THE REMOVAL OF MALACHITE GREEN (MG) USING POLYVINYL CHLORIDE (PVC)-BASED POLYMER INCLUSION MEMBRANES (PIMs)

by

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A report submitted in fulfillment of the requirements for the degree of Bachelor of Applied Science (Sustainable Science) with Honours

FACULTY OF EARTH SCIENCE
UNIVERSITI MALAYSIA KELANTAN

2020

DECLARATION

I declare that this thesis entitled "The Removal of Malachite Green (MG) using Polyvinyl Chloride (PVC)-based Polymer Inclusion Membranes (PIMs)" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ________________________________

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Date : ________________________________

ACKNOWLEDGEMENT

I would like to express my deepest appreciation to all those who provided me the possibility to complete this final year report. I would like to acknowledge with much appreciation the crucial role of Faculty of Earth Science which gives me an opportunity to conduct research of my interest.

Next, a special gratitude I give to my supervisor, Dr. Nurul Syazana binti Abdul Halim whose contribution in stimulating suggestions and encouragement, helped me to coordinate my final year project especially in writing this report.

Lastly, many thanks go to the lecturers of SEL program and laboratory assistants who invested their full effort in guiding me throughout the progress of my final year project. I must also appreciate the guidance given by seniors and friends whom helped me to improve my laboratory skills through their comment and advice.

The Removal of Malachite Green (MG) using Polyvinyl Chloride (PVC)-based Polymer Inclusion Membranes (PIMs)

ABSTRACT

Nowadays, various industries discharge their dyes effluent to the nearby streams. The point source where the dyes is being released caused exponentially increase in water bodies temperature which can kill aquatic organisms. Long term of exposure to the dyes by human can also cause serious health problems. The purpose of this research is to study the potential of polymer inclusion membranes (PIMs) in removing malachite green (MG). The PIM used in this study is made from polyvinyl chloride (PVC) as a base polymer and Aliquat 336 as a carrier, dissolved in Tetrahydrofuran (THF). The composition of carrier, initial dye concentration, pH and stirring speed were varied to determine the optimum condition for PVC PIM to remove MG in 24 hours. Result showed that 99 % of MG was successfully removed from aqueous solution using PVC PIM with 30 wt.% Aliquat 336. At the same time, the initial dye concentration of 10 ppm showed the highest percentage of removal with 99 % but, as the initial dye concentration increases, the extraction capability decreases. The removal of MG is more effective in slightly alkaline condition where pH 9 indicated the highest removal efficiency of MG. The suitable stirring speed which resulting in the highest MG removal efficiency was 250 rpm where, above that speed caused slight reduction in the removal rate. After optimization of all the parameters, about 98 % of removal efficiency had been reached. The PIMs were also characterized using Fourier Transformed Infrared Spectrometry (FT-IR) to determine the functional group presented in each of the components of PIM as well as fresh and used PVC PIMs. Finally, it was concluded that PVC PIMs associated with Aliquat 336 demonstrated outstanding extraction capabilities for the removal of MG from aqueous solution.

Penyingkiran Malakit Hijau (*MG*) dengan Menggunakan *Polymer Inclusion Membranes (PIMs)* Berasaskan *Polyvinyl Chloride (PVC)*

ABSTRAK

Pada masa kini, pelbagai industri melepaskan pengaliran keluar sisa pewarna ke sungai yang berhampiran. Titik sumber di mana pewarna dilepaskan menyebabkan peningkatan suhu air yang boleh membunuh organisma akuatik. Pendedahan kepada pewarna untuk jangka masa yang lama juga boleh mengakibatkan masalah kesihatan yang serius kepada manusia. Tujuan kajian ini dijalankan adalah untuk mengkaji potensi *Polymer Inclusion Membranes (PIMs)* dalam menyingkirkan malakit hijau (*MG*). *PIM* yang digunakan dalam kajian ini diperbuat daripada *polyvinyl chloride (PVC)* sebagai polimer asas dan *Aliquat 336* sebagai pembawa, yang dilarutkan dalam *Tetrahydrofuran (THF)*. Komposisi pembawa, kepekatan awal pewarna, pH dan kelajuan kacauan dipelbagaikan untuk menentukan keadaan optimum yang diperlukan oleh *PVC PIM* untuk menyingkirkan *MG* dalam masa 24 jam. Keputusan menunjukkan 99 % *MG* berjaya disingkirkan daripada larutan akueus menggunakan *PVC PIM* dengan kepekatan 30 wt.% *Aliquat 336*. Pada masa yang sama, kepekatan awal *MG* sebanyak 10 ppm menunjukkan peratusan penyingkiran paling tinggi sebanyak 99 %, tetapi apabila kepekatan awal pewarna meningkat, kemampuan pengekstrakan berkurang. Penyingkiran *MG* juga sangat efektif di dalam larutan yang sedikit beralkali, di mana pH 9 menunjukkan kecekapan penyingkiran *MG* tertinggi. Kelajuan kacauan yang sesuai yang menunjukkan kecekapan penyingkiran *MG* tertinggi adalah 250 rpm di mana, kelajuan yang melebihi kelajuan kacauan tersebut menyebabkan sedikit pengurangan kadar penyingkiran. Selepas semua parameter mencapai keadaan optimum, sebanyak 98 % kecekapan penyingkiran dapat dicapai. *PIM* juga dicirikan menggunakan *Fourier Transformed Infrared Spectrometry (FT-IR)* untuk mengenalpasti kumpulan berfungsi yang ada dalam komponen *PIM* serta *PIM* yang belum dan telah digunakan. Akhir sekali, dapat disimpulkan bahawa *PVC PIM* dengan *Aliquat 336* menunjukkan kemampuan pengekstrakan yang bagus untuk menyingkir *MG* daripada larutan akueus.

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LIST OF ABBREVIATIONS

B_2EHP	Bis-(2-ethylhexyl) phosphate
CAP	Cellulose acetate propionate
CTA	Cellulose triacetate
CTB	Cellulose tributyrate
CV	Crystal violet
D2EHPA	Di-(2-Ethylhexyl) phosphoric acid
DMA	Dynamic Mechanical Analysis
DOP	Dioctyl phthalate
ELM	Emulsion liquid membrane
FTIR	Fourier Transformation Infrared Spectroscopy
HCl	Hydrochloric acid
HNO_3	Nitric acid
LMG	Leucomalachite green
LLE	Liquid-liquid extraction
MB	Methylene blue
MG	Malachite green
NaOH	Sodium hydroxide
PIM	Polymer inclusion membrane
PVC	Polyvinyl chloride
PVDF	Polyvinylidene difluoride
SEM	Scanning electron microscopy
SLM	Supported liquid membrane
THF	Tetrahydrofuran

LIST OF SYMBOLS

wt.%	Weight percent
×	Multiply
-	Minus
%	Percentage
°C	Temperature (degree Celcius)
abs_i	Initial absorbance value of dye
abs	Final absorbance value of dye
cm	Centimeter
g/L	Gram per liter
HNO_{3i}	Initial abs value of HNO_3
HNO_3	Final abs value of HNO_3
mg/L	Milligram per liter
ml	Milliliter
$NaOH_i$	Initial abs value of NaOH
NaOH	Final abs value of NaOH
nm	Nanometer
ppm	Parts per million
R	Recovery factor
rpm	Revolutions per minute
T_g	Glass transition temperature

CHAPTER 1

INTRODUCTION

1.1 Background of research

Nowadays, various industries discharge their dyes effluents to the nearby streams. Point source where the dye is being released causes the exponentially increase of water bodies temperature to 90 ℃ (Xuan Nguyen & Van der Bruggen, 2015). This will lead to detrimental effects to the aquatic life as the concentration of oxygen will deplete, causing insufficient oxygen for the aquatic organisms to perform metabolic activity. Even long term exposure to the dye by human causes various health effects; irritation and respiratory problems such as asthma, sneezing and coughing (Hassaan & Nemr, 2017).

Malachite green (MG) is known to have high stability and strong recalcitrance which indicates its carcinogenic, mutagenic and teratogenic properties that can directly destruct living cell of human (Miyah et al., 2017). The MG pigment is visible in water even as low as 1 ppm (Iqbal & Datta, 2019) thus inhibit sunlight from entering water bodies that will literally kill aquatic lives. Therefore, treatment of dyes is necessary to overcome various environmental problems caused by them.

Conventional technology of dyes removal such as adsorption (Adeyi, Jamil, Abdullah, & Choong, 2019), photocatalytic degradation (Natarajan, Bajaj, & Tayade, 2018) and chemical oxidation (Türgay, Ersöz, Atalay, Forss, & Welander, 2011) have received wider acceptance in textile industrial effluents treatment due to their amenability of large-scale applications. However, the methods have disadvantage in term of the production, operation and maintenance cost that is relatively high. Thus, in comparison to those costly conventional technologies, the application of membrane-based extraction particularly polymer inclusion membranes (PIMs) with more significant advantages such as highly selective and low energy consumption is given considerable attention (Gherasim, Cristea, Grigoras, & Bourceanu, 2011). However, the study of PIM for dyes removal is still new and limited as there are many different types of dyes found in the environment which are still unexplored. In this study, PIM is used for removing MG, a cationic dye.

PIM is basically made up of base polymer, extracting agent or carrier and a plasticizer (Almeida, Cattrall, & Kolev, 2012; Gherasim et al., 2011). Poly(vinyl chloride) (PVC) and cellulose triacetate (CTA) are usually used as base polymers in PIM which act as a support system providing mechanical strength to the membrane (O'Rourke, Cattrall, Kolev, & Potter, 2009). CTA which has been used as base polymers in many PIMs production has shown poor chemical stability (Raut & Mohapatra, 2013), where it can decompose in highly strong acidic and alkaline solution thus it is not recommended for back extraction, one of the functions that can be performed by PIM. Meanwhile, PVC which is formed from monomer of vinyl chloride has long durability, lightweight as it is in powder form and non-flammable (O'Rourke et al., 2009). Thus, PVC is ideal to be applied for both extraction and back extraction whether in acidic or alkaline solution.

