperature were varied to determine the optimum removal of MB. The prepared membranes have been characterized using Fourier Transform Infrared Spectroscopy (FTIR) to detect the functional groups present on the membrane and the Scanning Electron Microscope (SEM) to gain insights into their surface morphology, structure, and composition. SEM is a versatile tool that enables researchers to examine the surface of materials at high magnifications and resolutions. From the result, the optimum conditions of extraction study are PIM with PVA 30-Aliquat 336, pH 4, 2 ppm of initial dye concentration and temperatures 55˚C. The result shows that PVA-based PIM incorporated with Aliquat 336 demonstrated excellent extraction capabilities of MB from aqueous solution. The maximum removal efficiency under optimum condition is 71.75% at pH 4. The FT-IR spectra show the presence of Aliquat 336, and PVA based PIM.

Pengingkiran Metilena Biru (MB) menggunakan Polymer Incusion Membrane berasaskan polivinil alcohol (PVA)

ABSTRAK

Dalam kajian ini, penyingkiran pewarna kationik (Methylene Blue; MB), yang bersifat karsinogenik dan merbahaya kepada kesihatan manusia dan alam sekitar, telah dilakukan daripada larutan akuatik mereka menggunakan membran penyertaan polimer (PIMs) yang terdiri daripada PVA sebagai polimer asas, Aliquat 336 sebagai pemikul, dan Dimetilformamida (DMF) sebagai pelarut. Komposisi pemikul, pH, kepekatan pewarna awal, dan suhu telah diubah suai untuk menentukan parameter optimum PIM berasaskan PVA untuk penyingkiran MB dalam masa 24 jam. Membran yang disediakan telah dicirikan menggunakan Spektroskopi Inframerah Transformasi Fourier (FTIR) untuk mengesan kumpulan fungsi yang hadir pada membrane dan Mikroskopi Elektron Pengimbasan (SEM) untuk memperoleh pemahaman terhadap morfologi permukaan, struktur, dan komposisi PIMs, SEM merupakan alat yang serba boleh yang membolehkan penyelidik mengkaji permukaan bahan pada pemerbesaran dan resolusi yang tinggi. Dari hasil kajian, keadaan optimum bagi kajian ekstraksi adalah PIM dengan PVA 30-Aliquat 336, pH 4, kepekatan pewarna awal 2 ppm, dan suhu 55˚C. Hasil menunjukkan bahawa PIM berasaskan PVA yang diintegrasikan dengan Aliquat 336 menunjukkan keupayaan ekstraksi MB yang sangat baik daripada larutan akuatik. Kecekapan penyingkiran maksimum di bawah keadaan optimum adalah 71.75% pada pH 4. Spektrum FT-IR menunjukkan kehadiran Aliquat 336, and PVA based PIM.

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LIST OF ABBREVIATIONS

2NPOE	2-Nitrophenyl octyl ether
CTA	Cellulose Triacetate
D2EHPA	Di-(2-ethylhexyl) phosphoric acid
DMF	Dimethyl Formamide
DMSO	Dimethyl Sulfoxide
FTIR	Fourier Transform Infrared
HCl	Hydrochloric acid
MB	Methylene blue
NaOH	Sodium Hydroxide
PIM	Polymer Inclusion Membranes
PVA	Polyvinyl Alcohol
PVC	Polyvinyl Chloride
PVDF	Polyvinylidene Fluoride
RBCs	Red Blood Cells
SEM	Scanning Electron Microscopy
SLM	Supported Liquid Membranes

LIST OF SYMBOLS

&	And
%	Percentage
˚C	Degree Celsius
wt.%	Weight by percentage
cm^{-1}	Wavelength

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Dyes come in two main types which are natural and synthetic. Natural dyes are obtained from various biological sources such as plants, animals, fruits, insects, and minerals. Although natural dyes were widely utilized in the past, synthetic dyes gained popularity due to their convenience and wider range of colours. However, the production of synthetic dyes often involves the use of chemicals like mercury, lead, chrome, copper, sodium chloride, toluene, or benzene, which are known to pose risks to human health (Manickam & Vijay, 2021). This raises concerns about the potential negative impact of synthetic dyes on ecosystems, as the improper disposal of untreated dyes into rivers can lead to water source contamination. Moreover, a significant portion (10-15%) of the dyes used in the colouring process is released into water bodies, exacerbating the problem. Consequently, when these pollutants find their way into nearby communities' water supplies, they introduce harmful substances that can have adverse effects on human health and pose threat to aquatic life (Kent, 2023).

Methylene blue (MB) is a synthetic dye widely used in various industries such as garment, textile, paper, and leather. It has a chemical formula of $C_{16}H_{18}N_3SCl$ and belongs to the class of heterocyclic aromatic compounds, characterized by its planar structure. MB is categorized as a cationic dye, imparting a blue colour, and it has a molecular weight of 319.85 g/mol. Its intricate structure makes it highly resistant to light and oxidation, posing challenges for its degradation. Furthermore, methylene blue (MB) is acknowledged as a substance that possesses mutagenic, carcinogenic, and toxic properties, as pointed out by Badri et al. (2018). Consequently, it is of paramount importance to eliminate MB from water sources in order to mitigate its harmful consequences.

Polymer inclusion membranes (PIMs) belong to the category of liquid membranes composed of a polymer along with a carrier and/or plasticizer. PIMs have become increasingly prominent in a wide range of applications, encompassing the extraction and retrieval of metal ions, as well as environmental remediation, as highlighted by Zulkefeli, N.S., Weng, S.K., and Abdul Halim, N.S. in 2018. The attractiveness of PIMs lies in their ability to selectively transport specific ions or molecules across the membrane while rejecting others. Moreover, PIMs exhibit remarkable stability, high selectivity, efficient performance, and long-lasting durability when compared to alternative liquid membranes (Sharaf & Yoshida, 2018). Although the potential of PIMs for dye extraction has been examined in recent research, most studies have focused on using polyvinyl chloride (PVC) and cellulose triacetate (CTA) as the primary polymers in PIMs. While successful applications have been reported with these polymers, some studies have identified drawbacks such as low temperature stability and a limited range of selectivity (Lin et al., 2014). Furthermore, there is a scarcity of comprehensive research exploring the potential of other polymers as alternative bases for PIMs.

Polyvinyl alcohol (PVA), is well known as a synthetic biodegradable polymer and possesses excellent mechanical properties. PVA has a good chemical resistance to a variety of substances, including acids, bases, solvents, and even potent oxidising agents (Lin et al., 2014). It is suitable for use in hostile chemical conditions because of this characteristic. Besides, PVA is resistant to high temperatures, has a high melting point, and exhibits good thermal stability. It is useful for applications that include high-temperature environments since it can endure temperature extremes without significantly degrading. Therefore, this study aims to produce PVA based PIM incorporated with Aliquat 336 as a carrier for the application of dye removal.

1.2 Problem Statement

Releasing untreated synthetic dyes like MB into rivers and streams can have significant environmental consequences. MB, being a cationic azo dye that readily dissolves in water, has the potential to pose risks to both human health and the environment if mishandled or improperly used. Inhalation of MB aerosols or powder, for instance, can lead to respiratory issues such as coughing, breathing difficulties, and respiratory distress, while direct contact with MB may cause skin irritation, allergic reactions, and eye irritation. (Badri et al., 2018).

Even at low concentrations, MB has been found to have detrimental effects on aquatic species, including fish and invertebrates. Discharging effluent containing MB into water bodies can pose a threat to aquatic ecosystems. In terms of ecotoxicity, MB has the potential to bioaccumulate in certain organisms and persist in the environment, thereby impacting the food chain (Tkaczyk et al., 2020). Therefore, it is essential to treat water sources containing MB to minimize its environmental impact.

While polymer inclusion membranes (PIMs) have been widely recognized for their benefits and achievements in extracting and reclaiming metal ions, there is a noticeable deficiency in research regarding their utilization for dye removal, as noted by Kaczorowska et al. (2022). Furthermore, most of PIM studies have concentrated on polymers like PVC and CTA, overlooking the potential of alternative polymers. Consequently, this investigation has been launched to assess the viability of using PVA as the foundational polymer for PIM in the context of eliminating methylene blue from water solutions.

1.3 Objective

The objectives of the study are:

a) To identify the best combination of Aliquat 336 concentration in PVA based PIM for MB removal.
b) To determine the optimum condition of PVA based PIM in removing MB dye.
c) To characterize the PVA based PIMs.

1.4 Scope of Study

The scopes of this study are:

a) To prepare PVA based PIMs with variation of Aliquat 336 concentrations as shown in Table 3.3 for MB removal.
b) To determine the optimum parameter for MB extraction by varying the pH (4, 6 and 12) and solution temperature (27, 35 and 55 ˚C).

c) To analyze the functional groups and morphological structure of PVA-based PIMs using Fourier transform infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM).

1.5 Significant of Study

This study holds significant importance as it contributes valuable findings towards the potential of PVA-based PIMs for the removal of MB dye. Additionally, previous studies primarily focused on utilizing CTA and PVC as the base polymer for PIMs. Hence, the outcomes of this study revealed the optimal combination of Aliquat 336 as a carrier in PVA-based PIMs for efficient MB removal. Moreover, this study has exposed the potential of PVA as the based PIM for dye removal. The findings from this research will be beneficial for researchers and help to explore the potential of other polymers for dye removal application and thus, offer an alternative treatment method.

CHAPTER 2

LITERATURE REVIEW

2.1 Dyes

Dyes can be in nature and synthetic form. Plants, insects, animals, and minerals are some of the sources of natural colours. These colours may be manufactured organically, making them non-toxic and eco-friendly. Examples of natural colours generated from plants include indigo and saffron. Natural colours may be made from both mineral and animal sources, such as ferrous sulphate and ochre found in rocks and some species of mollusks, shellfish, and insects (Kandisa & Saibaba KV, 2016).

