THE REMOVAL OF METHYL ORANGE USING PVC BASED POLYMER INCLUSION MEMBRANE

by

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DECLARATION

I declare that this thesis entitled "The Removal of Methyl Orange (MO) using PVC-based Polymer Inclusion Membrane (PIMs)" 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.

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The Removal of Methyl Orange (MO) using Polyvinyl Chloride (PVC)-based Polymer Inclusion Membrane (PIMs)

ABSTRACT

In this study, the removal of an anionic dye (Methyl Orange; MO), which is carcinogenic and harmful to human health and environment were carried out from their aqueous solution using polymer inclusion membrane (PIMs) consisting PVC as the base polymer, Aliquat 336 as carrier and tetrahydrofuran (THF) as the solvent. The composition of carrier, pH, initial dye concentration, stirring speed and temperature were varied to determine the optimum parameter of PVC-based PIM for MO removal within 24 hours. The transport of MO also was studied after the optimum conditions have been identified using sodium hydroxide (NaOH) and potassium chloride (KCl) as the receiving solution respectively. The prepared membranes have been characterized using Fourier Transform Infrared Spectroscopy (FTIR) to detect the functional group present on the membrane. From the result, the optimum conditions of extraction study are PIM with PVC 20-Aliquat 336, pH 4, 10 ppm of initial dye concentration, stirring speed at 100 rpm and temperature at 25ºC. The result show that PVC-based PIMs incorporated with Aliquat 336 demonstrated excellent extraction capabilities of MO from aqueous solution. The maximum removal efficiency under optimum condition is 99.61%. However, MO cannot be transported across the PVC PIM into the receiving solution. It can be concluded that NaOH and KCl is not suitable to be used as the receiving solutions. The FT-IR spectra show the presence of aliphatic hydrocarbon on the membrane surface which is functional group found in Aliquat 336, indicate the Aliquat 336 is a carrier in this experiment.

Penyingkiran Metil Oren (MO) menggunakan Polymer Inclusion Membrane berasaskan polivinil klorida (PVC)

ABSTRAK

Dalam kajian ini, penyingkiran pewarna anionik (Metil Oren; MO), yang bersifat karsinogenik dan berbahaya kepada kesihatan manusia dan alam sekitar dari larutan akueus dijalankan menggunakan polymer inclusion membrane (PIMs) yang terdiri daripada PVC sebagai polimer asas, Aliquat 336 sebagai pembawa dan tetrahidrofuran (THF) sebagai pelarut. Komposisi pembawa, pH, kepekatan awal pewarna, kelajuan kacauan dan suhu dipelbagaikan untuk menentukan parameter yang optimum bagi PIM berasaskan PVC untuk penyingkiran MO dalam tempoh 24 jam. Pengangkutan MO juga dikaji setelah keadaan optimum telah dikenalpasti dengan menggunakan natrium hidroksida (NaOH) dan kalium klorida (KCl) sebagai larutan penerimaan. Membran yang disediakan telah dicirikan dengan menggunakan Fourier Transform Infrared Spectroscopy (FTIR) untuk mengesan kumpulan berfungsi pada membran. Kondisi optimum kajian pengekstrakan adalah PIM dengan PVC 20-Aliquat 336, pH 4, 10 ppm kepekatan awal pewarna, kelajuan kacauan pada 100 rpm dan suhu pada 25ºC. Hasilnya menunjukkan bahawa PIM berasaskan PVC yang digabungkan dengan Aliquat 336 memperlihatkan keupayaan pengekstrakan MO yang sangat baik dari larutan akueus. Kecekapan penyingkiran maksimum di bawah keadaan yang optimum ialah 99.61%. Bagaimanapun, MO tidak boleh diangkut merentasi PIM ke dalam larutan penerimaan. Dapat disimpulkan bahawa NaOH dan KCl tidak sesuai untuk digunakan sebagai larutan penerimaan. Spektrum FT-IR menunjukkan kehadiran hidrokarbon alifatik pada permukaan membran yang kumpulan berfungsi yang terdapat di Aliquat 336, menunjukkan Aliquat 336 adalah pembawa.