A carrier such as Aliquat 336 will bind with targeted species when it passes PIM (Abdul Halim, Whitten, & Nghiem, 2016; Gherasim et al., 2011; Potter et al., 2006). According to Galan, Urtiaga, Alonso, Irabien, & Ortiz (1994), Aliquat 336 is a quaternary ammonium salt which is commercialized as a mixture of tri-nalkylammonium chlorides. In the study of membrane-based extraction, Aliquat 336 is likely a liquid ion ex-changer carrier (Giridhar, Venkatesan, Srinivasan, & Rao, 2006) which consists of a lipophilic cation and a hydrogen bond acceptor anion for commercial solvent extraction (O'Rourke et al., 2009). It also has three chains of alkyl groups which make it hydrophobic (Iqbal & Datta, 2019). A study by Abdul-Halim, Whitten, & Nghiem (2013) showed that Aliquat 336 can act as a plasticizer which will help to improve the solubility of the carrier. However, additional plasticizer in PIMs is not necessary if the carrier itself can act as plasticizer (O'Rourke et al., 2009).

The extraction and back extraction experiment using PIM is usually conducted in a batch study where the PIM is being put in the selected aqueous solution to perform extraction within the allocated time and under suitable parameters. PIM can also promote extraction and back extraction to perform continuously on both sides of the membrane. In addition, PIMs have high diffusion coefficients and affordable in term of production cost (Gherasim et al., 2011).

At the same time, a research conducted by Salima, Ounissa, Lynda, & Mohamed, (2012) has proved that PIM is able to extract methylene blue (MB) from an aqueous feed phase. The efficiency of the extraction process depends on the pH of the aqueous solution, concentration of the carrier in PIMs, stirring speed and initial concentration of dye itself. By optimizing these conditions, 93% of MB was successfully removed from the aqueous solution. However, this study is focusing on the ability of PVC PIM to remove MG in aqueous solution.

1.2 Problem statement

From industrial sectors such as textile, paint, printing and dyeing to the medicine production, the presence of dye as waste in nearby streams is undeniable. Dyes do not easily break down by degradation process (Messaoudi, Khomri, & Bentahar, 2016). Thus, rapid accumulation of dyes on water surface will prevent sunlight from reaching the aqueous water bodies, causing aquatic life to die due to depletion of oxygen. Moreover, the structure of dye itself which contains aromatic amine will lead to cancer and allergic to the contacted human if they are being exposed to dyes for long time (Güzel, Sayğili, Sayğili, & Koyuncu, 2014; Zahoor, 2012).

Many industries such as textiles and painting release dyes to their surrounding water source. About 500000 tons of the dyes were discharged as effluents during the dyes production without proper treatment (Rehman, Sayed, Khan, & Khan, 2017). The existence of dye in water may result in critical health effects to the living creatures and cause serious environmental problems. Hence, dye must be removed from the water bodies because human consume water throughout their basic daily routines such as bathing and drinking.

In correspondence to this problem, a study on the removal of MG was conducted using PVC PIMs. Many studies have proved the capabilities of different types of base polymer such as CTA associated with Aliquat 336 in PIMs to remove metal ions, yet only few studies are conducted using PVC. Even the study of PVC as base polymer in PIM for removing dyes is also limited. Most of the PIMs studies focus on removing metals and organic compound, instead of dyes which also can be detrimental. Hence, PVC incorporated with Aliquat 336 was prepared to study the potential of this PIM in extracting MG. Besides, other parameters that affect the removal rate of MG was also optimized.

1.3 Objectives

The objectives of this research are:

i. to determine the optimum parameters for the removal of MG from aqueous solution.
ii. to identify the functional groups in PIMs by means of Fourier Transformed Infrared Spectrometry (FT-IR).

1.4 Scope of study

The scopes of this study are:

i. to prepare PIMs using PVC as a base polymer and Aliquat 336 as a carrier for the removal of MG from aqueous solution.
ii. to study on the effect of carrier concentration (20, 30, 40 and 50 wt.%), pH (2, 5, 7, 8 and 9), initial MG concentration (10, 20, 30 and 40 ppm) and stirring speed (100, 150, 200, 250 and 300 rpm) on the removal efficiency of the PVC PIM.
iii. to characterize the functional groups in PVC PIM using Fourier Transformed Infrared Spectrometry (FT-IR) at 600-4000 cm^{-1}.

1.5 Significant of study

The discharge of dyes into the environment poses detrimental health effects either to the human or aquatic organisms (Messaoudi et al., 2016). Hence, advanced technology is needed for treating water that has been contaminated with dyes. Recently, PIM becomes a promising technique for environmentally friendly separation of dyes due to its potential of selective separation (Almeida et al., 2012) and high mechanical strength (Witt, Radzyminska-Lenarcik, Kosciuszko, Gierszewska, & Ziuziakowski, 2018). PVC and CTA have been used extensively as base polymer in PIMs for metal ion (Nghiem et al., 2006), gold (Bonggotgetsakul, Cattrall, & Kolev, 2015) and antibiotics separation (Benavente, Romero, Vázquez, Anticó, & Fontàs, 2018). However, study using PVC as base polymers in PIMs, incorporated with Aliquat 336 as a carrier for dyes removal is very limited. To best of our knowledge, there is no study reported on the extraction of dyes using PVC PIM, along with exceptional of plasticizer.

Hence, this study which focuses on the potential of PVC PIM incorporated with different concentration of Aliquat 336 for the removal of MG is very important in PIM studies to discover the strength of PVC to prepare a thin film yet still mechanically strong and functionality of Aliquat 336 as a carrier to bind with targeted MG. This study offers the potential of significant improvement to the overall speed of MG extraction process as well as the simplicity of PIM preparation itself and unitary nature process of removal compared to the readily conventional technologies for dyes separation.

CHAPTER 2

LITERATURE REVIEW

2.1 Dye

Dye can be easily detected in water even at less than 1 ppm because it is usually appears in various colors (Hamidzadeh, Torabbeigi, & Shahtaheri, 2015; Zahoor, 2012). Once the water is contaminated with dye, a lot of efforts are needed to remove the dyes, even the existing conventional methods face challenges in fully removing the dye. This is because dye is an oxidizing agent which resists aerobic bio-oxidation (Güzel et al., 2014). Many inefficient traditional wastewater treatments such as precipitation and electrochemical techniques cannot recover water which has been contaminated by dye.

Chromophores and auxochromes made up the molecules of dye. Chromophores causes the dye to be presentable in colors, while auxochromes improves the color appearance (Sharma & Sanghi, 2012). The dye undergoes slow degradation process that made it persists in the environment for a long time. Realizing that dye poses disastrous effects to human health, thus many wastewater treatment technologies were applied yet the effectiveness of the technologies still cannot tolerate the invasive discharging of dyes into the water bodies.

Dyes can be produced as natural or synthetic. Natural dyes are derived from plant sources such as bark, roots, wood, berries, leaves and lichens. Meanwhile, synthetic dyes are aromatic compounds produced by chemical synthesis, where their aromatic rings structure contains a hetero atom with a lone pair of electrons and also different functional groups (Appusamy, John, Ponnusamy, & Ramalingam, 2014). Dye can be further classified according to the fiber type and the way it is being applied to the substrate. As for fiber type, there are dyes which are used for cotton, nylon and polyester while for the method of application, there are reactive dyes, acid, basic, azoic dyes and direct dyes (Gregory, 2012).

Dye can also be divided into cationic, anionic and non-ionic by determining the charge on the molecules. Anionic dyes are negatively charged (contain more electrons), while cationic dyes are positively charged (contain more protons). However, non-ionic dyes are neutral which means that it has equal number of positive (proton) and negative charges (electron). The most hazardous type of dye based on the molecule charge is cationic dye (Güzel et al., 2014) due to their synthetic origin and structure of aromatic ring which contains delocalized electrons (Appusamy et al., 2014).

One of the examples of cationic dye is crystal violet (CV). CV is an artificial basic cationic dye (Hamidzadeh, Torabbeigi, & Shahtaheri, 2015) which is in the triphenylmethane group (Zahoor, 2012). It is widely used for poultry additive, printing, veterinary medicines (antifungal) and textiles dyeing (Güzel et al., 2014; Zahoor, 2012). The stability and persistence of CV in the environment due to its poor biodegradability made it classified as recalcitrant molecule (Chen, Liao, Cheng, Yen, & Chung, 2007). Besides, its cationic properties made the CV as carcinogenic, mutagenic and teratogenic (Miyah et al., 2017). The cationic CV which is positively charged can interact with negatively charged membrane thus, make it a way to enter the cell and accumulate in the cytoplasm (Rehman et al., 2017).

Another example of hazardous basic cationic dye which is used in this study is malachite green (MG). MG is a water soluble dye which appears as green crystalline powder (Culp & Beland, 1996; Raval, Shah, & Shah, 2017) and is designed for dyeing silk, paper and leather. It is also widely be used as food coloring agent, food additive and medical disinfectant (Raval et al., 2017). Meanwhile, MG is also illegally used as a fungicide, anti-protozoan and disinfectant in fish farming industries (Adeyi et al., 2019). Molecular structure and short description of MG was shown in Figure 2.1 and Table 2.2.

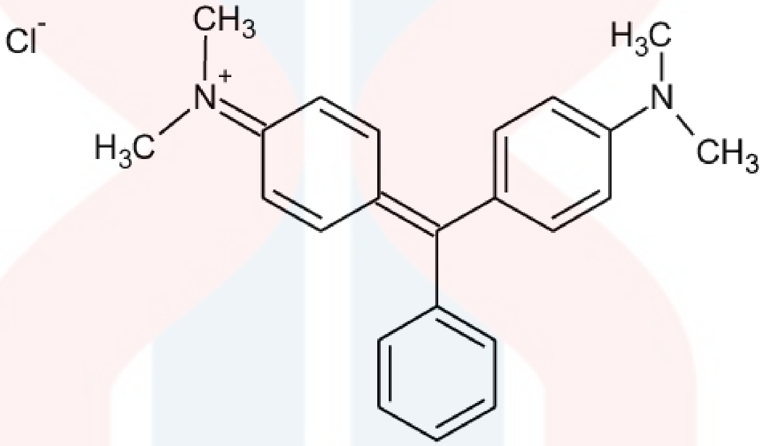

Figure 2.1: Molecular structure of malachite green. (Source: Tara et al., 2019)

Table 2.2: Description of malachite green.