Synthetic dyes play an increasingly significant role in our modern lives and are derived from organic compounds. They find applications in various fields, including industry and commercial sectors such as the paint industry, as well as in the development of photoredox catalysts and fluorescent tracers. Chemists have devised several methods to facilitate the synthesis of intricate synthetic organic pigments, enhancing their complexity and diversity (Ziarani et al., 2018). Within this context, MB is a type of heterocyclic compound that belongs to the thiazine dye family. Thiazine dyes, along with dyes from other categories, are commonly employed in the textile industry to dye fabrics, imparting vibrant and luminous colours.

2.1.1 Methylene blue dye

MB also known as Methylthioninium chloride or Swiss blue, is an organic chloride salt compound widely utilized in medicine and biology as a dye for microscopic visualization. Its chemical formula is $C_{16}H_{18}ClN_3SCl$, and was first discovered in 1876 by German chemist Heinrich Caro (Mehlhorn, 2016). Traditionally, MB has been extensively used in Africa for the treatment of malaria, but with the introduction of chloroquine and other drugs, the usage has been discontinued (Trape JF, 2001). With a molecular weight of 319.85 g/mol, MB has the potential to cause harm to red blood cells (RBCs) and impair the oxygen-carrying capacity of blood, posing significant health risks when consumed orally or administered intravenously. As a thiazine dye with basic properties, MB selectively stains cellular components with negative charges, such as nucleic acids. The molecular structure of MB is depicted in Figure 2.1 (Mehmet, 2014).

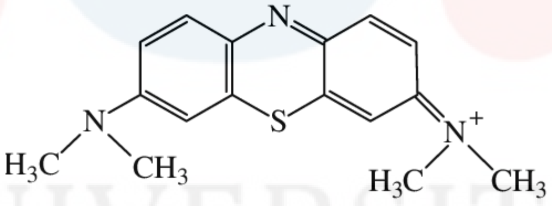

Figure 2.1: Structure of MB (Mehmet, 2014).

2.2 Liquid membrane

Supported liquid membranes (SLMs) and polymer inclusion membranes (PIMs) are two types of liquid membranes commonly used for separating metals from aqueous solutions. In SLMs, the liquid membrane phase is held in place by capillary forces within the pores of a microporous polymeric or organic film (Dżygiel & Wieczorek, 2010). This configuration provides support to the membrane. On the other hand, PIMs offer advantages over SLMs as they combine extraction and stripping processes in a single stage and exhibit greater stability (Salima, 2012). Therefore, PIMs are preferred due to their flexibility and adaptability.

2.2.1 Polymer inclusion membranes (PIMs)

PIMs are composed of a liquid phase and a polymer (López-López et al., 2010). The extractant/carrier that binds the target species through complexation or ion-pair formation is present in the membrane's liquid phase. The common base polymer used for PIMs were cellulose triacetate (CTA), polyvinyl chloride (PVC) and polyvinylidene fluoride (PVDF), which serves as the membrane's skeleton and gives mechanical strength (Pereira et al., 2019).

A plasticizer or modifier can be introduced to the membrane structure to improve the PIM's flexibility or make the extracted species more soluble in the membrane's liquid phase. Even certain extractants also exhibit plasticizing properties such as Aliquat 336 (Fontas et al., 2006). The inclusion of a plasticizer modifies the physical and mechanical properties of the membrane, leading to improved performance in certain applications. Plasticizers are substances added to polymers to improve their flexibility, processability, and durability. The plasticizer that is commonly used in PIMs is (2-nitrophenyl octyl ether (NPOE). NPOE is often used as a nonpolar solvent in liquid-liquid extraction processes. It can selectively extract nonpolar and slightly polar compounds from aqueous solutions or other polar solvents (Keskin et al., 2023). It can be advantageous due to its compatibility with certain polymers and its ability to improve the membrane's performance.

Carrier or extractant is responsible for transport across the PIM complex. Generally, a carrier will act as an ion exchanger by forming an ion complex between carrier and metal ions (Almeida et al., 2017). The carrier is soluble in membrane and aids the transportation of metal ions from the feed phase to receiving phase across the membrane (Taylor et al., 2014). However, the amount of carrier used in PIMs must reach a certain concentration to be able to function and ensure the transport efficiency of target ions and enhance the membrane selectivity. There are several kinds of extractants/carriers, including carriers that are acidic, basic, neutral, macrocyclic, and macromolecular. According to Barlah Rumhayati et al. (2019), the quaternary ammonium compound Aliquat 336 is a basic carrier that may be utilised to separate metal anionic complexes. The optimum of carrier concentration can be identified by performing the extraction study.

2.3 Studies on dye removal using PIM.

A novel polymer inclusion membrane (PIM) was successfully developed using polyvinylidene fluoride (PVDF) as the base polymer, tricaprylmethylammonium chloride (Aliquat 336) as the ion carrier, and 2-nitrophenyloctylether (2NPOE) as the plasticizer. This PIM was utilized in the extraction of methylene blue dye from aqueous solutions in the study, employing the casting evaporation method. PVDF is known to be soluble in various solvents such as dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO) when dissolved in water (Sellami, Kebiche-senhadji, et al., 2020). Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer that is commonly used as a glue, thickener, film former, and other applications. Due to its water-soluble nature, the most common solvent for polyvinyl alcohol is water itself. When dissolved in water, PVA forms a viscous solution that can be used for various purposes. The alternative solvents for PVA that are not water-based is might consider using polar solvents such as dimethyl sulfoxide (DMSO) or dimethylformamide

(DMF). These solvents can also dissolve PVA, but they are typically used in more specialized applications.

In a study conducted by Salima et al. (2012), an investigation was carried out to eliminate a basic dye called methylene blue (MB) from aqueous solutions. This was accomplished using polymer inclusion membranes (PIMs) composed of Cellulose Triacetate (CTA) as the primary polymer, 2-nitrophenyl octyl ether (2-NPOE) as the plasticizer, and di-(- ethyl hexyl) phosphoric acid (D2EHPA) as the carrier. The findings of the study indicated that the most effective extraction of MB occurred at a pH level of 6, with a dye concentration of 250 ppm, resulting in nearly complete recovery of methylene blue (93%).

Not only that, an ionic dye (Methyl Orange; MO) removal have been deliberately studied using PVC based PIM. Achieving optimal conditions, a remarkable removal efficiency of 99.61% was obtained (Nursyahirah Binti Majdi, 2020). In the context of PVC-based PIM studies, chloroform and THF were employed as alternatives to DMF (Sellami, Kebiche-Senhadji, et al., 2020). Commonly used extractants, such as Aliquat 336, Cyanex 272, and di-(2-ethylhexyl) phosphoric acid (D2EHPA), are frequently utilized during PIM preparation (Sellami, Kebiche-Senhadji, et al., 2020).

PVA membranes have been extensively explored and employed a number of separation processes, including waste treatment, drinking water, and oil or water separation (Shi et al., 2016). This is because of their exceptional chemical and physical stabilities. To fulfil the requirements, it is possible to provide PVA membranes with certain surface properties. However, no previous studies have investigated the utilization of Polyvinyl Alcohol (PVA) as the foundation for Polymer Inclusion Membranes (PIM) in the context of dye removal. This research aims to explore the effectiveness of PVA as a potential agent for the removal of dyes, contributing valuable insights to the field of water treatment and environmental remediation.

2.4 Characterization of PIM

The PIM can be characterised for its morphology, functional group, mechanical strength and other. The morphological structure is a common method to observe the structure surface of PIMs and this can be done using scanning electron microscopy (SEM). SEM is a potent imaging method that employs a concentrated electron beam to look at a sample's surface and near-surface features. Detailed, high-resolution pictures of the sample surface are produced using SEM. At magnifications ranging from extremely low to extremely high, it may disclose surface topography, morphology, and minute features (Iben Nasser et al., 2016).

Besides surface morphology, the functional group of the PIMs was also characterised using Fourier transform infrared (FTIR) analysis as a spectroscopic technique utilized for identifying modifications in the overall structure of biomolecules by detecting alterations in functional groups (Eid, 2021). By examining absorption bands in the FTIR spectrum, it becomes possible to identify specific chemical groups present in a substance. Each functional group possesses distinct vibrational frequencies, allowing for the determination of the presence of chemical groups. FTIR spectroscopy provides insights into the composition of molecules by analysing their characteristic vibrations and chemical bonds. Therefore, valuable information regarding the surface components of the membrane could be directly obtained through FTIR analysis (Amir & Anjum, 2013).

CHAPTER 3

MATERIAL AND METHOD

3.1 Material and Equipment

The material and apparatus used in this study are listed in Table 3.1 and 3.2 respectively.

Table 3.1: List of materials used in the experiment.

Materials	Supplier
Polyvinyl alcohol (PVA)	Sigma-Aldrich
Methylene Blue (MB)	Sigma-Aldrich
Distilled water	Conrad Electronic International
Aliquat 336	Sigma-Aldrich
Dimethyl formamide (DMF)	Sigma-Aldrich

Table 3.2: List of apparatus used in the experiment.

Apparatus	Supplier
Uv-vis spectrophotometer	Hach Company
FTIR	Shimadzu Corporation
pH meter	Hanna Instrument (M) Sdn Bhd
Hot plate stirrer	SHCHEER Lab Instrument
Digital Orbital Shaker	Shimadzu Corporation
Scanning Electron Microscopes (SEM)	Shimadzu Corporation

3.2 Preparation of polymer inclusion membrane

This investigation involved the synthesis of PVA-based polymer inclusion membranes (PIMs) with different Aliquat 336 as listed in Table 3.3. The preparation process involved dissolving 1 g of PVA polymer in 10 mL of DMF solvent at room temperature. The solution was heated to 75˚C and swirled with a magnetic stirrer until it completely dissolved. Then, the Aliquat 336 were added to the mixture in the proportions specified in Table 3.3. A homogenous solution was formed by continuing to stir. The final mixture was carefully transferred to a petri plate and then placed in fume to let the DMF evaporate slowly for at least 72 hours. The last step was to delicately remove the PVA-based PIMs from the petri dish so they could be studied in greater detail.