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LIST OF ABBREVIATIONS

2NPOE	2-Nitrophenyl octyl ether
CTA	Cellulose Triacetate
COD	Chemical oxygen demand
Co(II)	Cobalt (II)
D2EHPA	Di-(2-ethylhexyl) phosphoric acid
DMAc	Dimethylacetamide
DMF	N, N-Dimethylformamide
FTIR	Fourier Transform Infrared Spectroscopy
MO	Methyl orange
MB	Methylene blue
NMP	N-Methyl-2-pyrrolidone
PIM	Polymer Inclusion Membrane
PVC	Polyvinyl chloride
RB 19	Reactive Blue 19
Sc	Scandium
SEM	Scanning Electron Microscope
SLM	Supported Liquid Membrane
TGA	Thermogravimetric analyses
THF	Tetrahydrofuran
TOC	Total organic carbon
Zn(II)	Zinc(II)

LIST OF SYMBOLS

&	And
%	Percentage
ºC	Degree Celcius
wt.%	Weight by percentage

CHAPTER 1

INTRODUCTION

1.1 Background of study

Synthetic dye such as MO has been vastly applied in huge number of industries such as textile, food, printing and pharmaceutical industries. Diversities of dyes and chemicals are used in textile industry to make the shade of fabrics more attractive. Dyes are also required for dyeing and printing of cotton fibres (Benkhaya, Harfi, & Harfi, 2018). Nowadays, synthetic dyes have become a good option for the textile manufacturers due to their timeliness of production and their variety of colours in comparison with natural dyes (Enniya & Jourani, 2017). The rapid growth of these industries had driven the increasing usage of synthetic dyes to accelerate the production in the industries.

There are two types of dyes which are natural and synthetic dyes. Natural dyes are mostly non-substantive and the mordants are required to apply the natural dyes on the textile. Metallic salt commonly acts as mordants and it has an affinity for both the colouring matter and the fibre (Samanta & Konar, 2011). Meanwhile, synthetic dyes are dyes that manufactured using chemical compounds. These dyes can be classified based on their chemical structure (indigo dyes, nitro dyes, azo dyes, anthraquinone dyes, nitrated dyes, phthalein dyes, triphenyl methyl dyes, and etc.) and depend on how the dyes were used in the textile industry (Benkhaya et al., 2018). Despite of their useful application in industries, the improper disposal of dye wastewater into the environment lead to several harmful consequences. Complex structure found in synthetic dye such as MO making them high resistant to light and oxidation, difficult to be degraded, mutagenic, carcinogenic and toxic in nature (Badri et al., 2018). Not only that, the bright colour of these dyes prevents the penetration of sunlight and oxygen into the water sources thus, result in disruption of photosynthesis activity (Jalil et al., 2010). Later, the aquatic life will be hugely affected as their food sources become scarce. Therefore, appropriate treatment methods for dye wastewater is necessary in order to reduce the environmental impact caused by disposal of untreated dyes.

Dye treatment or removal can undergo various techniques such as biological treatment, chemical treatment and physical treatment. Biological treatments normally involve the accumulation of microbes such as algae, fungi, bacteria and yeast which able to degrade various dyes whilst chemical methods involved the processes like coagulation, flocculation, filtration, precipitation, electrokinetic and traditional oxidation methods by oxidizing agents. For physical treatment, adsorption by using activated carbon is one of the examples (Karthik, Saravanan, & Nadu, 2014). However, these conventional treatments have some drawbacks. Hence, the study of other means to remove dye have been investigated.

Nowadays, membrane technology has a great concern among the researchers due to its potential to be performed in dye removal. According to Salima, Ounissa, Lynda, & Mohamed, (2012) membrane technology is an affordable, effortless and good substitute for colour separation and dye treatment in textile wastewater. Among membrane technologies, liquid membrane is more reliable and act as the lead role in separation, purification or analytical application in different areas, such as effluent treatment, biomedicine and hydrometallurgy. There are a few types of liquid membrane such as supported liquid membranes (SLMs), emulsion liquid membranes (ELMs), bulk liquid membranes (BLMs), and polymer inclusion membranes (PIMs). Among these, PIM has gained the most attention due to its high stability, good selectivity, efficiency and durability (Sharaf & Yoshida, 2018). They also reported that PIM is made from base polymer, a carrier and addition of plasticizer if necessary. A study by Sharaf & Yoshida (2018) stated that the PIMs was chosen to be focused because it is highly stable, very selective, efficient and durable. Hence, this study aims to prepare PVC based PIMs for the removal of dyes.