IUPAC name	4-{[4-(dimethylamino)phenyl](phenyl) methylidene}-N,N-dimethylcyclohexa-2,5-dien-1-iminium chloride (Soni, Kumar, Patel, & Kumar, 2016)
Appearance	Green crystalline powder (Culp & Beland, 1996; Raval et al., 2017)
Chemical formula	$[(C_{23}H_{25}N_2)(C_2HO_4)]_2.(C_2H_2O_4)$ (Wanyonyi, Onyari, Shiundu, & Mulaa, 2014)
Other names	Aniline green, Basic green 4, Diamond green B, Victoria green B (Raval et al., 2017)
Maximum wavelength	617 nm (Ling et al., 2017)

However, MG is reasonably poisonous and cause irritant, where even a little exposure to MG may cause vomiting, jaundice, and tissue necrosis (Iqbal & Datta, 2019). In aquaculture industries, MG which is supposed to be used as bacterial treatment is suspected to be easily absorbed by fish and other marine species and later can metabolically be transformed to the lipophilic leucomalachite green (LMG), which can persist for a long time in edible fish tissues (Andersen, Turnipseed, & Roybal, 2006). Therefore, the development of wastewater treatment specifically in dye removal is urgently needed for environmental safety and benefits of health.

2.2 Conventional method for dye removal

There are many physical, chemical and biological methods that have been conducted to remove MG in water bodies. The examples of these methods are coagulation, ozonation, photocatalysis and sonication (Raval et al., 2017). Biological treatment or biodegradation is the weakest method among all the methods available since dye has low biodegradability, and some cannot be degraded naturally at all (Rehman et al., 2017).

Chemical oxidation and membrane filtration are examples of common physicochemical processes that be applied to remove dyes from water. Among all, latter is the most effective methods to remove dye and color in wastewater. However, an accumulation of sludge will be formed after the dyes have been fully removed thus, causing the turbidity of the water to increase (Sivarajasekar & Rajoo, 2015).

Meanwhile, activated carbon also get attention to be used as dye adsorbent because it has high adsorption capacity of organic materials (Miyah et al., 2017). According to the study conducted by Sartape et al. (2017), *Limonia acidissima* (wood apple) shell can also be used as adsorptive agent. Unfortunately, the production cost is expensive and not relevant to be used in large scale industries (Sivarajasekar & Rajoo, 2015).

2.3 Membrane technology

Membrane technology is manipulating the characteristic of several membranes which is semi-permeable. The principle of membrane technology is the membrane will act as specific filter that trap targeted species in water that pass through it (Banerjee, Das, Das, & Mukhopadhyay, 2018). There are many water treatment techniques that uses the concept of membrane technology such as nanofiltration, reverse osmosis, microfiltration, ultrafiltration, membrane distillation and liquid membrane.

The application of membrane technology in various industries such as wastewater treatment, medicines and food processing has becoming a norm and is acceptable by human well-being, proven by many researches. Membrane technology has the potential of separating either metals or organic substances from water. Membrane extraction allows facilitated transport, which resulting in the simultaneous extraction and back extraction throughout the membrane (O'Rourke et al., 2009).

Other than that, membrane technology has high efficiency, good flexibility and low cost (Judd, 2003). Membrane technology is known to be an environmentally friendly technology in the aspect of its impact to the environment, land usage and energy consumption. Without any doubt, membrane technology is proven to potentially contribute to the significant changes in the field of wastewater treatment.

Nanofiltration or specifically polymeric nanofiltration is another alternative for removing dye in water constituents. It is commonly been used in producing drinking water. In the field of water treatment, it plays crucial role in removing hardness and synthetic organic compound. Since 1990, nanofiltration shows promising success in removing dye discharged by industries (Xuan Nguyen & Van der Bruggen, 2015).

In comparison to the readily conventional methods, PIM is an environmentally friendly method for removing dyes in water due to its reusability thus, it does not contaminate the water after the extraction process takes place (Gherasim et al., 2011). Next, PIM has high selectivity in separating targeted solutes from aqueous solution (Almeida et al., 2012). During the extraction process, PIM plays the role as organic phase which storing targeted solutes in its membrane. It is also capable of allowing extraction and back extraction process to be conducted continuously. To be concluded, this technology is not only effective for removing dye, but it is safe and does not cause detrimental effects to the aquatic organisms.

2.4 Polymer inclusion membrane

PIMs are homogenous, flexible and colorless membrane (O'Rourke et al., 2009), constructed by dissolving carrier, base polymer and plasticizer in volatile organic compound (VOC) (Benavente, Romero, Vázquez, Anticó, & Fontàs, 2018; Gherasim et al., 2011). PIM is usually be used to extract targeted ions or molecules from aqueous solution (Gherasim et al., 2011).

PIM has numerous other terms such as gelled liquid, solvent polymeric membranes and polymer liquid. PIM has the characteristics of transparent, homogenous stable and permeable (O'Rourke et al., 2009). Next, PIM can be reuse again and the production cost is affordable. Compared to other liquid membranes such as supported liquid membrane (SLM) and emulsion liquid membrane (ELM), the mechanical resistance and chemical stability of PIM is better. For selective separation process, PIM can extract one single targeted species whilst the porous membrane only separate solutes with the same size (Gherasim et al., 2011). All these characteristics promises that PIM is a considerable potentially method for recovering dye-contaminated water.

Polymer inclusion membranes (PIMs) represent the capability of membrane-based extraction for the selective removal of organic compounds such as dyes from aqueous solutions. The transport of such compounds across PIMs can be described as the simultaneous extraction and back-extraction process combined in a single stage. The transport of cationic dyes and the possibility of their selectivity of extraction are determined by how the cations react with the carriers and the structure and stability of the membranes being formed (Ulewicz & Radzymińska-Lenarcik, 2011)

2.4.1 Base polymer

The role of base polymer is more likely a back bone of any polymer inclusion membrane, where it gives strength to the structure of the membrane (Almeida et al., 2012), making it strong and stable for any kind of extraction, in any experimental conditions. Many previous studies of PIMs used poly(vinyl chloride) (PVC) and cellulose triacetate (CTA) as base polymers due to their thermoplastic properties which can easily dissolved in organic solvent resulting from no crosslinking between polymer strands of both PVC and CTA (Zulkefeli, Weng, & Abdul Halim, 2018).

PVC which is formed from a vinyl chloride monomer as shown in Figure 2.3, has non-flammable characteristic and high stability. It is also light and compatible with many types of plasticizer (O'Rourke et al., 2009). PVC based membrane can be used for removing targeted species in both acidic and basic solution. Meanwhile, CTA has good stability, excellent flux (Darvishi, Karimi Sabet, & Esfahany, 2018) and mechanically strong because of its crystalline structure, however it is chemically weaker than PVC (Gherasim et al., 2011). The contrary of these two is PVDF which is formed during polymerization process of vinylidene difluoride (Ji, Liu, Hashim, Abed, & Li, 2015). PVDF has low solubility in major common organic solvent such as tetrahydrofuran (THF) (Li et al., 2013), thus a long time is required to produce PVDF-PIM.

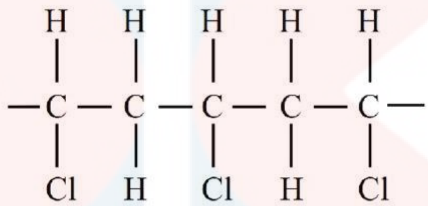

Figure 2.3: Molecular formula of polyvinyl chloride. (Source: Arahman, Fahrina, Wahab, & Fathanah, 2018)

2.4.2 Carrier and plasticizer

The role of carrier in PIMs is to extract and transport solutes in the form of ions or chemicals from aqueous solution. This is be done by binding of the carrier to the targeted ions during transport pass (Yildiz, Manzak, Aydin, & Tutkun, 2014). During the extraction process, the carrier will transport targeted ions from source solution into the receiving phase (Gherasim et al., 2011) through facilitated transport which eventually will offer in the improvement of overall transportation speed (O’Rourke et al., 2009).

On the other hand, additional plasticizer helps to decrease hydrogen bonds of the polymer chain thus, ensure the flexibility of the membrane. The combination of plasticizer along with base polymers will resulting in good compatibility and elasticity, low volatility, toxicity and viscosity of the PIMs. However, a study proved that the plasticizer is an expensive substance thus, the dismissal of the plasticizer in PIM would lead to significantly reduction of cost.

There are certain carriers that can act as a plasticizer such as D2EHPA and Aliquat 336. According to Gherasim et al. (2011), PIMs that contain 50 wt.% of D2EHPA result in better extraction of targeted solutes than plasticized PIMs. Meanwhile, Aliquat 336 has widely been used as a carrier in PIMs. This ionic liquid has meaningful properties to be an ideal carrier as well as replacing the role of actual plasticizer.

Aliquat 336 (tricaprylylmethylammonium chloride) (Vincent & Guibal, 2001) which is made up of mixture of quaternary ammonium chlorides (Van Roosendael, Regadío, Roosen, & Binnemans, 2019) consists of a hydrogen bond acceptor anion and a lipophilic cation which can form heteroconjugate anion when neutral molecule is extracted (O'Rourke et al., 2009). The chemical structure of Aliquat 336 is shown in Figure 2.4. According to Sakai, Cattrall, Potter, Kolev, & Paimin (2000), 30 to 50 wt.% of Aliquat 336 must be included in PIM for successfully extraction of solutes that passed through it. If the concentration of carrier lower than 20 wt.%, there will be no extraction occur. The rate of extraction exponentially increases when the concentration of carrier reaches a maximum of 50 wt.%, referring to the percolation threshold (O'Rourke et al., 2009).