Table 3.3: PVA-based PIM with different composition of Aliquat 336.

PVA-based PIM ID	**PVA (%)**	**Aliquat 336 (%)**
PVA (A)	70	30
PVA (C)	50	50

3.3 Preparation of methylene blue (MB) standard dilutions.

In order to make a typical methylene blue (MB) dilution curve, a volumetric flask was used to dissolve 0.1 g of MB powder in 100 ml of distilled water, resulting in a 10 ppm starting solution of MB. Dilutions of 2,4,6,8, and 10 ppm were made from this 10 ppm stock solution. Afterwards, a UV-Vis spectrophotometer was used to detect the absorbance of these different MB standard dilutions at a wavelength of 635 nm. In the Appendix, you may see the graph that shows the outcomes of the MB standard dilutions.

3.4 Extraction of methylene blue using PVA based PIM

3.4.1 The effect of initial dye concentration

The behavior of methylene blue (MB) was the primary focus of an extraction investigation that utilized PVA-based polymer inclusion membranes (PIMs). The first step was to cut the PVA-based PIMs into smaller pieces and place them in a beaker with 200 ml of a neutral pH MB solution that had a concentration of 6 ppm. The dye solution was vigorously mixed at a speed of 150 rpm throughout the experiment. For the purpose of evaluating MB absorption, samples were taken at 0, 30, 60, 120, 180, 240, and 1440 minute intervals and subjected to a UV-Vis spectrophotometer set at a 635 nm wavelength. Utilizing Equation 3.1, we ascertained the efficacy of MB removal. The PVA-based PIM that showed the most efficacy in MB removal was chosen for further studies based on the results.

$$\text{Removal efficiency, E (\%)} = \frac{C_i - C_f}{Cf} \times 100\% \qquad (3.1)$$

Where;

C_i = Initial concentration of methylene blue

C_f = Final concentration of methylene blue

3.4.2 The effect of pH solution

Following the experiment, a pH investigation was conducted to determine the most suitable pH condition for removing MB. The same extraction procedure described in section 3.4.1 was performed, but with pH solutions of 4 and 8. The pH of the MB solutions was adjusted by adding HCl and NaOH. Throughout the experiment, the MB solution was stirred at a rate of 150 rpm and maintained at room temperature. Samples were collected at various time intervals (30, 60, 120, 180, 240 and 1440 minutes) and subjected to UV-Vis analysis. The removal efficiency of MB was then calculated using Equation 3.1. The optimum pH value was selected for the subsequent study.

3.4.3 The effect of solution temperature

Temperature has a major impact on how effective the removal process was. In the experiment, two distinct temperatures, 35 and 55 ˚C, were used. Using the optimal pH from the prior investigation, the same extraction procedures as described earlier were employed. After that, after 30, 60, 120, 180, 240, and 1440 minutes, the samples were taken and analyzed using UV-Vis.

3.5 Characterization of PVA based PIM

3.5.1 Fourier infrared spectroscopy (FTIR)

The PVA-based polymer inclusion membrane (PIM), which incorporated different compositions of Aliquat 336, underwent characterization using Fourier Infrared Spectroscopy (FTIR). This analytical technique enabled the detection of a wide range of functional groups present in the sample by analyzing the obtained spectrum. FTIR spectra were acquired using an FTIR-8400S spectrophotometer from Shimadzu, with measurements taken in the range of 4000-400 cm^{-1} and a resolution of 4 cm^{-1} (Salima et al., 2012).

3.5.2 Scanning electron microscopy (SEM)

The PVA-based polymer inclusion membrane (PIM) containing varying concentrations of Aliquat 336 was characterized using scanning electron microscopy (SEM). SEM enabled the visualization of the size and morphology of the sample. Before the commencement of the extraction studies, the components of the PIM were subjected to SEM examination. The SEM analysis was conducted using a Shimadzu Corporation model, with voltage settings ranging from 0.5 to 30 kV. The average diameter and surface characteristics of the sample were observed at a magnification of x500.

CHAPTER 4

RESULT AND DISCUSSION

4.1 The study of MB extraction

4.1.1 Effect of different PVA PIMs composition

At the outset, the research focused on analyzing PVA-based polymer inclusion membranes (PIMs) with different concentrations of Aliquat 336 to determine the optimal combination for removing methylene blue (MB). The extraction solution used contained 6 ppm of MB at a pH level of 7. The findings of this investigation are depicted in Figure 4.1.

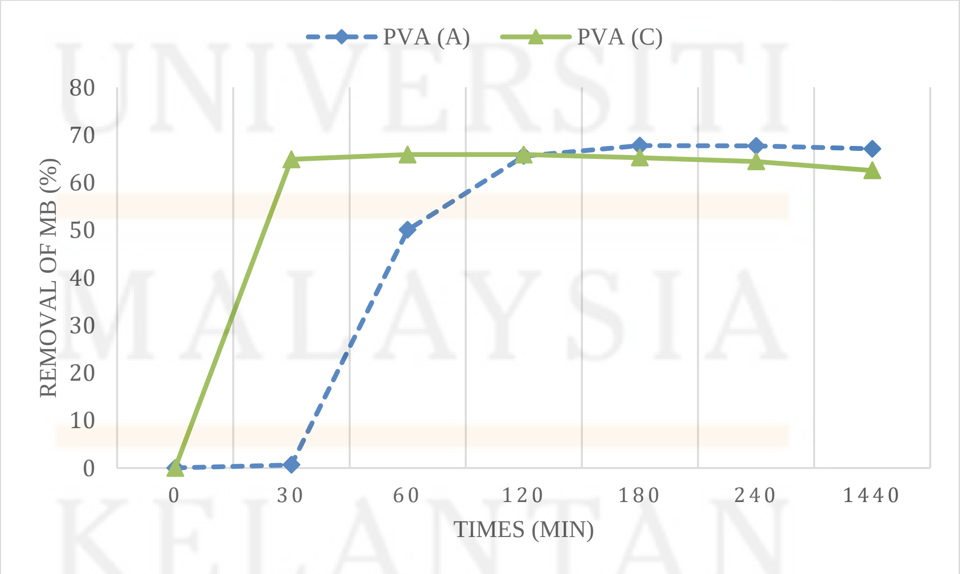

Figure 4.1: Effect of Aliquat 336 concentration on the removal efficiency of MB.

Figure 4.1 shows that after 2 hours of extraction, all PVA PIMs removed more than 50% of the MB. Since the PVA PIMs have carrier material, MB extraction is still possible. After two hours of extraction, the results reveal that PVA (C) had a tendency to lose some of their initial removal efficiency. On the other hand, PVA (A) stabilised at 67% removal even after 24 hours of extraction, though it was slightly slower

The results also showed that the MB removal effectiveness is unaffected by increasing the carrier content (Aliquat 336). The removal percentage was identical with PVA (A), which contains 30 wt.% of Aliquat 336, even though PVA (C) have greater carrier contents of 45 wt.%. Consistent with this result was the study by Salima et al. (2012), which found that adding a larger carrier concentration to PIMs did not improve the removal efficiency beyond a certain point; instead, it slowed down the extraction process.

Moreover, Taylor et al., (2014) stated that an increase in concentration of a carrier will increase the viscosity of the carrier in membrane phase and thus increase the membrane resistance. Once the membrane reaches a state of saturation with the carrier, there is a likelihood that the carrier might be deposited onto the membrane surface. This deposition has the potential to diminish the removal efficacy and impede the transport properties of the membrane by disrupting its homogeneous structure (Mitche et al., 2008). Therefore, based on the finding of this study, the PVA (A) PIM with 30 wt.% of Aliquat 336 was chosen for study as it already reaches the suitable carrier content with the highest MB removal percentage.

4.1.2 Effect of pH

After reviewing the pH data, we settled on a 2 ppm MB concentration as the sweet spot for optimal performance and maximum removal rate. The process of color removal can be controlled by adjusting the pH level. Bazrafshan, Zarei, Nadi, and Zazouli (2014) explained that this is due to the fact that it affects the adsorbent's charge or ions, the level of ionization of various pollutants, the dissolution of functional groups on the adsorbent's active sites, and the molecular structure of dye compounds. Figure 4.2 displays the results of an investigation into the effect of pH on MB extraction for PVA (A) and PVA (C) at pH 4, 7, and 12.

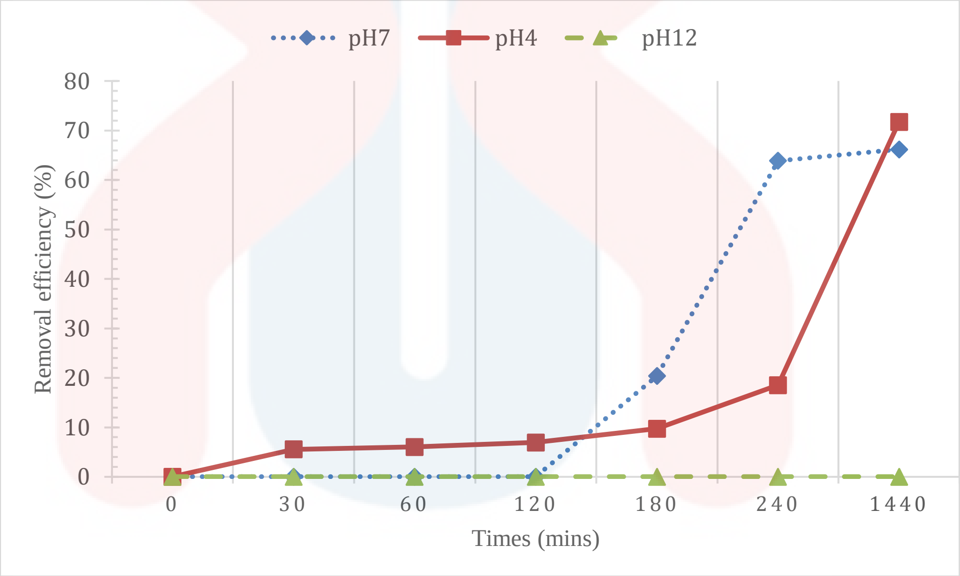

Figure 4.2: Effect of pH on the removal of MB.