1.2 Problem statements

The disposal of untreated synthetic dyes such as MO into receiving streams can cause severe damage to the environment. MO is an anionic azo dye and soluble in water. It shows mutagenicity, carcinogenic properties, stable and have low biodegradability in nature (Sejie & Nadiye-tabbiruka, 2016). Besides, when skin comes into contact with dyes, it may cause an allergic or irritant reaction. Through inhalation it may cause gastrointestinal irritation with nausea, vomiting and diarrhoea. Hence, it is obligatory to develop effective methods to inhibit the pile up of hazardous dye in the environment, either to less harmful compounds or achieve complete neutralization before being discharged into water sources.

Not only that, the environment can be seriously affected as well. The flowing of effluent as the runoff along the soil will eventually cause them to be absorbed into the soil and result in soil infertility. The discharge of untreated dye into drains and rivers will deteriorate the water quality making it unfit to be used by human for domestic purpose like drinking, washing, cooking and etc. The effluent which flows in the drains will damage sewerage pipes, which leads to leakage in drains and burden the human to repair the broken pipelines and maintain the operation. The contaminated water in particular region is very risky because it will attract bacteria and viruses to breed intensely which later can cause infectious diseases (Kant, 2012). The pollutants found in wastewater containing dye can be found in form of organic and inorganic chemicals. These organic and inorganic chemicals are relatively high and they were characterized by high chemical oxygen demand (COD) and total organic carbon (TOC) values (Azami, Bahram, & Nouri, 2012). Therefore, it is necessary to treat the wastewater with dye residues.

Several methods have been applied for dye treatment such as advanced oxidation and electrocoagulation. Nevertheless, these methods show some drawbacks in term of high cost and sludge problem (Sharma & Kaur, 2018). Biological treatment which use microorganisms such as bacteria and fungi for bio-desorption process have demerits when the rate of MO removal is moderate. A study showed that the colour purification of textile dye effluent like methyl orange are 76.15% & 55.92% during batch and continuous mode respectively on 5th day by using *Schizophyllum commune* (Karthik et al., 2014). This result does not show promising performance as it took 5 days to achieve the removal rate over than 50%. Hence, better techniques are required to overcome the disadvantages of this method.

Recently, PIMs comprises of based polymer and carrier have been successfully used in many metals ions extraction study. The usage of PVC PIMs with Aliquat 336 in extraction of inorganic anions such as Cl^-, $NO3^-$, SCN^-, $ClO4^-$, and SO_4^{2-} have been performed and exhibit good results (Barlah Rumhayati et al., 2019). However, the study on the PVC based polymer incorporated with Aliquat 336 is finite especially in

MO removal. Hence, the potential of PVC PIM to remove MO is essential to be studied in order to find out its capability toward dye removal.

1.3 Objectives

The objectives of this study are:

1. To identify the optimum concentration of Aliquat 336 in PVC based PIM for removal of MO in aqueous solution.
2. To determine the optimum condition of PVC based PIM by varying the methyl orange concentration, pH of feeding solution, stirring speed and temperature in extracting study.
3. To characterize the PVC based PIM using fourier transform infrared spectroscopy (FTIR).

1.4 Scope of Study

The study focused on the preparation of PVC based PIMs incorporated with Aliquat 336. Different Aliquat 336 concentration was used (0, 10, 20, 30, 40 and 50 wt%) to determine the best PVC PIM for MO extraction. Besides, other parameters that affect the extraction such initial feed concentration (10, 20, 30, 40 and 50 ppm), pH (2, 4, 6, 7 and 9), stirring speed (100,150, 200, 250 and 300 rpm) and temperature (20, 27, 35, 45, and 50 °C) was also determined. Next, by using the optimised condition, the transport of methyl orange in PVC based PIM was studied. Lastly, the characterization study was conducted using FTIR for Aliquat 336, PVC and also PVC based PIM before and after extraction to compare the functional group in each component.

1.5 Significance of study

Dyes contamination is a global problem which can result in poor water quality and lead to surface water scarcity issue. Poor water quality also can result in severe adverse health effect in human such as skin irritation. Hence, this study is very important as it aimed to remove the dye from wastewater. Moreover, advanced technology is required for dyes removal to ensure the water sources are desirable to be used. For a few decades, PIMs notably have been tested to be a better option than ion exchange and liquid-liquid extraction methods to extract and recover various metal ions (Zulkefeli, N.S., Weng, S.K., Abdul-halim, N.S., 2018). The application of PVC as base polymer in PIMs have widely discussed for metal ion extraction. However, the study on the PVC PIM with Aliquat 336 for MO removal is scarcely reported.