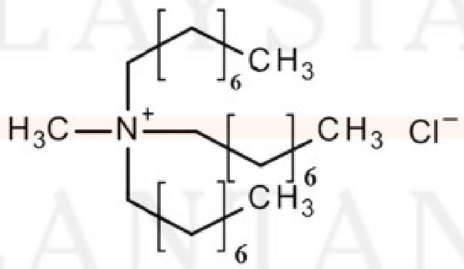

Figure 2.4: Chemical structure of Aliquat 336. (Source: (Lupa, Cocheci, Pode, & Hulka, 2018)

The molecular structure of Aliquat 336 is the most important factor that influences the membrane selectivity due to its specific and conformational interactions (Nghiem et al., 2006) with targeted species. In the removal study of metals and dyes, the complex or ion pair formed between the targeted species and Aliquat 336 is retained in the PIM thus causing extraction process to occur across the membrane.

A study by Benavente et al. (2018) proved that the use of ionic liquid such as Aliquat 336 as carriers gives mechanical strength to PIM as well as improving its flexibility. Hence, the additional of plasticizer in PIM is unnecessary for this case. This type of carrier has physicochemical properties such as lipophilicity, high viscosity, can interact with dipole-dipole interactions, strong hydrogen bond and exists in the form of liquid at room temperature that enables it to replace plasticizer (O'Rourke et al., 2009).

In addition, Aliquat 336 is classified as a plasticizer when it is being used with PVC because it can transform brittle PVC into plastic. The additional of Aliquat 336 will soften the PVC, indicating that Aliquat 336 does not achieve the plasticization by forming a solid solution with PVC and depressing its T_g. However, it achieves plasticization through the formation of a sponge like structure of PVC, containing Aliquat 336 in the sponge pores (Abdul-Halim et al., 2013).

Moreover, a study by (Sakai et al., 2000) showed contradiction result regarding the role of plasticizer where the transport of thiourea through the PIM containing organic compound plasticizer resulting in slow rate of extraction compared when Aliquat 336 itself is being used as plasticizer. This is because thiourea can dissolve in Aliquat 336. This study proved that diffusion coefficient of substance in carrier is important to increase the efficiency of PIM for removing contaminant from water.

2.5 Previous study of PIM for dye removal

Many studies have shown that PIMs are successful in removing and recovering metal ions. Due to its capabilities, research in PIMs has been expanded in other application such as removal of dyes from wastewater. Recently, a study conducted by Salima, Ounissa, Fadila, & Mohamed (2016) showed more than 99 % of red bordeaux acid dye and yellow erionyl dye have been removed using CTA based PIM incorporated with Aliquat 336 under optimized conditions.

There was also another study by Ling, Bukhari, & Suah (2017) which used PIM for the removal of MG from real and synthetic wastewater. The PIM uses poly(vinyl) chloride (PVC) as the base polymer, bis-(2-ethylhexyl) phosphate (B2EHP) as carrier and dioctyl phthalate (DOP) as plasticizer. The extraction study was successfully removing more than 98 % of MG from wastewater.

Although the above studies have shown interesting results however the study on PIMs for the removal of dyes is still new and limited. The potential of PIMs in extracting many other dyes are remain unknown considering that there are variety types of dyes and extractants available in the market. Therefore, this study which focuses on the potential of PVC PIMs incorporated with Aliquat 336 for the removal of MG can benefit the industries.

2.6 Characterization of PIM

According to Cole (2008), infrared spectroscopy is a complement to X-ray diffraction and transmission electron microscopy. In his study, overall degree of intercalation or exfoliation in polymer nanocomposites was identified using infrared spectroscopy to quantify the degree of orientation for the polypropylene matrix and the reinforcing clay in blown nanocomposite films.

In conjunction with that, Fourier Transformed Infrared Spectrometry (FT-IR) is used for identifying the interaction of the components in PIMs (Gherasim et al., 2011). In this study, FT-IR is useful for studying the interaction between Aliquat 336 and PVC after being mixed together with THF either they have new covalent interactions or electrostatics interactions (Yildiz, Manzak, Aydin, & Tutkun, 2014) to determine the filtration performance of PIMs.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials and methods

The materials and apparatus that were used in this study are listed in Table 3.1 and 3.2 respectively.

Table 3.1: List of materials used in the experiment.

No	Materials	Brand
1	PVC polymer	Aldrich
2	Aliquat 336	AL0159 Alpha Chemika
3	Tetrahydrofuran	R & M Chemicals
4	Malachite Green	Minerals-water.ltd
5	Filter paper	Whatman qualitative filter paper No. 2 Camlab UK
6	Distilled water	Favorit® W4L Water Distiller
7	Nitric acid	R & M Chemicals.
8	Hydrochloric acid	R & M Chemicals
9	Sodium hydroxide	R & M Chemicals
10	Parafilm	Parafilm "M" Laboratory Film Bemis
11	Disposable macro cuvette (10 mm)	P 0037 Cuvette Macro 10mm
12	Disposal plastic dropper (3 mL)	Plastic Eye Dropper Set Transfer Graduated Pipettes Nalgene

Table 3.2: List of apparatus used in the experiment.

No	Apparatus	Brand
1	Glass petri dish	Favorit® Petri Dish
2	Magnetic stirrer	Multi-position Magnetic Stirrer (MS-H-S-10)
3	20 mL beaker	HmbG Bboro 3.3 100mL

Table 3.2 (Continued)

4	UV-Vis spectrophotometer	Hach DR 6000 UV VIS Spectrophotometer
5	Orbital shaker	Lab Companion Shaking Incubator Model SI-600R
6	Volumetric flask 100 mL and 25 mL	NS HmbG DIN A In 20°C
7	FT-IR	PerkinElmer, 1750X-PerkinElmer Inc.
8	Conical flask 250 mL	Schott Duran 250 mL
9	Micropipette (10-100 µL)	Eppendorf Research Plus
10	Micropipette (100-1000 µL)	Eppendorf Research Plus M11681C 1000
11	Hotplate stirrer	Thermo Scientific Cimarec Stirring Hot Plates
12	Fume hood	Laboff Fume Cupboard
13	Spatula	K 1145 Spatula - Stainless Steel
14	Weighing balance	Mettler Toledo B3002-S Balance
15	Measuring cylinder	Favorit® 100mL
16	Reagent bottle	Reagent bottle Rs 62/250ml
17	Forcep	Laboratory Tools Adson Thumb Forceps by Delta Med Surgical
18	pH meter	Hanna HI 2211 Microprocessor-based pH/mV/°C Bench Meters

3.2 Preparation of MG solution

0.1 g of MG powder was dissolved in the 100 ml distilled water using 100 m/L volumetric flask thus producing 1000 ppm of MG stock solution. Further dilution was conducted to obtain 10, 20, 30 and 40 ppm for the calibration curve purpose. Calibration using standard MG solutions were conducted prior to each batch of analysis. The linear regression coefficient for all calibration curves obtained were greater than 0.97.

3.3 Preparation of PIM

The PIM was prepared using poly(vinyl chloride) (PVC) as base polymer and Aliquat 336 as a carrier. For this study, various concentration of Aliquat 336 (20, 30, 40 and 50 wt.%) was mixed with PVC in 10 mL of tetrahydrofuran (THF) to produce 500 mg of polymer solution, which is equal to one sheet of PIM. The solution was stirred using a magnetic stirrer until it become homogenous. During the stirring process, the beaker was covered with parafilm. Finally, the mixed polymer solution was poured into a 9 cm diameter of petri dish and be covered with filter paper for overnight at room temperature to form a PIM at slow rate. The next day, the PIM was peeled from the petri dish and was further used for extraction experiments.

3.4 Extraction study of MG

For the extraction experiments with MG, the PVC associated with (10, 20, 30 and 40 wt.%) Aliquat 336 based PIM were cut into smaller pieces and placed in a 10 ppm of MG solutions. The extraction solution was set at room temperature (27 °C) and the pH was set neutral (7). The extraction solution was stirred at 150 rpm and the samples of aliquots were taken 7 times within 24 hours for analysis using UV-Vis spectrophotometer at 617 nm (Miyah et al., 2017). The removal efficiency was calculated using Equation 3.1. From the result, the optimum Aliquat 336 content in PVC PIM was determined based on the highest removal efficiency and was used in further experiment.

$$Removal\ efficiency, E\ (\%) = \frac{abs_i - abs}{abs_i} \times 100\% \qquad (3.1)$$

Where,

abs_i = Initial abs value of dye

abs = Final abs value of dye

The extraction experiments were repeated to study the effect of initial dye concentration, pH and stirring speed on the removal of dye. For determining the initial dye concentration, the optimum Aliquat 336 which was determined from the previous experiment was used in extracting 10, 20, 30 and 40 ppm of MG while the temperature, pH and stirring speed were set to the control setting. After determining the optimum initial dye concentration, the experiment was followed by the extraction of MG for determining the optimum pH. The pH was determined by studying variation pH of MG solution which were 2, 5, 7, 8 and 9. The pH of MG were adjusted using HCl and NaOH. The optimum Aliquat 336 concentration and initial dye concentration to be used were taken from the previous experiment while the speed was maintained at 150 rpm. Lastly, the optimum stirring speed for MG extraction were varied to 100, 150, 200, 250 and 300 rpm accompanied with all the optimized parameters. The optimum concentration of Aliquat 336, initial dye concentration, pH and stirring speed were then being determined by tabulating yield point graph.

3.5 Characterization of PIMs

3.5.1 Fourier transformed infrared spectroscopy (FTIR)

Infrared spectra were recorded in the transmission mode, in the range of 600 to 4000 cm^{-1} (Gherasim et al., 2011; Nidheesh, Gandhimathi, Ramesh, & Singh, 2012). The functional groups in PVC, Aliquat 336 and PVC PIM with Aliquat 336 was determined by doing comparison to the existing standard functional groups in fresh PIM and changing of functional groups in used PIM (Ling et al., 2017).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 The study of MG extraction

4.1.1 The effect of Aliquat 336 concentration

The removal efficiency of MG using PVC PIM at different Aliquat 336 concentration was first studied in order to determine the best PVC PIM with carrier content. The obtained results shown in Figure 4.1 shows that all PVC PIMs have successfully removed more than 99 % of MG after 23 hours regardless the Aliquat 336 content.