The study revealed that acidic solution (pH 4) is more effective for MB removal where the removal rate managed to increase to 71.76% after 24 hours of extraction. Meanwhile, in alkaline solution no MB removal was observed. While pH 7 showed the second highest reading of removal percentage which is 66.20%. This result contradicts with a study by Ijagbemi et al., (2010) who reported that MB removal was better in alkaline solution. From their study they observed that MB can be removed in alkaline solution because alkaline consists of hydroxide ion (OH^-) which negatively charges that can attract with MB which is positively charged ion. Nevertheless, there was reduction in MB concentration as pH increases.

The enhanced extraction at acidic pH levels is attributed to the influence of hydroxyl ions, which promote the formation of extractable target complex species within the organic membrane phase, functioning as counter-ions. It can be proven by a study Coşkun et al., (2019) when MB is a cationic dye, and its solubility and stability are influenced by pH. In general, MB is more soluble and stable in acidic solutions. In acidic conditions, the positively charged MB molecules are more likely to interact with negatively charged surfaces, such as certain adsorbents or membranes. Acidic pH can enhance the adsorption of MB onto surfaces with a net negative charge.

When MB becomes acidic, it undergoes a reduction reaction, leading to a colour change. The reduction involves the acceptance of protons (H^+) and electrons (e^-) by the MB molecule (Hu et al., 2013). In the case of MB, the reduction reaction converts the oxidized form (blue) into the reduced form (pale). Possibly, the H+ ion competes with MB, which also has a positive charge, to form a complex with the Aliquat 336 carrier which is a negatively charged. As a result, the removal of MB becomes low. When the pH increases and the concentration of H^+ ions decreases, the removal of MB also increases at that time. The reduced form of MB is typically colourless or pale compared to the blue colour of the oxidized form. This colour change is exploited in various applications, including the use of MB as an indicator in redox titrations. The reduction reaction in acidic conditions is reversible, and the blue colour can be restored by exposing the reduced form to oxidizing conditions.

When comparing pH 4 and 6, the elimination percentage is lowest at pH 12. Therefore, it follows that methylene blue (MB) cannot be efficiently attracted in an alkaline solution, regardless of the period. These findings point to an acidic pH range as an optimal extraction environment for MB. The presence of hydroxide ions (OH^-) causes a conflict between positively charged nitrogen atoms (cationic nitrogen) and the negatively charged carboxylate group (COO^-) when the pH value is more than 7, as stated by Ijagbemi et al. (2010). One carbon atom (C) is doubly bound to one oxygen atom (O) and another oxygen atom (O) with a negative charge is singly bonded to form this carboxylate group. Because of this rivalry, MB ions are able to adsorb more effectively on the adsorbent surface, and their aggregation is decreased. As a result, an acidic pH environment is more likely to eliminate MB than an alkaline one. Acidic conditions are necessary for the color shift that accompanies MB decrease.

4.1.3 Effect of temperature

The experiment was conducted at a temperature of 35 ˚C and 55 ˚C at an acidic MB solution. The interaction between the removal efficiency and the temperature is given in Figure 4.3. From the result, increasing the temperature of MB solutions to 35 ˚C and 55 ˚C does not increase the MB removal or no removal was observed compared to at room temperature. Although MB removal managed to achieve 35.17% at 180 minutes but, the removal rate suddenly drops and no removal of MB was detected.

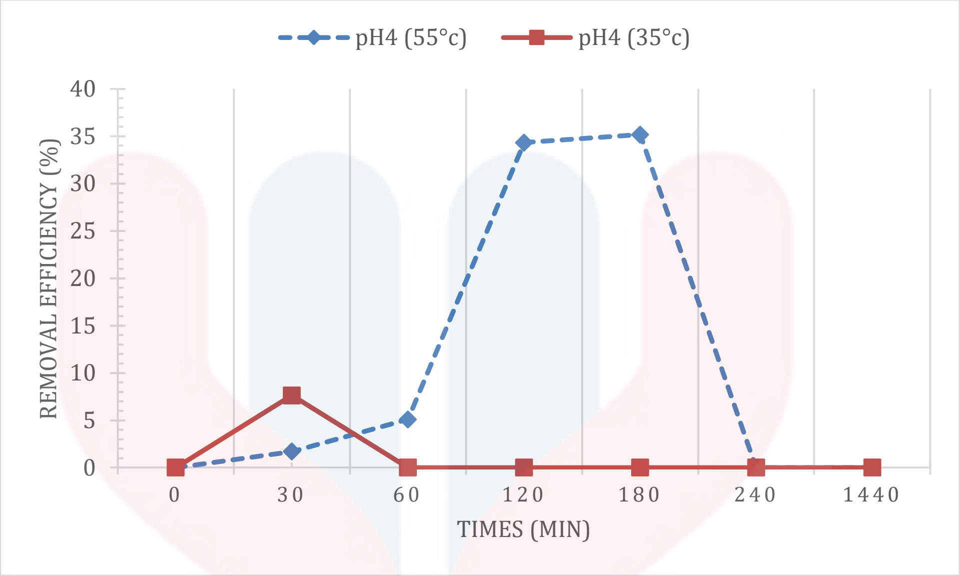

Figure 4.3: Effect of temperature on the removal efficiency of MB.

As stated by Silva et al. (2020) study, a rise in temperature results in a reduction in the adsorption of MB dye, highlighting that the adsorption process is more favorable at lower temperatures. When the temperature is elevated, the binding forces between the active sites on the adsorbent and the molecules of the adsorbate diminish. Consequently, the attraction of the ion carrier complex weakens, causing a slowdown in the removal process. This phenomenon likely extends to the membrane surface, where the strength of the adsorption sites on the membrane decreases as the temperature increases.

4.2 Characterization of PVA PIMs

The adsorption process is significantly impacted by the functional groups within an adsorbent material. Therefore, it is crucial to identify the specific types of functional groups present in the adsorbent material. The use of the FTIR spectrum proves beneficial in anticipating the nature and characteristics of these functional groups within the adsorbent material. Figure 4.4 shows the FT-IR spectra of Aliquat 336, PVA (A) and PVA (C).

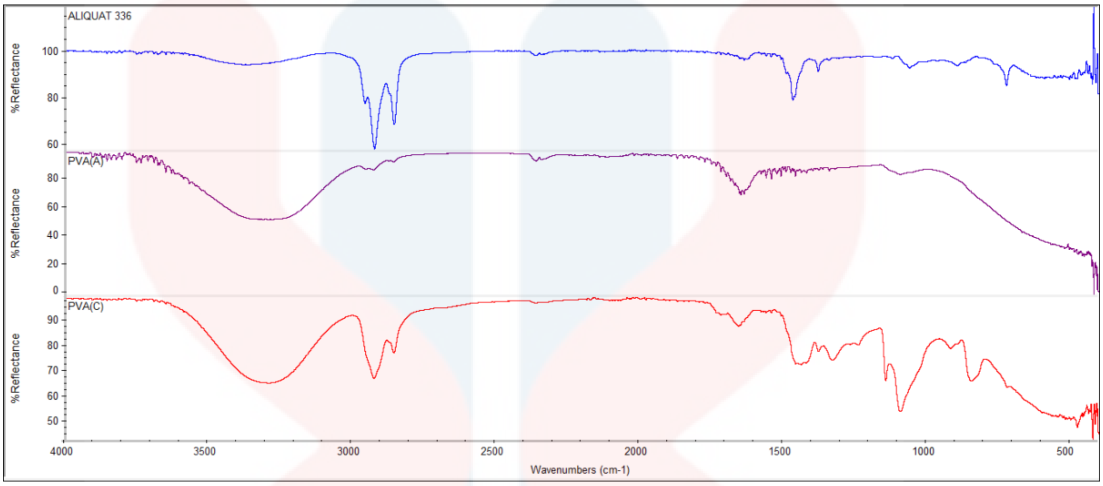

Figure 4.4: FT-IR spectra of Aliquat 336, PIM with PVA (A), and PVA (C).

The results obtained for Aliquat 336 revealed an absorption peak located at 3365.14 cm^{-1}, which can be attributed to the stretching vibration modes of the aliphatic hydrocarbon group, as discussed by Benosmane et al. (2022). Aliphatic compounds are a category of hydrocarbon compounds that consist of carbon and hydrogen atoms arranged in straight chains, branched structures, or non-aromatic rings. Infrared spectroscopists encounter aliphatic groups in various compounds, and the key vibrational modes of interest include C-H stretching, typically occurring around 3000 cm^{-1}, and -CH deformation modes, typically found at approximately 1460 cm^{-1} and 1380 cm^{-1}, as noted by Guan et al. (2019).

The presence of atoms directly linked to aliphatic groups can result in noticeable deviations from typical frequency values. Specifically, adjacent atoms with higher electronegativity tend to shift the positions of spectral bands towards higher frequencies. For example, the vibration linked to the asymmetric stretching of CH^3 groups typically occurs within the range of 2975 - 2950 cm^{-1}, and the absorption corresponding to CH2 groups takes place at approximately 2930 cm^{-1} (Paramasivam et al., 2011).