Therefore, this study which concentrate on the possibility of PVC PIM with various concentration of Aliquat 336 for MO removal is very significant in order to find out the ability of PVC based PIM with Aliquat 336 as a carrier to extract targeted MO species. This study offers the simplicity of membrane preparation process and provide notable improvement of the efficiency for removal of MO in comparison with readily conventional techniques for dye treatment. Not only that, this study is important as it contribute to the identification of optimum parameters which can influence the removal efficiency in order to maximize the removal rate of MO.

CHAPTER 2

LITERATURE REVIEW

2.1 Dye and its classification

Dye can be derived from two sources which are natural sources and chemical compounds. Plants, insects, animals and minerals are the sources of where natural dyes came from. Most of the natural dyes are harmless and safe for environment as it can be derived naturally. Dyes derived from plant sources are usually coming from indigo and saffron. Animal sources also could give human the natural dye sources and it can be derived from some species of mollusks or shellfish and insects while from minerals the example of sources can come from ferrous sulfate, ochre etc. (Kandisa, Kv, Shaik, & Gopinath, 2016). Some example of natural dyes are carotenoid, flavonoids and quinone dyes. Caretenoids can be derived from dandelions and sunflower while flvonoids often found in fruits, leaves and flowers of plants. Quinone dye are derived from benzoquinone, naphthoquinone and anthraquinone which used in dyeing textiles, cosmetics and food industry (Krizova, 2015).

Synthetic dyes are aromatic compounds which contain delocated electrons and different functional group at their aromatic ring and its production process undergo chemical synthesis (Carmen & Daniela, 2018). Aromatic compounds are any compound that contains a benzene ring or has certain benzene-like properties. They also reported that synthetic dyes can be classified into direct, vat, basic, acid, reactive, metal complex, disperse, sulphur and mordant dyes. The classification of dyes is based on their molecular structure and characteristics of application. Considering only general structure of dye, textile dye can be divided into main three groups which are anionic, cationic and non-ionic dyes (Carmen & Daniela, 2018). Synthetic and natural dyes are different in term of sources they are derived from. Normally, the chemicals that can be found in synthetic dyes are copper, lead, mercury, toluene, chromium, benzene and sodium chloride (Hassaan & Nemr, 2017). The exposure to the synthetic dye can be harmful to human health because this dye contains dangerous chemical mixture.

Industries which use dyes for colouring their products are textile, printing, carpet, paper, leather etc. (Kandisa et al., 2016). Synthetic dye like azo dyes is among the highest synthetic colorants consumed by industries and mainly used to dye the cotton (Hassaan & Nemr, 2017). The dyeing process will leave amount of wastewater with dye residues because not all dyes are attached to the fabrics. Some portion of residual dyes will be washed out and goes to the waterways. The concentration of residual dyes is very high in textile effluents (Hassaan & Nemr, 2017). The dye effluent from this industry will end up trapped in the waterways and disturb aquatic ecosystem. (Kandisa et al., 2016).

2.1.1 Azo dyes

Dyes can be defined as natural or chemical substances prepared to be absorbed or adsorbed by, to react with or attached to the any surface or materials in order to give colour to that material with some degree of permanence (Buonanno et al., 2014). Azo dye are compounds characterized with the presence of one or more azo groups (N=N), normally at number of one or four, linked to phenyl and naphthyl radicals (Ventura-camargo & Marin-morales, 2015). The chemical structure of azo dye was given as shown in Figure 2.1. The role of azo group is to stabilize the dye and form a conjugated system which very often absorbs visible light (Buonanno et al., 2014). In aqueous solution, azo dye become acidic due to the presence of the linkage N=N, which reduces the possibility of unpaired electron pairs in nitrogen atoms (Ventura-camargo & Marin-morales, 2015).