The extraction of dye across the PIM was caused by the ion ex-changer carrier in the PIM which is Aliquat 336. This is because when the PIM and MG is in contact with each other, a dynamic equilibrium is established between them (Das, Pal, Saha, & Maji, 2009) which is caused by the electrostatic force of attraction. The part of MG dye molecule which has electron-rich oxygen atom (Cl^{-1} ions) interacts with the nitrogen atom of the amine group of Aliquat 336 (Iqbal & Datta, 2019) to form neutral ion pair complex (Ling et al., 2017). At the same time, the positive charge on the tertiary nitrogen ions in MG also attracted to the negative charge presented in Aliquat 336 as proved in a study by Ling et al. (2017) where nitrogen ions in MG moved towards the negatively charged B2EHP thus causing the dyes molecules to be extracted from the aqueous solution and adsorbed to the PIM.

From Figure 4.1, PVC PIM associated with Aliquat 336 achieved more than 97 % of dye removal after 24 hours for all PVC PIMs. However, PVC PIM with 30 wt. % of Aliquat 336 was chosen for the further used because it exhibited the fastest removal efficiency of MG (71 %) after one hour compared to the other PIMs.

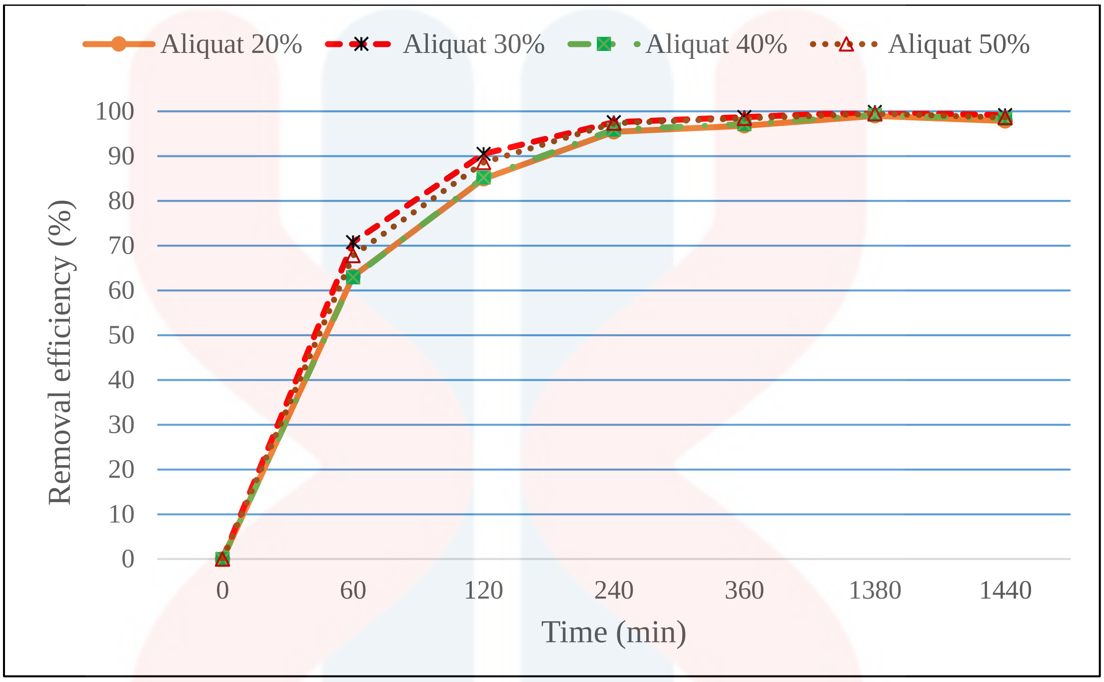

Figure 4.1: The removal efficiency of MG using PVC PIMs with different Aliquat 336 concentrations.

4.1.2 The effect of initial dye concentration

The effect of different initial dye concentration ranging from 10 to 40 ppm were studied and the results are shown in Figure 4.2. The optimum 30 wt.% of Aliquat 336 PVC PIM was used with pH 7, temperature of 27 °C and stirring speed of 150 rpm. From the figure, the removal efficiency of MG decreased with the increasing of dye concentration. It was found that at 10 ppm of MG, the removal efficiency was more than 97 % within 4 hours of extraction. After 4 hours, the removal efficiency was constant which attributed to the equilibrium attainment (Adeyi et al., 2019). Meanwhile at higher concentration, the PVC PIM is quickly saturated and thus decrease the effectiveness of membrane area (Salima et al., 2012). This finding is similar with a study conducted by Kebiche-Senhadji, Tingry, Seta, & Benamor (2010) which proved that the increasing concentration of metallic ions used in transport experiment caused increasing of fluxes, where among the ranges of initial concentration of Cr(VI) studied, concentrations higher than 30 ppm showed the limit value of transport flux due to the saturation at the carrier sites. Therefore 10 ppm was selected for further study.

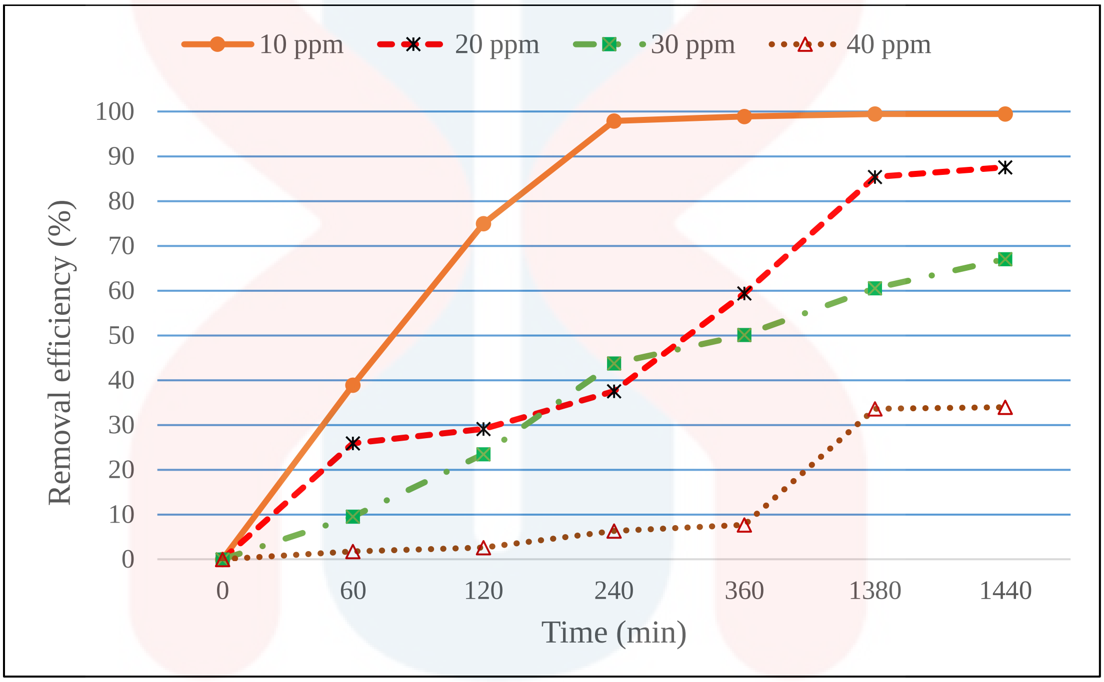

Figure 4.2: The removal efficiency of MG using PVC PIMs with different initial dye concentration.

4.1.3 The effect of pH in aqueous solution

The initial pH of dye which also influences the rate of extraction was studied ranging from pH 2 to 9 only. However, pH of MG that is more than 9 was neglected in this study because the immediate fading and loss intensity of MG colour within 10 minutes was observed when the pH of MG was adjusted using NaOH thus this will eventually affect the result of MG extraction efficiency starting from the initial time. The fading of MG in alkaline condition can be attributed to the conversion of MG dye molecule into its carbinol compounds that causes it to lose its chromophore due to the presence of OH^- ions in the alkaline condition (Iqbal & Datta, 2019).

The relationship between pH of MG and the percentage of removal was given in Figure 4.3. The maximum percentage of removal occurred at pH 9 with 99 % of extraction efficiency whereas pH 7 and pH 8 exhibited more than 96 % of dye removal. However, pH 9 was chosen as the optimum pH because the dye removal showed the fastest removal rate with highest extraction efficiency after 60 minutes. At lower pH (pH 2 and pH 5), the percentage of removal was the lowest because of the formation of H^+ in acidic solution which causing them to compete with the cationic MG molecule that will eventually create barrier to transfer the dye molecule on the PIM surface (Iqbal & Datta, 2019). In contradiction to a study by Ling et al. (2017), the optimum pH for MG removal was observed at acidic condition but different carrier was used. To be concluded, MG can be best extracted in pH between 7-9 which is neutral to slightly alkaline, where too alkaline pH (more than 9) will affect the study of MG removal efficiency.