According to Sellami et al. (2020), the Aliquat 336 spectrum displays two distinct bands at 2922 cm^{-1} and 2853 cm^{-1}, which can be ascribed to the C-H groups. Furthermore, signals originating from the quaternary ammonium group are detected at 1466 cm^{-1} and 1377 cm^{-1}. The presence of a broad peak at 3373 cm^{-1}, characteristic of O-H groups, indicates the existence of some trapped moisture within the Aliquat 336 sample. The symmetric vibration of CH^3 groups is observed in the range of 2885-2865 cm^{-1}, while absorptions associated with CH^2 groups typically fall within the range of approximately 2870-2840 cm^{-1}.

In the case of PVA (A) blended with Aliquat at a concentration of 30 wt.%, the IR spectra display absorption peaks positioned at 3274.41 cm^{-1}. This indicates that PVA (A) has effectively demonstrated its intended functionality, which includes the presence of functional groups from both the carrier and the base polymer. While PVA (C) with Aliquat 50% exhibit adsorption peak 3293.36 cm^{-1} indicating the C-H stretching of the aliphatic CH group and alcohols compound which contain the hydroxyl (-OH) group. Alcohol compounds are categorized into primary, secondary, or tertiary types based on the count of additional carbon atoms bonded to the carbon atom linked to oxygen. In the condensed phase, these molecules engage in hydrogen bonding with each other. This hydrogen bonding significantly elevates the boiling points of alcohols compared to alkane molecules with an equivalent number of carbon atoms. The stretching of the -C-O bond and the deformation of the -OH group display characteristic vibrations, typically occurring in the range of 1050 cm^{-1} to 1150 cm^{-1}. Then, the PIM with PVA -70% Aliquat 30% which is PVA (A) was further used in the extraction study using MB solution.

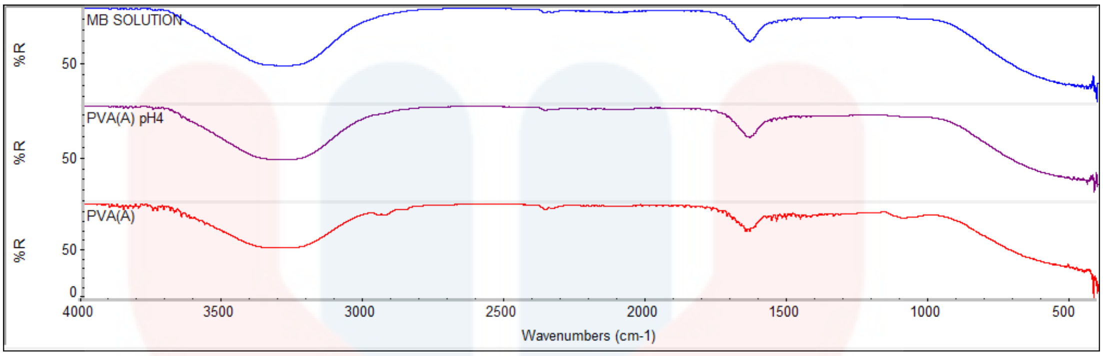

Figure 4.5: FT-IR spectra of PIM with PVA(A) before and after extraction.

The MB solution has functional groups which are aliphatic primary amides. The IR spectrum of this PIM shows adsorption peaks located at 3273.89 cm^{-1}, which is attributed to N-H stretching vibration modes of the aliphatic primary amides. Erina, (2016) describes that the MB solution vibrations peak of bonded OH groups at 3236 cm^{-1} is shifted to 3214 cm^{-1}. This band becomes a broad (70-80 cm^{-1}) structureless shoulder (Ovchinnikov et al., 2016).

Table 4.1: Peak values and the corresponding radical in different components.

Materials	Peak Value (cm^{-1})	Corresponding radical
Aliquat 336	3365.14	CH_2
	3000	C-H
	1460 and 1380	-CH
	2975-2950	CH_3
PVA (A)	3285.70	CH_2
	2923.63	CH^2
	1088.91	-OH
	1417.86	-CH
	2924.49	CH_2
	2855.43	CH
PVA (C)	1436.87	C-H
	1092.39	-CH
	3293.36	CH^2
	1050	-C-O
PVA (A) after extraction	3273.89	N-H
	3277.41	N-H

4.2.1 Characterization of PIM using SEM

The SEM images of all membranes (Figure 4.6) show uniform surfaces and appear dense with no apparent pores. In Figure 4.6 are represented the morphology of PIMs obtained in a scanning electron microscope (SEM) at the magnification x500.

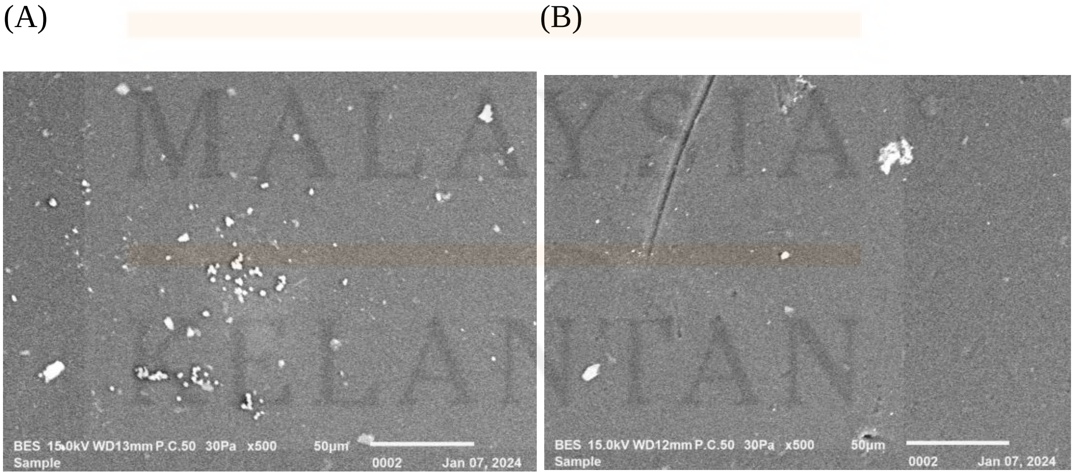

Figure 4.6: SEM image of PVA A (A) and PVA C (B) in magnification x500.

Examined at 500x magnification in the scanning electron microscope (SEM), the sample revealed stunningly detailed surface structures. At 500x magnification, intricate patterns and textures became discernible, capturing a high-resolution image that offered insight into the samples surface topography.

The image of all PIMs shows in Figure 4.7. The polymer inclusion membrane (PIM) is a composite material composed of a polymer matrix embedded with ion carriers, supported on a porous material. This layer is often present in polymer inclusion membranes and contains plasticizers like organic solvents. These plasticizers improve the flexibility and overall performance of the membrane.

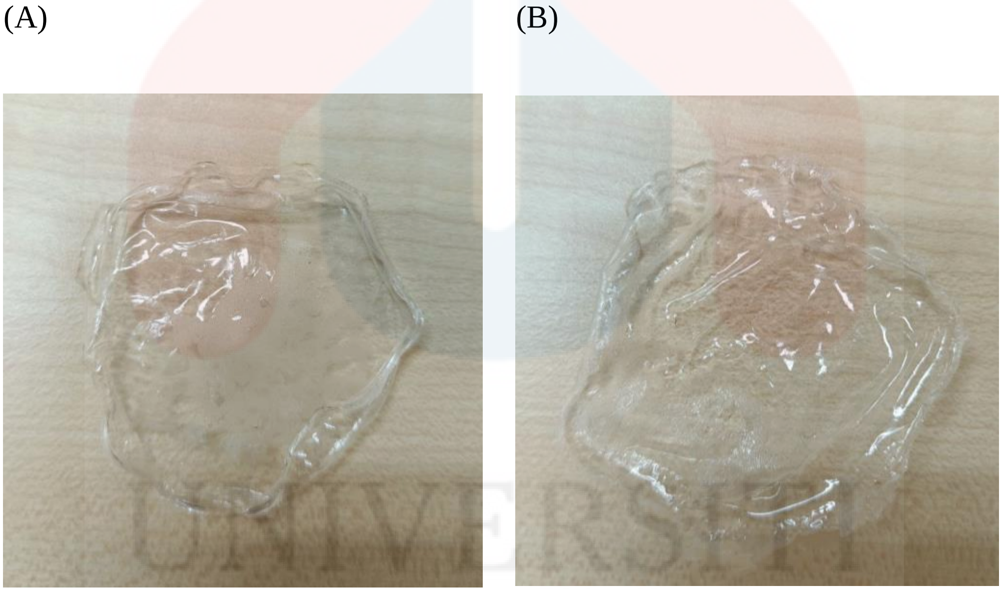

Figure 4.7: The images of PVA A (A) and PVA C (B).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This research employs PVA-based PIMs to eliminate MB from water solutions due to the adverse impact MB poses on the environment**.** The result of the study showed that the extraction of MB using PVA PIMs achieved 71.76% under acidic pH. The maximum condition to achieve removal efficiency are optimal pH level, appropriate adsorbent selection and dosage, contact of times, and temperature controls. There are several parameters studied which are carrier concentration, pH, initial dye concentration and temperature. The optimal setting is valuable for maximizing the removal rate of MB from an aqueous solution within a short timeframe. According to the research findings, the best conditions for extracting MB from the solution involve the use of PIM with PVA (A), maintaining a pH of 4, having an initial dye concentration of 2 ppm, and operating at a temperature of 55˚C. These conditions were identified as they yielded the highest removal efficiency. Following the characterization process, it was observed that the PVA PIM used in the extraction displayed the same adsorption peak as the virgin PVA PIM, albeit with the addition of olefins functional groups. In summary, the successful removal of MB from the aqueous solution was confirmed through FT-IR and SEM characterization.