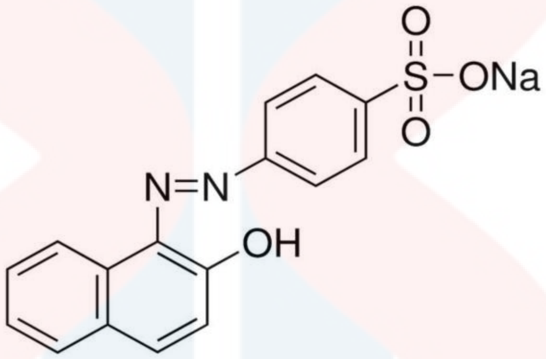

Figure 2.1: The chemical structure of azo dye orange II

Azo dyes were hugely applied in textile industry to colour the polyester, nylon and cellulose diacetate, dyeing the leather, paint, plastic, cosmetic and food and are also used as additive in products derived from the petroleum. The manufacturers tend to choose azo dyes due to some excellent properties. They are versatile, present broad range of colour, easily synthesized, have excellent fixative and have high degree of permanence to fabrics in comparison to natural dyes (Ventura-camargo & Marin-morales, 2015). The vibrant colour of azo dye (eg; MO) make the shades of fabrics and food looked attractive and appealing. However, the azo dye can pose danger to environment and human health. In some cases, the dye can be carcinogenic due to the presence of aromatic amines in azo group (Buonanno et al., 2014). So, it is vital to identify the advanced treatment of this dye as their structure is complex and cannot be easily degraded.

2.1.2 Methyl orange (MO)

MO which grouped in azo dyes commonly act as indicator in acid-base titrations. Mostly, it is applicable for the titration of a strong acid like hydrochloric acid with a strong base in the concentration range from 0.01 to 0.001 mol L^{-1}. MO have transition interval from $3.0 \leq pH \leq 4.4$, the exhibited the changes of colour from red to yellow, and within the transition interval the mixed colour is orange (Kahlert, Meyer, & Albrecht, 2016). In laboratory, it is in powder form and must be diluted for standard solution preparation. This orange-coloured dye usually appear as red in acidic solution and yellow colour in alkaline solution and has an absorbance maximum at 464 nm (Azami et al., 2012). The IUPAC name of this dye is Sodium p-dimethylamino azobenzenesulphonate and having molecular formula as $C_{14}H_{14}N_3NaO_3S$. This dye is classified as azo dye due to the presence of azo group (N=N) found in their chemical structure. Figure 2.2 shows the molecular structure of methyl orange dye (Buonanno et al., 2014).

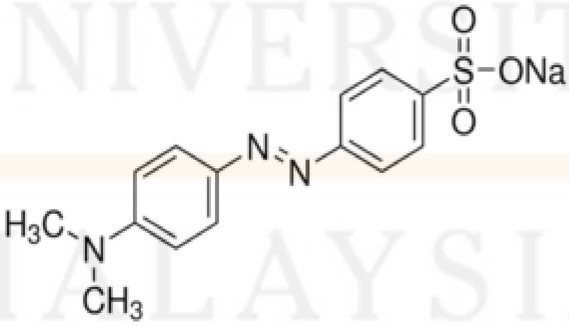

Figure 2.2: The molecular structure of MO azo dye.

Despite the useful application of MO in many fields, the harmful effect of this dye cannot be disregarded. The production of MO for various purposes will cause its release to the environment through various waste streams. Hence, there would be increasing concentration of dye in the water bodies. The long exposure to this dye and dermal contact can lead to lung cancer and skin irritation respectively. This dye also can accidentally enters the body through ingestion and metabolizes into aromatic amines by intestinal microorganisms which can even lead to intestinal cancer (Smita, Dipika, & Shraddha, 2016). Due to its awful consequences, MO must be treated before being discharged to the environment or being treated if MO was found out in water sources.

2.2 Treatment of dyes

There are various of physical, chemical and biological method for dye removal. Physical methods include adsorption, ion exchange and filtration/coagulation methods etc. whereas chemical methods include ozonisation, photocatalytic reactions etc. (Kandisa et al., 2016). Biological techniques such as bioremediation normally use living organism such as microbes to decolorize and metabolize the dyes. Hence, screening out microorganisms in order to identify their characteristics which suitable for the specific dye and it seems to be complicated to be applied (Singh, Singh, & Singh, 2015).

According to Haddad et al., (2014) conventional methods for the removal of dyes in effluents do not able to eliminate the colours completely. The secondary product from these conventional processes sometimes tend to exist as other pollutants which require high cost for treatment. Kandisa et al. (2016) reported that physical methods like ion exchange and reverse osmosis are restricted to be applied in huge scale industries due to expensive initial capital, operational and maintenance cost even it showed good performance for removal process of pollutants from industrial wastewater.