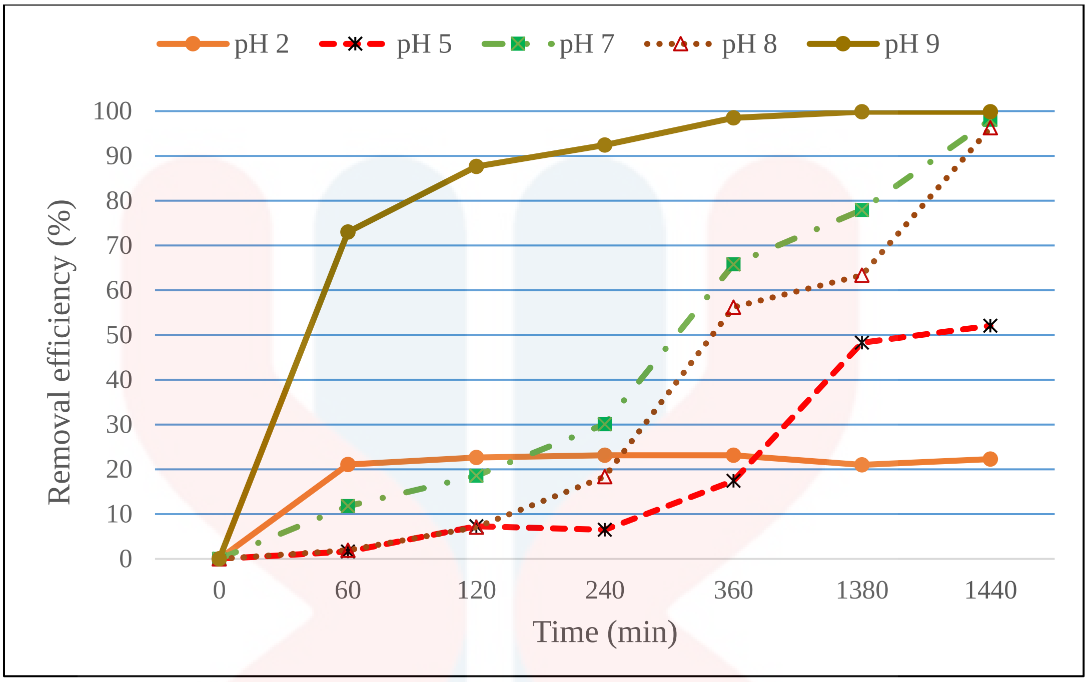

Figure 4.3: The removal efficiency of MG using PVC PIMs with different pH.

4.1.4 The effect of stirring speed

The result in Figure 4.4 indicates the influence of stirring speed on the extraction efficiency of MG. Stirring speed is the driving force that affects the contact time between targeted species and PIM. In this study, the stirring speed study used was in of ranged 100 to 300 rpm. From Figure 4.4, the result shows that as stirring speed increased, the percentage of MG removal also increased where the optimum was obtained at 250 rpm. When 300 rpm was applied, there was a slight reduction on the removal rate due to the decrease of permeability, consequence of the turbulence caused by stirring (Salima et al., 2012). Overall, the ranges of stirring speed studied resulting in more than 97 % of MG removal from the aqueous solution after 24 hours.

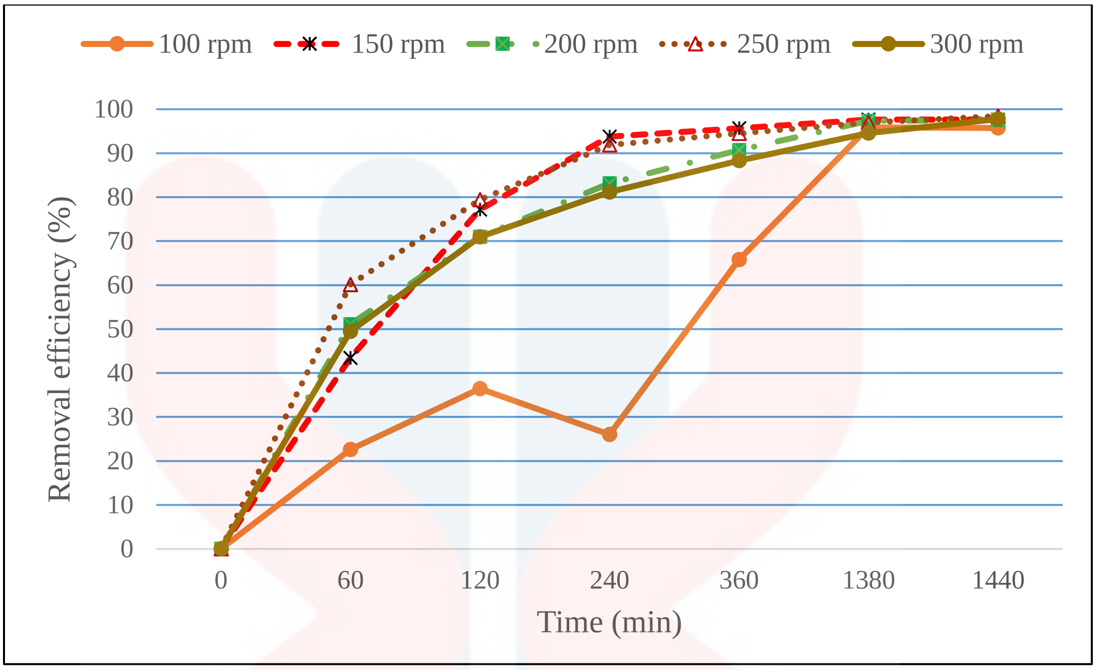

Figure 4.4: The removal efficiency of MG using PVC PIMs with different stirring speed.

4.2 Characterization of PIMs

4.2.1 FTIR analysis

The obtained results in Figure 4.5 indicate that Aliquat 336 shows strong absorption bands at 1466 cm^{-1}, 2853 cm^{-1}, 2922 cm^{-1} and 2954 cm^{-1} which correspond to the CH_2 and C–H (CH_2). Aliquat 336 is proved at the peak obtained at 2954 cm^{-1} which shows the presence of H-bond with free amine group (Iqbal & Datta, 2019). The spectrum of PVC however exhibits a sharp peak at 606 cm^{-1} and 682cm^{-1} which can be attributed to the C−Cl stretching. C−C band also exhibited at 1243 cm^{-1} while the peak at 1425 cm^{-1} corresponds to the CH_2. The aliphatic hydrocarbon in PIM with 30 wt.% of Aliquat 336 is shown in the vibrational mode of 2924 and 2855 cm^{-1} which indicates C–H. There is also –CH deformation modes around 1465cm^{-1} and 1252 cm^{-1} shown by PVC PIM with 30 wt.% Aliquat 336. It can be concluded that PVC PIM with 30 wt.% Aliquat 336 concentration contains all the functional groups of

Aliquat 336 and PVC. For PVC PIM with 0 wt.% Aliquat 336, there is no absorption band for the functional groups in Aliquat 336 appear where the peak is only be obtained at 1252 cm^{-1} which indicates C−C.

Figure 4.6 indicates that there is no significant change in peaks assigned in fresh and used PVC PIM. The small shifting of stretching of used PVC PIM can be attributed to the interaction of Aliquat 336 in PIM and components in MG. The two small weak peaks at about 2924 cm^{-1} and 2855 cm^{-1} observed in the spectrum shows the stretching vibrations of CH^{3-} and CH^{2-} group as found in a study by St John et al. (2011). The peak values and the corresponding radical are summarized in Table 4.7.

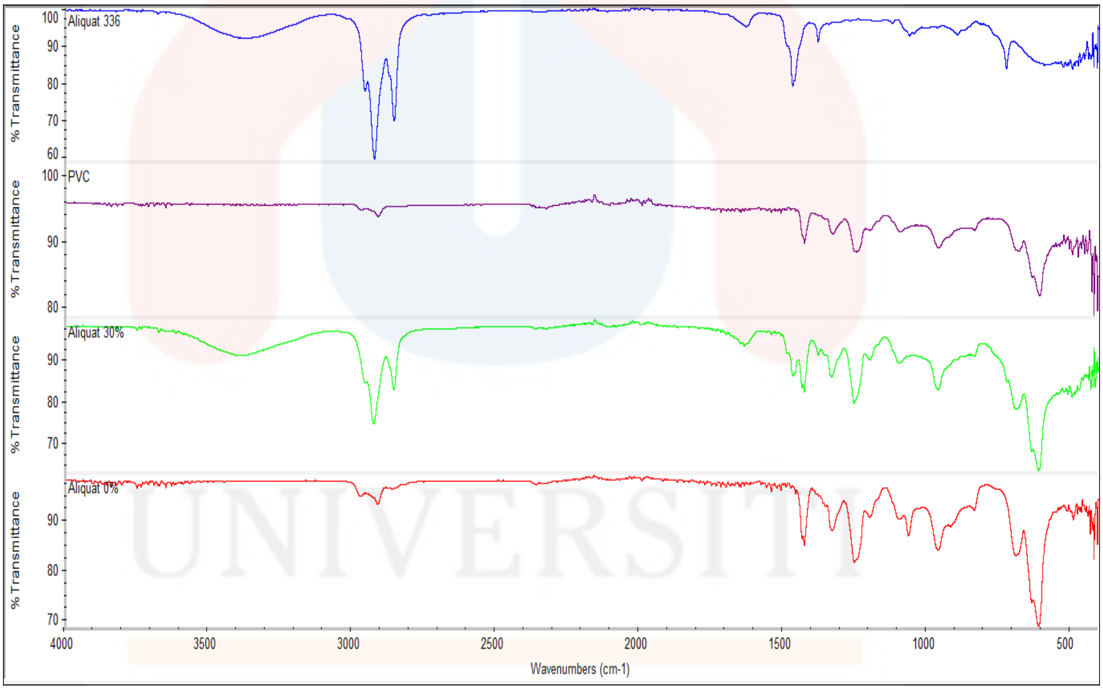

Figure 4.5: FTIR spectra of Aliquat 336, PVC and PVC PIM with 0 wt.% and 30 wt.% Aliquat 336.