5.2 Recommendations

After completing this research, some recommendations are suggested to improve the future study. To improve the efficiency of dye removal during the extraction process, various modifications can be contemplated. For instance, altering the carrier used in PIMs, where Tri-n-octylamine (TOA) can serve as an alternative carrier, and it's essential to customize TOA within PIMs to optimize its capacity to facilitate the transport of specific substances through the membrane. Customizing TOA can enhance its stability within the polymer matrix and improve compatibility with the membrane material. This is essential for preserving the long-term integrity and performance of the PIM. Change based polymer to Polyvinylidene fluoride (PVDF) which is often employed in various water treatment processes, including the removal of dyes. PVDF has a considerable surface area, enabling efficient adsorption of dye molecules onto its surface. The polymer matrix offers binding sites for dye molecules, resulting in their extraction from the water. Next, the characterization of the membrane can be enhanced by using other instruments such as X-ray Diffraction (XRD). XRD is a technique used to analyze the crystalline structure of materials by measuring the diffraction of X-rays. It can provide information about the crystallographic phase, crystallite size, and crystal orientation of the membrane, which can be important for understanding its mechanical and chemical properties.

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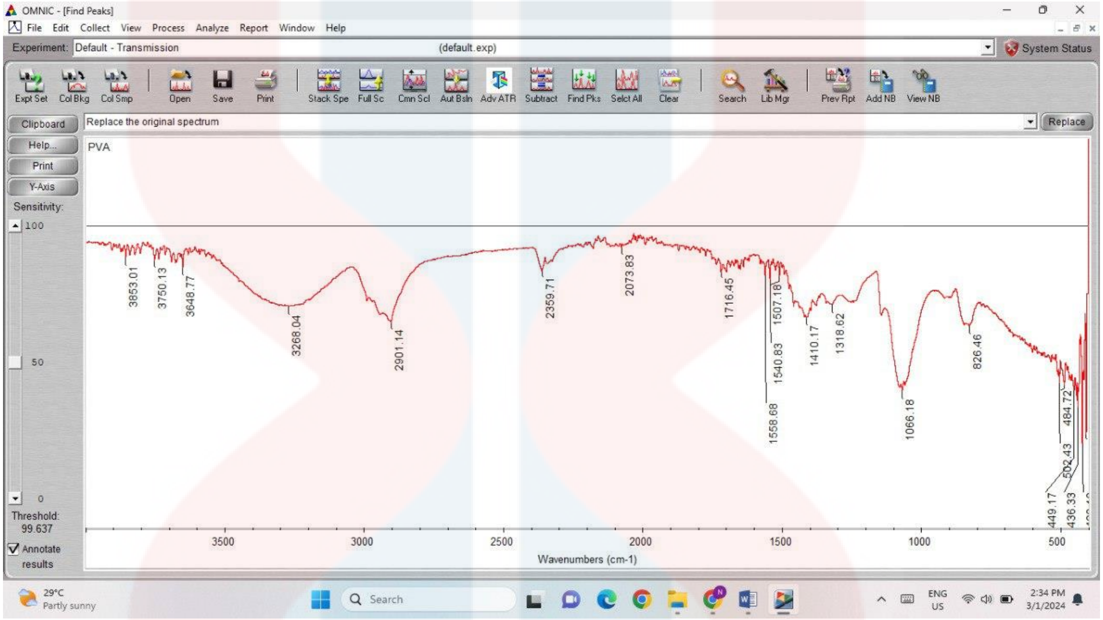
APPENDIX A



OMNIC - [Find Peaks]

Experiment: Default - Transmission (default.exp)

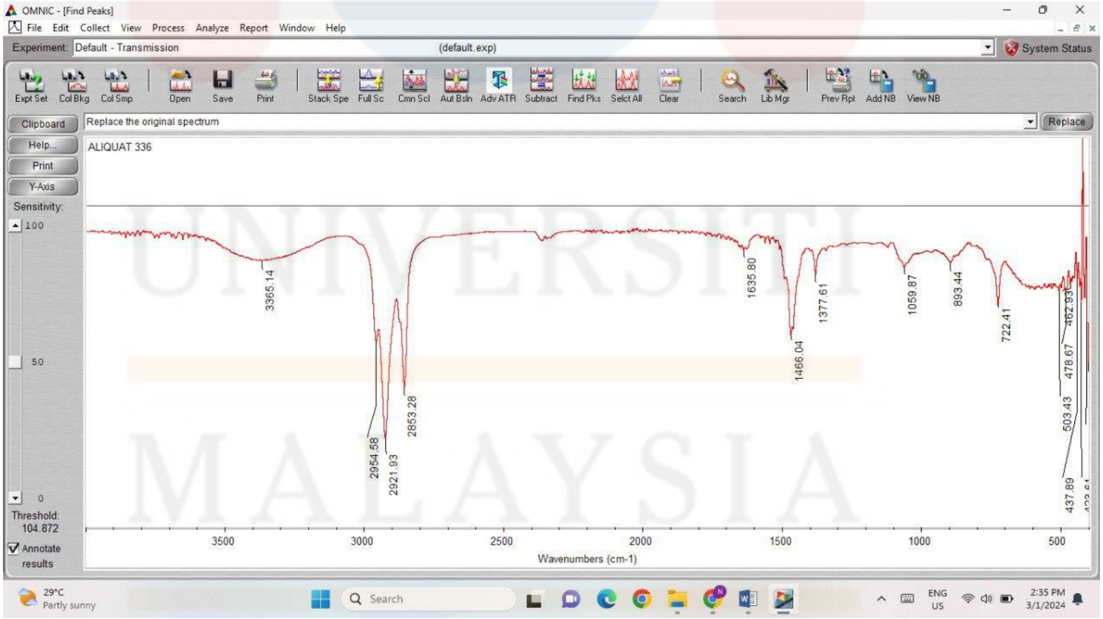
Replace the original spectrum

Sensitivity: 100

Threshold: 99.637

☑ Annotate results

Figure A-1: Peak value of PVA (3268.04 cm^{-1})



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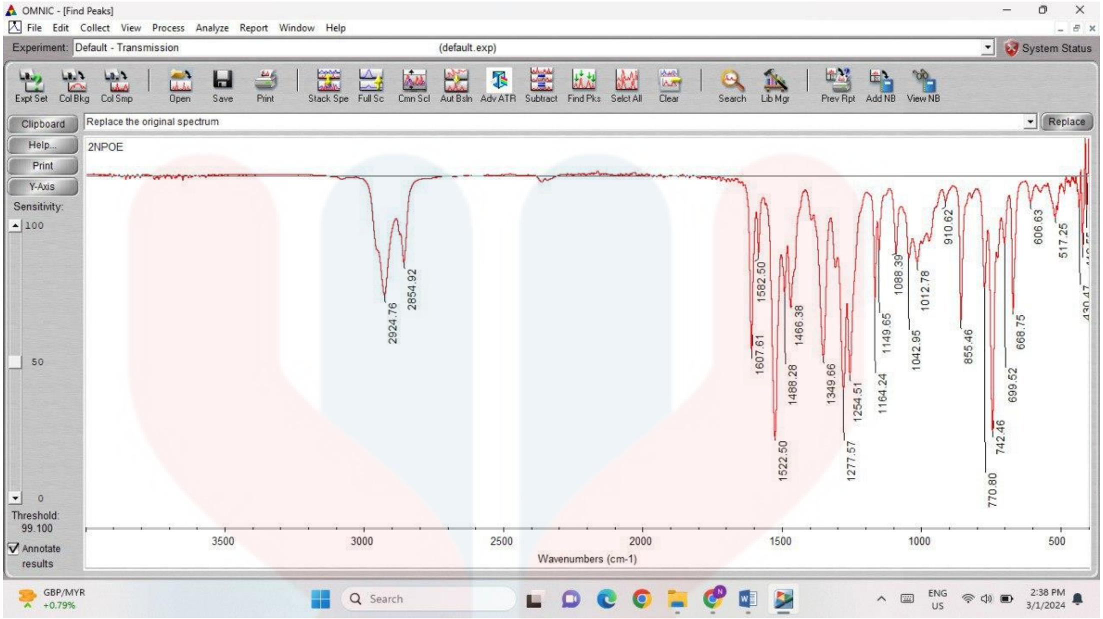
☑ Annotate results

Figure A-2: Peak value of Aliquat 336 (3365.14 cm^{-1})



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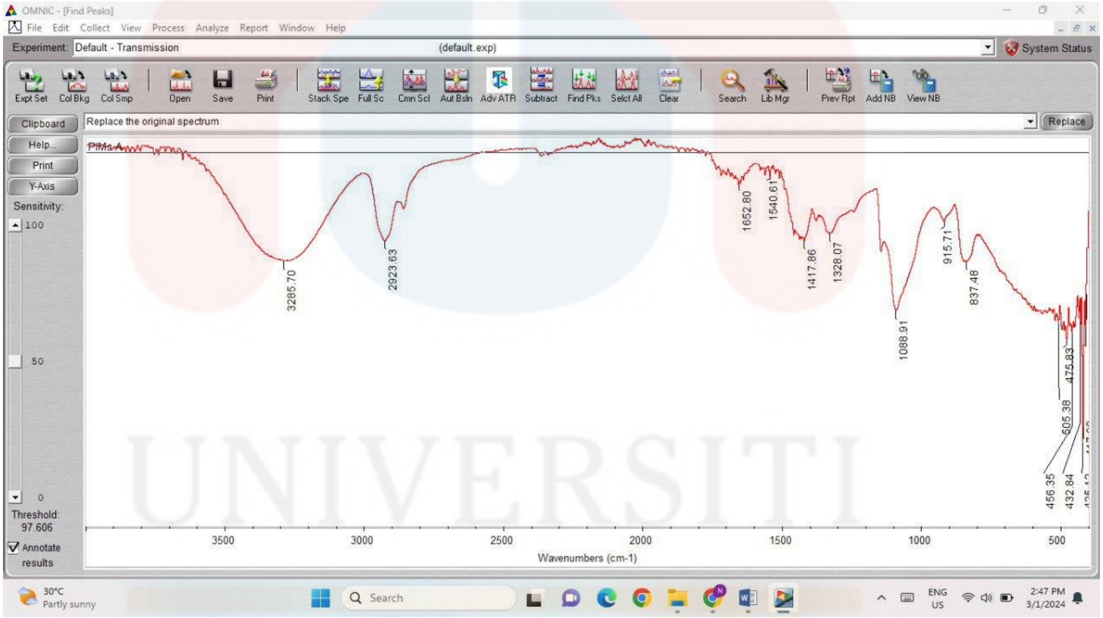
Threshold: 99.100