Liquid membranes particularly polymer inclusion membrane (PIMs) has shown excellent capabilities in removing and recovering metal ions. Besides, PIMs have acquired an important role in multiple areas such as biomedicine, ion selective electrodes and effluent treatment for separation, purification or analytical application purpose (Salima et al., 2012). Due to its excellent stability and selectivity, recent researchers have shown interest in exploring the potential of PIMs in removal of dye application.

2.3 Polymer inclusion membrane

There are a few types of liquid membranes for metal separation from aqueous liquors, such as supported liquid membranes (SLMs) and polymer inclusion membranes (PIMs). Wieczorek (2010) stated that a supported liquid membrane (SLM) is one of the three-phase liquid membrane systems in which the membrane phase (liquid) is held by capillary forces in the pores of microporous polymeric or inorganic film. The immobilized liquid is a membrane phase and a microporous film serves as a support for the membrane. Salima et al., (2012) mentioned that SLMs system combine the extraction and stripping processes in one step but have been disadvantages in term of lack of stability compared to PIMs. So, PIMs is preferred as it can maintain versatility and flexibility.

PIMs also have been used successfully for selective separation of both inorganic and organic chemical species (Cho, Cattrall, & Kolev, 2018). It is also applicable in separation of Zn(II) and ions of other metal and have been a recent platform employed for wastewater treatment, separation and recovery of target metals (Radzyminska-Lenarcik & Ulewicz, 2019). A polymer inclusion membrane (PIM) is usually prepared by solvent evaporation casting from a homogeneous solution of a polymer, extractant and/or plasticizer, in a suitable solvent (e.g. tetrahydrofuran (THF) for PVC based PIMs and chloroform for CTA-based PIMs). The polymer mixed with extractant in certain solvent can be casted onto glass plate to form a flat sheet membrane or poured into petri dish to form transparent with a soft surface membrane (Almeida, Cattrall, Kolev, & In, 2017).

The base polymer were used as it act as skeleton which can provide mechanical strength to the membrane and PVC and CTA are examples of base polymer commonly used for membrane preparation. The role of extractant/carrier is to bind the targeted species by complexation or ion-pair formation (Almeida et al., 2017). Aliquat 336, Cyanex 272, di-(2-ethylhexyl) phosphoric acid (D2EHPA) are often used as extractant in PIM's preparation (Cho et al., 2018). Aliquat 336 composes of large organic cation associated with chloride ion. The chemical structure of Aliquat 336 is shown in Figure 2.3. This extractant is suitable to be used both in acidic and slightly alkaline medium due to the permanent positive charge present at its ammonium structure (BASF, 2015). For this reason, it can form salt with anions over a wider pH compared to to primary, secondary and tertiary amines (Taylor et., 2014). Cyanex 272 is applicable for extraction of Co(II) and Zn(II) (Regel-rosocka & Masalska, 2016). Meanwhile, PIMs containing either PC-88A or Versatic 10 as the carrier or extractant have been studied for selective separation and recovery of Sc (Sharaf & Yoshida, 2018).

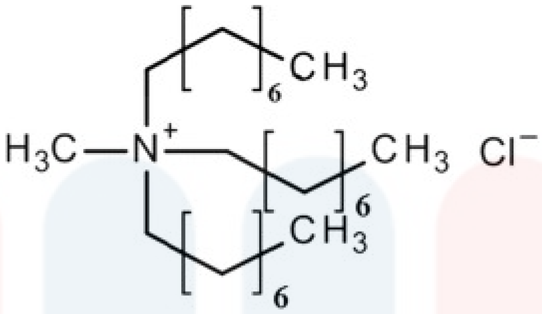

Figure 2.3: The chemical structure of Aliquat 336

On the other hand, plasticizer is added into a PIM to increase the flexibility and achieve homogeneity or to increase the solubility of the extracted species in the membrane liquid phase (Cho et al., 2018). Plasticizer will penetrate into the polymer molecules and mitigates the intermolecular forces. So, the distances between the polymer molecules will be greater (Witt, Radzyminska-lenarcik, & Kosciuszko, 2018). PIMs do not require the addition of a plasticiser if ammonium salts and phosphoric acid esters are the carrier ingredients, such as in quaternary, because they already have plasticising properties (Taylor et al., 2014). Aliquat 336 is a common phase transfer catalyst and an ionic liquid itself (Mikkola & Sjo, 2006) which also have plasticizer properties consisting of a mixture of quaternary ammonium chlorides and has been widely devoted in studies of PIMs. It also emphasized that Aliquat 336 is a good plasticizer for PVC (Almeida, Cattrall, & Kolev, 2012). Considering the great properties of Aliquat 336 as an extractant and plasticizer at the same time, it is vital to find out the incorporation of Aliquat 336 in PVC for methyl orange removal.