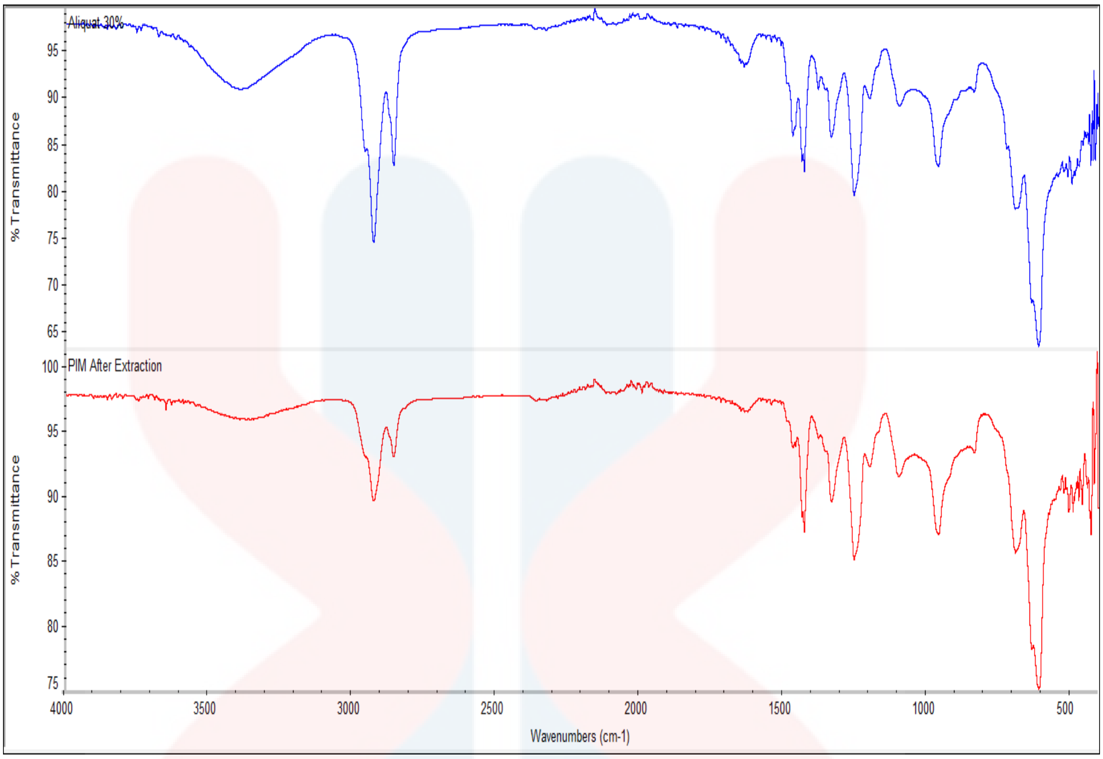

Figure 4.6: FTIR spectra of fresh and used PIM with 30 wt.% Aliquat 336.

Table 4.7: Peak values and the corresponding radical in PIM.

Materials	**Peak value (cm^{-1})**	**Corresponding radical**	**Reference**
Aliquat 336	1466	CH_2	(Haque et al., 2017)
	2853	C–H (CH_2)	(St John et al., 2011)
	2922	C–H (CH_2)	(St John et al., 2011)
	2954	C–H (CH_2)	(St John et al., 2011)
PVC	606	C−Cl	(Pandey, Joshi, Mukherjee, & Thomas, 2016)
	682	C−Cl	(Ling et al., 2017)
	1243	C−C	(Rajendran, Uma, & Mahalingam, 2000)
	1425	CH_2	(Rajendran et al., 2000)
PIM with 0 wt.% Aliquat 336	1252	C−C	(Rajendran et al., 2000)
PIM with 30 wt.% Aliquat 336	610	C−Cl	(Pandey et al., 2016)
	1252	C–H	(Haque et al., 2017)
	2855	C–H (CH_2)	(St John et al., 2011)
	2924	C–H (CH_2)	(St John et al., 2011)

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Membrane technology particularly polymer inclusion membrane (PIM) which is made up of PVC as base polymer and Aliquat 336 as a carrier is an effective as well as environmentally friendly method for extraction of MG. The results from this research shown the excellent removal of MG from aqueous solution when optimum conditions were applied. The efficiency of the extraction depends on four parameters which are the concentration of Aliquat 336, initial dye concentration, pH and stirring speed. By using the best PVC PIM with 30 wt.% Aliquat 336, 10 ppm of MG, pH 9 and 250 rpm of stirring speed, the extraction efficiency achieved 98 % after 24 hours. The characterization of PVC PIM using FT-IR indicated PVC and PVC PIM with 0 wt.% Aliquat 336 do not have functional groups that belong to Aliquat 336. However, PVC PIM with 30 wt.% Aliquat 336 has the functional groups of both PVC and Aliquat 336.

5.2 Recommendations

The surface and the composition of PIM can be further evidenced by scanning electron microscopy (SEM) to determine the morphological structure of PIMs which is beneficial for the future studies regarding various types of carrier and base polymers that are potentially be used for PIM studies. SEM analysis also can be used for studying the variation of interior structure of the PIM at various extractant content. The structural characterization of PVC PIM with Aliquat 336 is also suggested to be performed by using Dynamic Mechanical Analysis (DMA) to study the viscoelastic behavior of PVC in PIM that made it suitable to be used for providing mechanical in many PIM studies.

It is also highly recommended to study on the removal of MG taken from real wastewater to study on the potential of PVC PIM associated with Aliquat 336 in removing real MG discharged to the water bodies as the concentration of MG released by the industries might vary from the synthetic MG, thus proving the capability of PIM to be used in removing dyes released from large scale industries.

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APPENDIX A

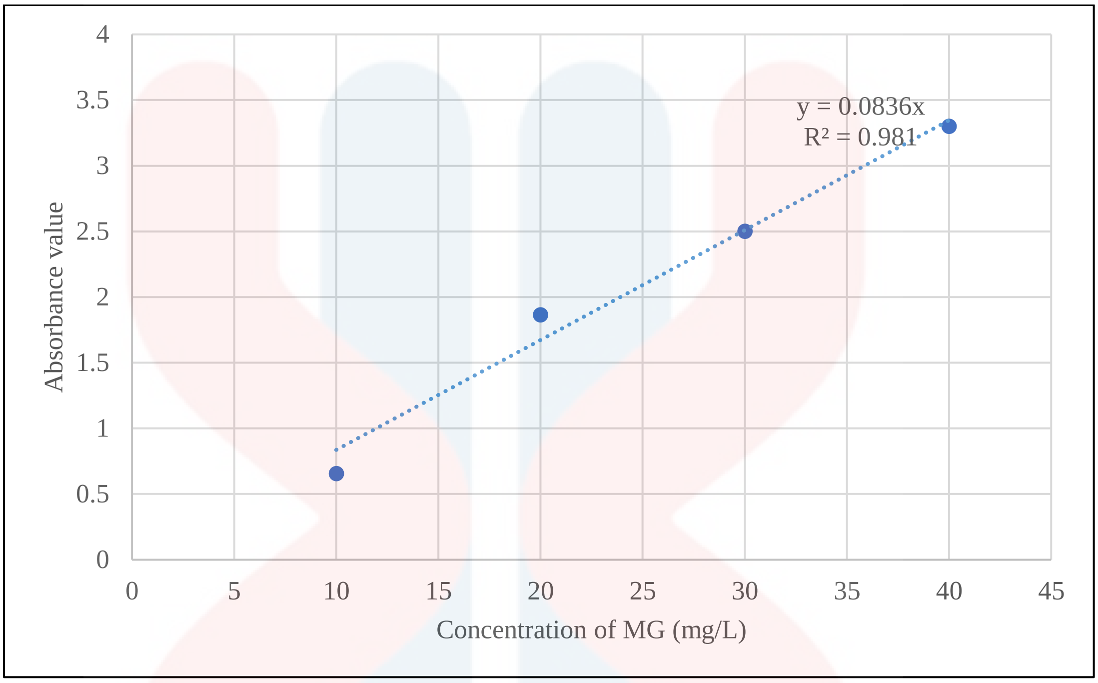

Figure 1: Calibration curve of MG for determining optimum aliquat concentration.

Table 2: Raw data of MG extraction in 24 hours for determining optimum aliquat concentration.

Time (min) \ Concentration of aliquat (wt.%)	Aliquat 20%	Aliquat 30%	Aliquat 40%	Aliquat 50%
0	0.781	0.695	0.736	0.745
60	0.288	0.203	0.273	0.24
120	0.118	0.066	0.109	0.085
240	0.036	0.017	0.03	0.02
360	0.025	0.009	0.021	0.012
1380	0.008	0.001	0.006	0.004
1440	0.017	0.006	0.012	0.01

APPENDIX B

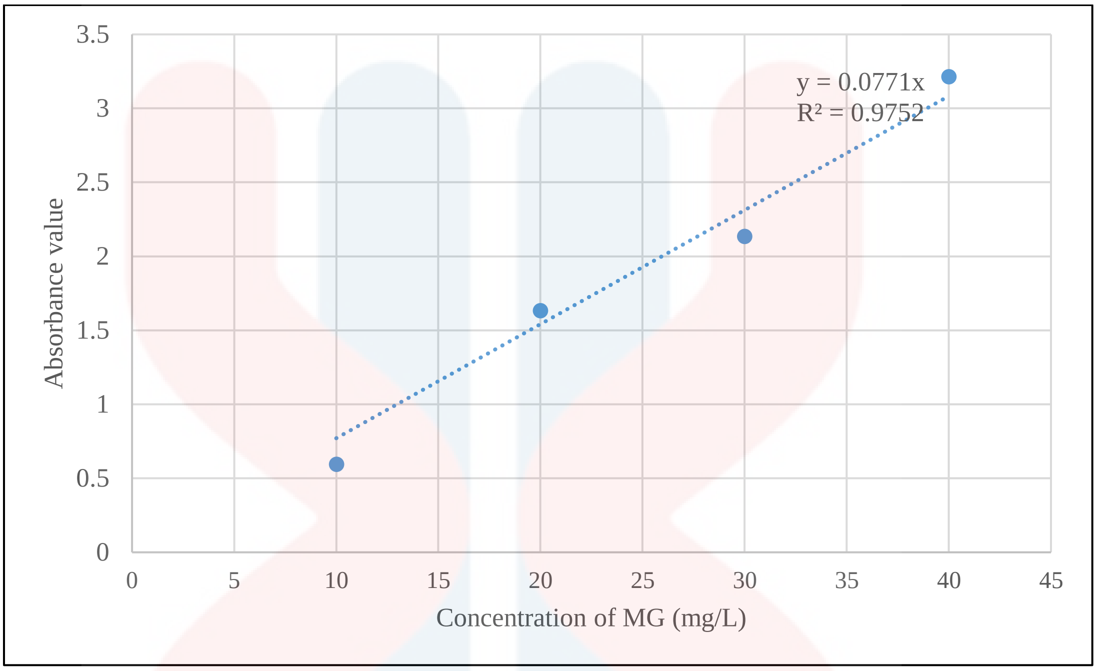

Figure 3: Calibration curve of MG for determining optimum initial dye concentration.