☑ Annotate results

Figure A-3: Peak value of 2NPOE (2924.76 cm^{-1})



Experiment: Default - Transmission (default.exp)

Replace the original spectrum

Threshold: 97.606

☑ Annotate results

Figure A-4: Peak value of PIMs A (3285.70cm^{-1})

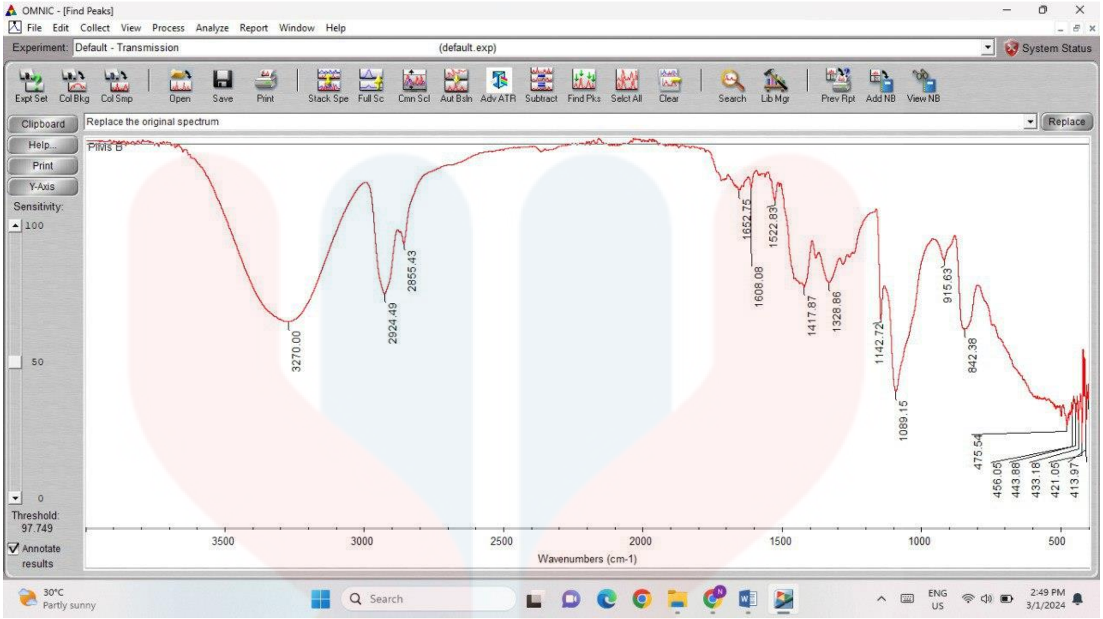


Figure A-5: Peak value of PIMs B (3270.00 cm^{-1})

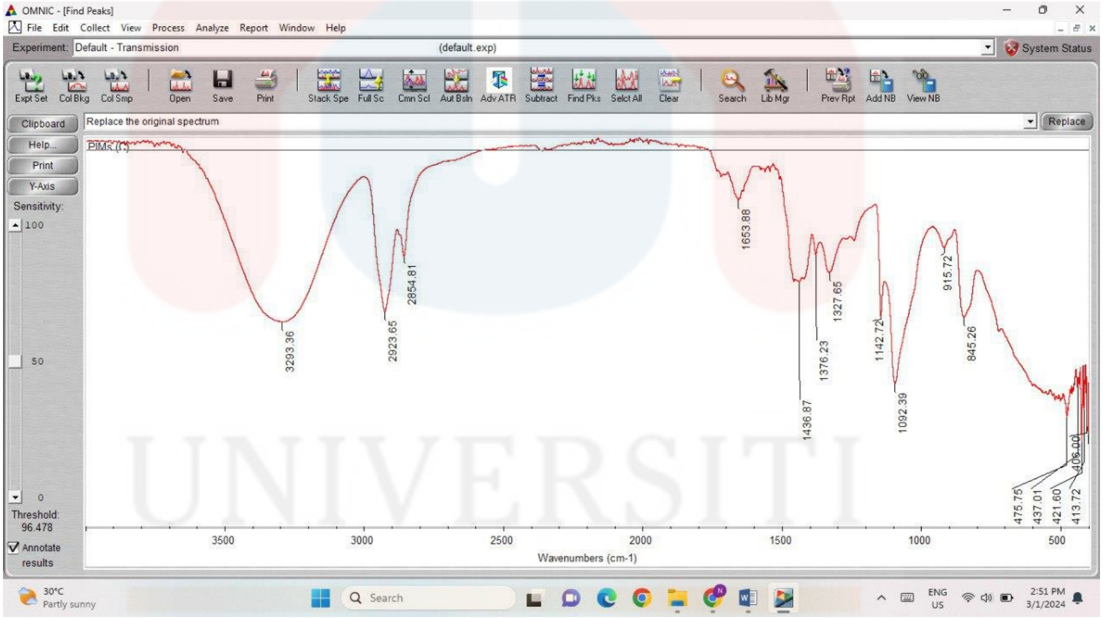


Figure A-6: Peak value of PIMs C (3293.36 cm^{-1})

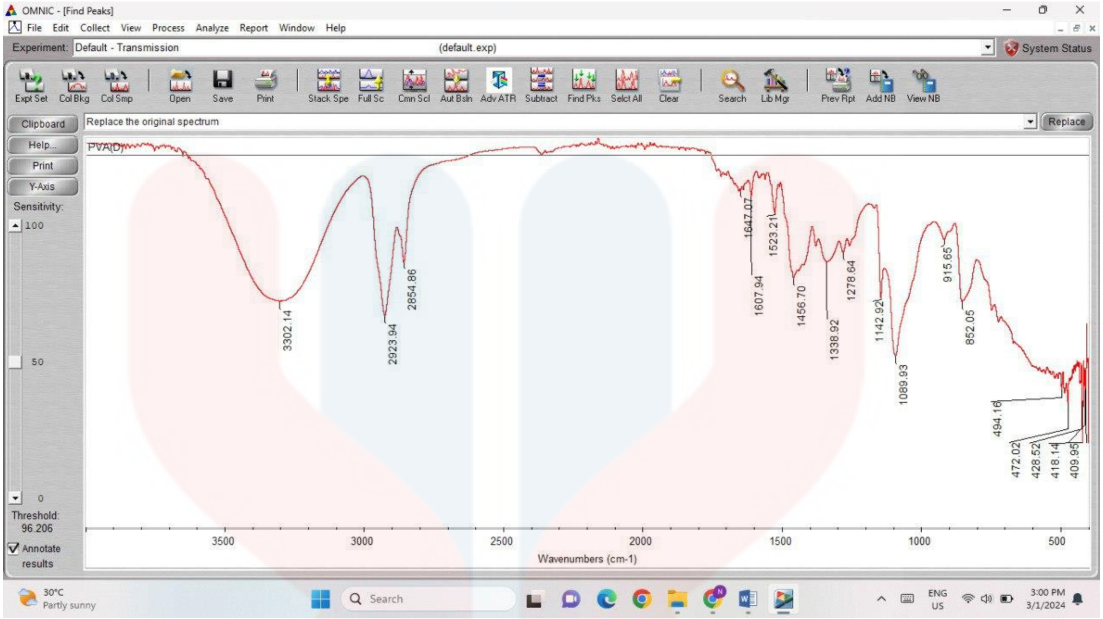


Figure A-7: Peak value of PIMs D (3302.14 cm^{-1})

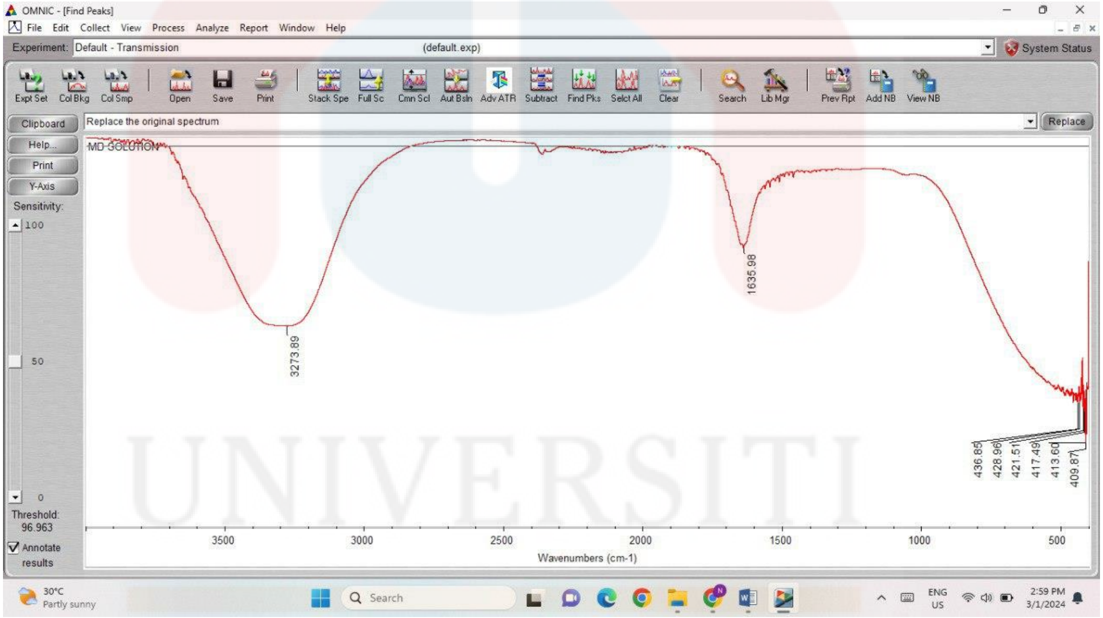


Figure A-8: Peak value of MB solution (3273.89 cm^{-1})