2.3.1 Aliquat 336 as a carrier

Carriers is normally a complexing agents or ion exchangers which responsible for the transport across PIM complex or the formation of ion pair between the metal ion. The carrier is soluble in the membrane and facilitates the metal ion transport across the membrane (Taylor et al., 2014). The chemical structure of the carrier can control the rate of transport of the target ion through the PIM thus determining the target ion transport efficiency and membrane selectivity. The types of extractant/carrier can be divided into acid carrier, basic carrier, neutral carrier, macrocyclic and macromolecular carrier. Aliquat 336 is a basic carrier from group quaternary ammonium which can be used to separate metal anionic complexes (Barlah Rumhayati et al., 2019). For the PIM system, the concentration of carriers affects the transport of metal ion through the membrane. The quaternary ammonium carrier like Aliquat 336 will react as an anion exchanger by forming ion pairs with the target ion (Barlah Rumhayati et al., 2019). The optimum of carrier concentration can be identified by performing the extraction study. Lower amount of carrier used is more desirable because carriers are generally notably expensive.

2.4 Transport experiment

In this experiment, transport cell consisting two compartments, feeding and receiving compartment respectively. The feeding cell consist of the dye solution which would be transferred to the receiving phase while the receiving cell consist of a solution which can transport the dye into it. The concentration gradient of species or carrier complex formed within the membrane will enable the transport across the membrane as it will act as driving force for the movement of carrier or ion in the solution (Almeida et al., 2017).

In this study, MO as a model of anionic dyes have been selected to be transported across the PIM. The mechanism of facilitated transport in this study can be supported by other literature. According to Hajarabeevi et al. (2009), a study on the transport of cationic dyes across SLM have been conducted. The positively charged dye will diffuse from the from feed phase to the membrane interface through aqueous boundary layer. At the feed membrane interface, cationic dye will form neutral ion pair complex with the carrier. Then, due to the potential gradient the complex will diffuse through the PIM into the receiving phase between feed and receiving phase. The dye ion is exchanged with a proton at the receiving-membrane interface. The dye ion will be released into the receiving phase. This transport mechanism can be implemented for this study as the previous study also used dyes and same type of membrane. Both PIM and SLM are liquid membrane even they have slight dissimilarity in term of capability to remove dyes.

2.5 Previous studies on PIM for dye removal.

Initial dye concentration, pH of feed solution, stirring speed and temperature are some of the parameters that always be discussed by the previous literature in this field of study. According to Lakshmi et al., (2015) a study on removal of Reactive Blue 19 (RB-19), a textile dye using PIM with ionic liquid have been carried out. This study discovered that PIM adsorbed higher percentage of RB 19 when the concentration of dye is lower. In this study, it also mentioned that effect extractant concentration (Aliquat 336), the pH of feeding solution, initial dye concentration and stirring speed were the crucial factor in dye removal efficiency.

Not only that, cationic dye (methylene blue; MB) removal have been deliberately studied using PIM. A study by Salima, Ounissa, Lynda, & Mohamed (2012) show that CTA was used as a base polymer, 2-Nitrophenyloctyl ether (2NPOE) was used as plasticizer and D2EHPA was as the carrier. D2EHPA as the extractant transfers MB species from an aqueous feed phase into a solid organic phase (PIM). In this study, the recovery of MB is almost achieved 93% under the optimum parameter. The result obtained proved that PIM can be applied in the dye removal study as it showed outstanding performance.

2.6 Characterization of PIM

Several techniques are required in order to characterize the PIM for example scanning electron microscope (SEM), Thermogravimetric analyses (TGA) and FTIR. SEM can be used to illustrate the surface morphology of membrane. The cross section of membrane can be seen either the surface is dense or not and how porous the membrane is.The TGA was developed the linkage between specific temperature and height of mass changes to the degradation of a specific compound or fragment of it (Kebiche-senhadji et al., 2011). The degradation of the component can be identified at particular temperature after the percentage of mass losses of component and these will be notified from thermogram (Iben et al., 2016).