Table 4: Raw data of MG extraction in 24 hours for determining optimum initial dye concentration.

Time (min) \ Concentration of MG (mg/L)	10	20	30	40
0	0.71	1.583	2.198	3.425
60	0.434	1.173	1.988	3.364
120	0.178	1.122	1.682	3.335
240	0.015	0.989	1.237	3.208
360	0.008	0.643	1.097	3.162
1380	0.004	0.231	0.867	2.275
1440	0.004	0.197	0.724	2.262

APPENDIX C

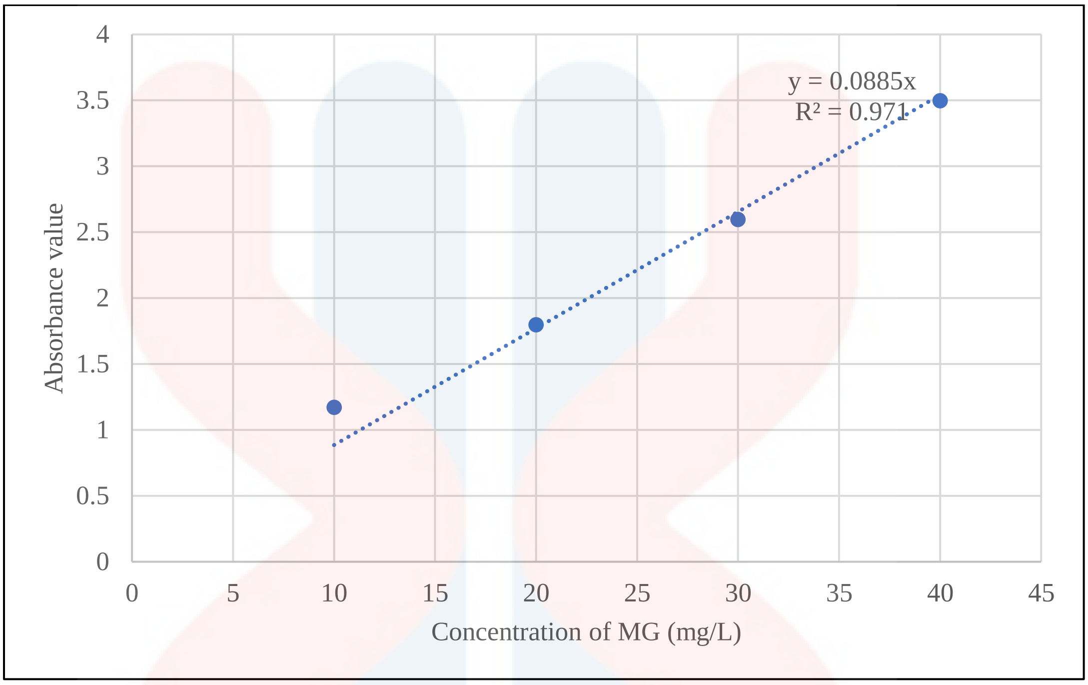

Figure 5: Calibration curve of MG for determining optimum pH.

Table 6: Raw data of MG extraction in 24 hours for determining optimum pH.

Time (min) / pH	pH 2	pH 5	pH 7	pH 8	pH 9
0	1.386	1.097	1.082	0.897	1.101
60	1.094	1.079	0.955	0.880	0.297
120	1.072	1.017	0.883	0.833	0.136
240	1.066	1.026	0.761	0.732	0.084
360	1.065	0.906	0.371	0.392	0.017
1380	1.095	0.567	0.239	0.328	0.001
1440	1.077	0.526	0.021	0.033	0.002

APPENDIX D

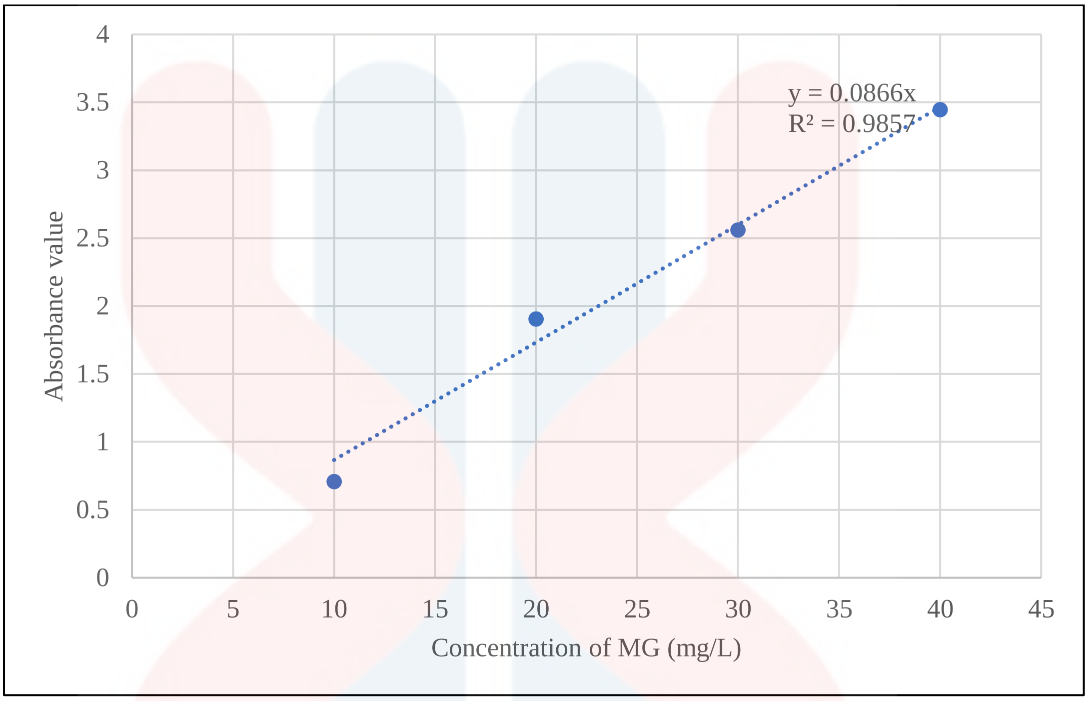

Figure 7: Calibration curve of MG for determining optimum stirring speed.

Table 8: Raw data of MG extraction in 24 hours for determining optimum stirring speed.

Time (min) / **Stirring speed (rpm)**	**100**	**150**	**200**	**250**	**300**
0	0.894	1.068	0.569	0.967	0.984
60	0.692	0.604	0.278	0.386	0.497
120	0.568	0.244	0.165	0.199	0.285
240	0.661	0.066	0.096	0.078	0.185
360	0.306	0.046	0.053	0.053	0.115
1380	0.037	0.025	0.015	0.029	0.053
1440	0.038	0.025	0.014	0.015	0.022

APPENDIX E

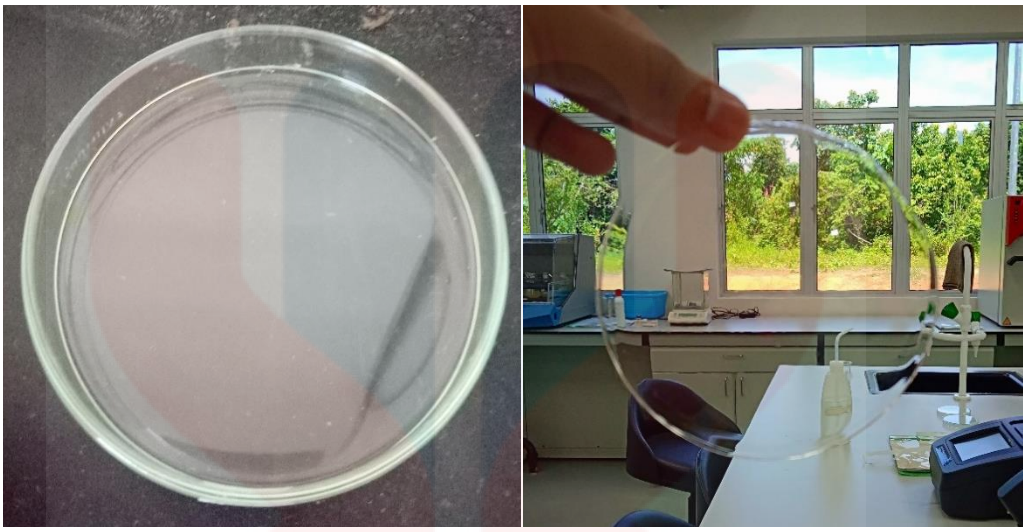

Figure 9: Fresh PVC PIM associated with 30 wt.% Aliquat 336 before being used for extraction of MG.

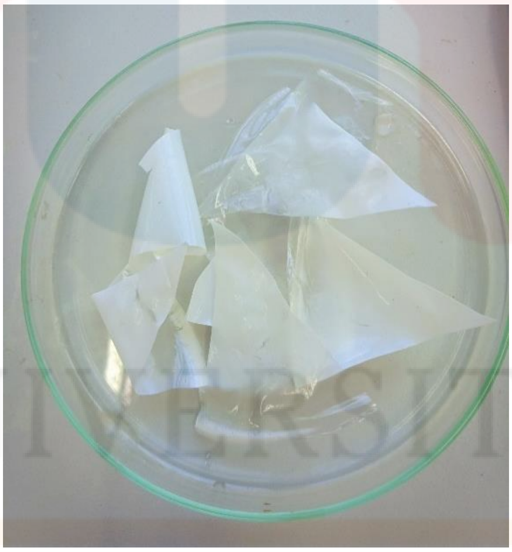

Figure 10: PVC PIM with 30 wt.% Aliquat 336 after being used for extraction of MG.