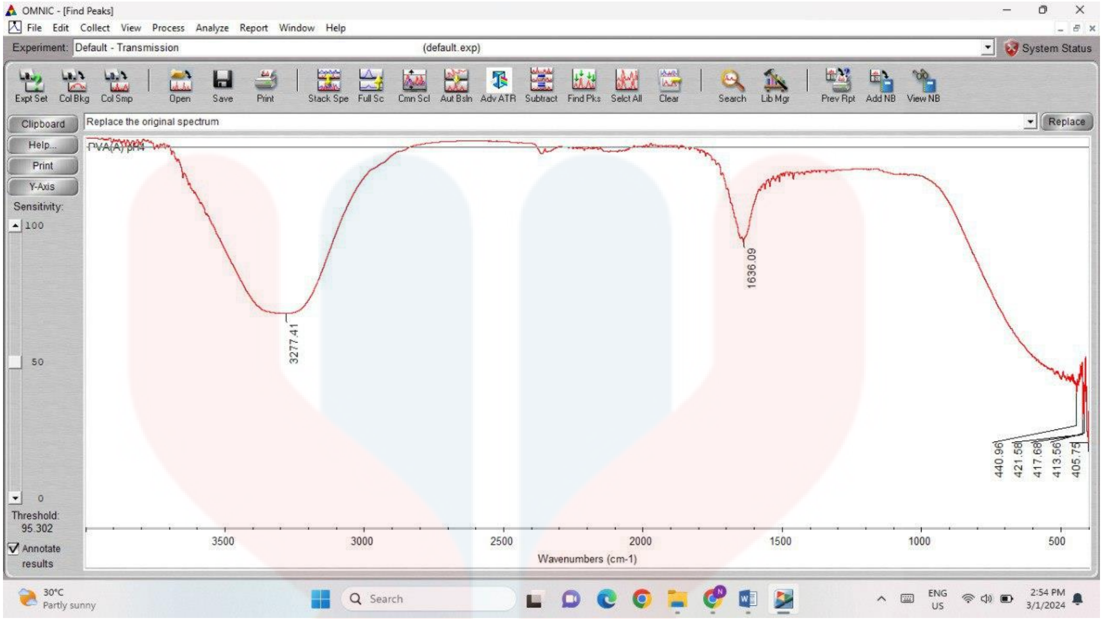


Figure A-9: Peak value of after extraction (3277.41 cm-1)

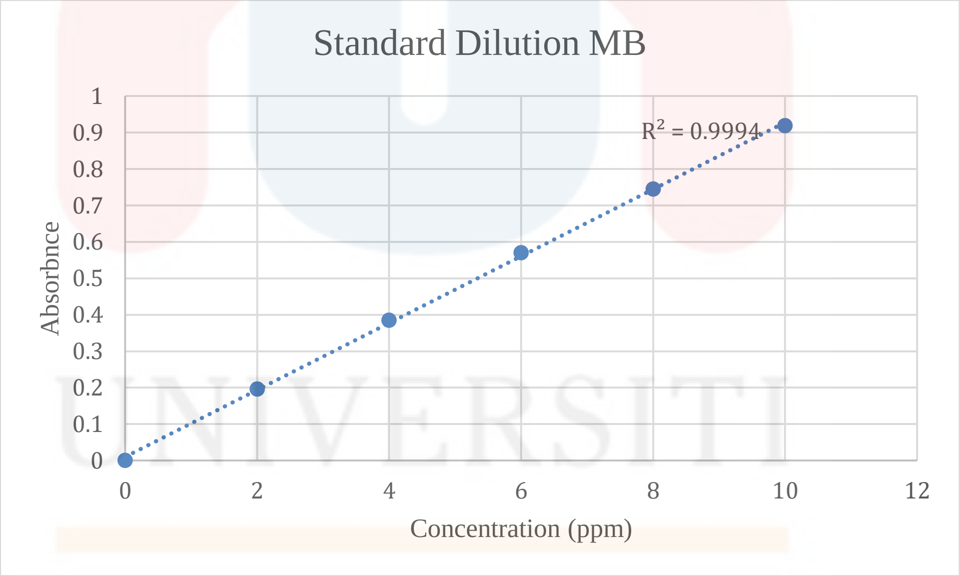


Figure A-10: Standard dilution of methylene blue (MB)

APPENDIX B

Figure B-1: The PVA PIM preparation process

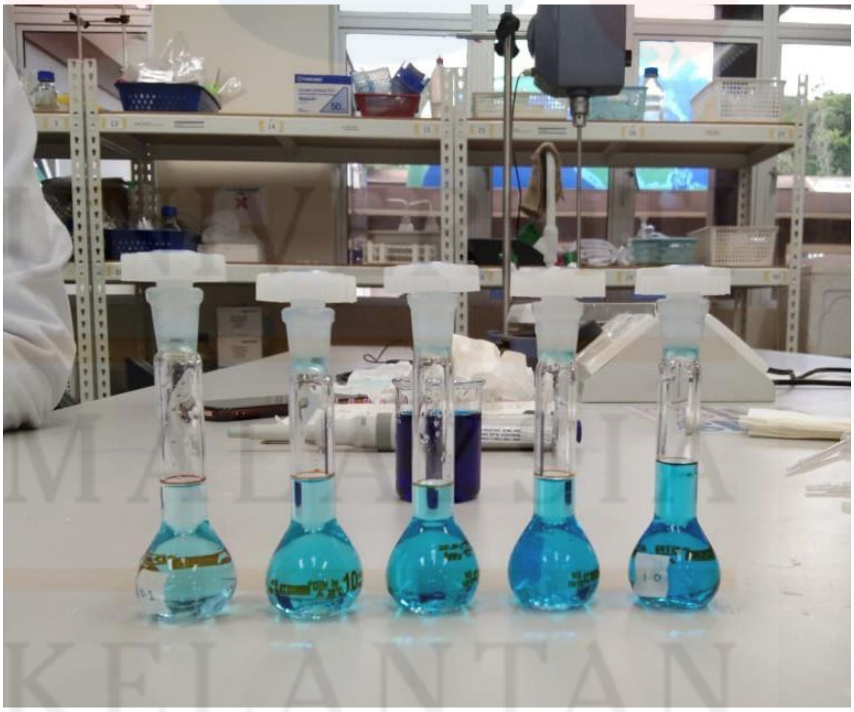


Figure B-2: The dilution of 100 ppm stock solution into different concentrations

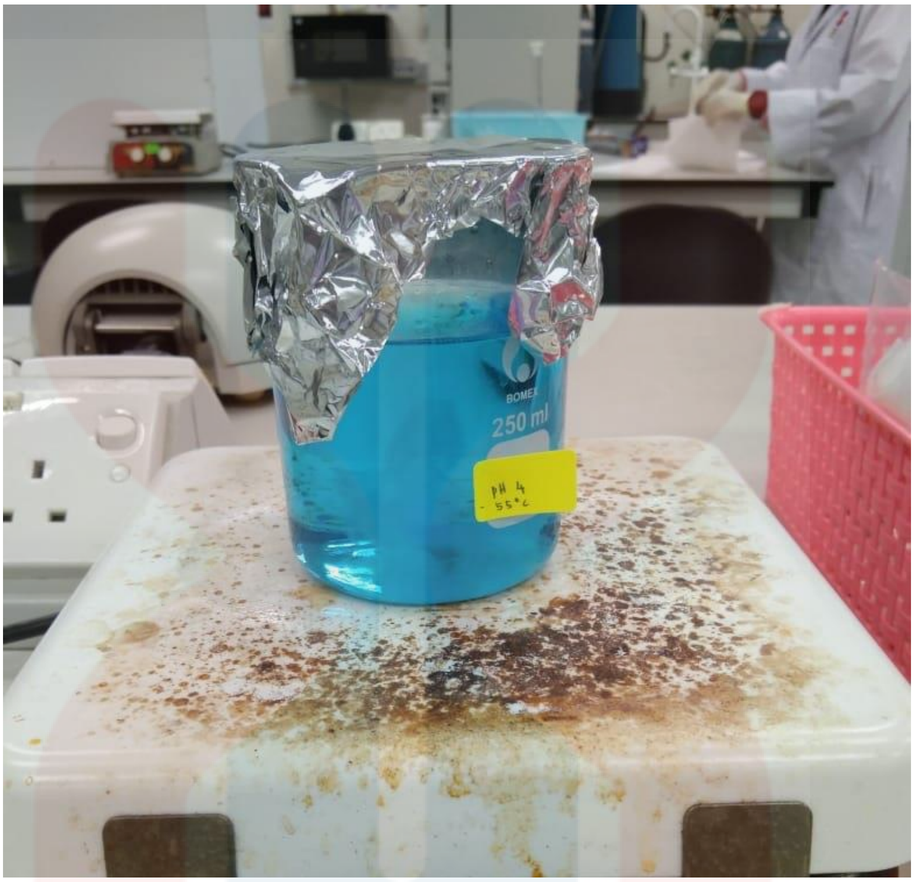


Figure B-3: The MB solution containing acidic pH (pH 4) was stirred on a hotplate (55°C)