Meanwhile, FTIR is a technique used to detect a range of functional groups of a sample. It provide information on the basis of chemical composition and physical state of the whole samples and is sensitive to changes in molecular structure (Amir & Anjum, 2013). The wave number to measure the absorption band of the component present are usually from 400 to 4000 cm^{-1} (Kebiche-senhadji et al., 2011). Using FTIR spectra, the component can be detected at certain peak. For example, the vibration at band around 1596 cm^{-1} attributed to the C=C-C ring, which readily indicates that the sample contains aromatic ring (Elumalai & Muthuraman, 2015). The information will be given directly to the user when the software of FTIR installed to the computer.

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CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

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

Table 3.1: The list of materials used in the experiment.

Materials	Supplier
Polyvinyl chloride (PVC)	Sigma-Aldrich
Aliquat 336	Sigma-Aldrich
Tetrahydrofuran	Sigma-Aldrich
Methyl orange	Sigma-Aldrich
Sodium hydroxide	Sigma-Aldrich
Distilled water	Conrad Electronic International
Sodium hydroxide	Sigma-Aldrich
Potassium chloride	Sigma-Aldrich

Table 3.2: The 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

3.2 Preparation of polymer inclusion membrane

In this study, the polyvinyl chloride (PVC) based polymer inclusion membranes (PIMs) was prepared by dissolving PVC polymer and various Aliquat 336 concentrations (0, 10, 20, 30, 40 and 50 wt.%) in 10 mL of tetrahydrofuran (THF). Table 3.3 presents the PIMs identification and composition. The total weight of Aliquat 336 and PVC were 500 mg. The polymer mixture was stirred using magnetic stirrer until it becomes homogenous. During the process, the beaker was covered with parafilm. After that, the solution was poured into a petri dish and covered with filter paper until it formed a plasticised membrane called PVC PIM. Next, the PVC PIM was peeled from the petri dish for further used in the extraction and transport study.

Table 3.3: The PIMs identification and composition

PVC PIM identification	PVC (mg)	Aliquat 336 (mg)	Composition (wt.%)
PVC 0	500	0	50:0
PVC 10-Aliquat 336	450	50	40:10
PVC 20-Aliquat 336	400	100	30:20
PVC 30-Aliquat 336	350	150	20:30
PVC 40-Aliquat 336	300	200	40:10
PVC 50-Aliquat 336	250	250	50:10

3.3 Preparation of MO standard solution

A stock solution of 1000 ppm MO was prepared by dissolving 0.1 g of MO powder into 100 ml distilled water using volumetric flask. Then, the stock solution was diluted to 100 ppm of MO. Next, 100 ppm of MO were diluted again to prepare different initial methyl orange concentration (10, 20, 30, 40 and 50 ppm) for calibration purpose. The linear regression coefficient obtained in this study were greater than 0.97.

3.4 The extraction study of methyl orange

The extraction study was conducted in a batch mode according to previous research (Abdul-halim, Whitten, & Nghiem, 2013). The first parameter studied was Aliquat 336 concentration. In order to study the effect of Aliquat concentration, the PIMs with different Aliquat 336 concentration were used to identify the best extractant content. The 0.50 g of PVC PIM with different Aliquat 336 concentration (0 wt.%, 10 wt.%, 20 wt.%, 30 wt.%, 40 wt.% and 50 wt.%) were cut into smaller pieces and placed in the conical flasks containing 100 mL of 20 ppm of extraction solution (MO) respectively. The feed solution with small pieces of PIM in it was stirred continuously using orbital shaker at 150 rpm and 2 mL of aliquot were taken 6 times within 24 hours for analysis using uv-vis spectrophotometer at 464 nm wavelength (Azami et al., 2012). The experiment was conducted at room temperature. The removal efficiency were determined by using the Equation 3.1 (Salima et al., 2012). The extraction studies were repeated to study the other parameters such as pH, initial dye concentration, stirring speed and temperature.

$$\text{Removal efficiency (R)} = \frac{A_o - A_t}{A_o} \times 100 \qquad (3.1)$$

Where;

A_o : Initial absorbance value in the aqueous solution (Abs)

A_t : Absorbance value in the aqueous solution at the time interval (Abs)

3.4.1 The effect of other parameters on the removal efficiency

Next, the effect of pH was studied by varying different pH in feeding solution (2, 4, 6, 7 and 9) to determine the optimum pH for removal of MO and the optimum Aliquat 336 identified from previous experiment was used. The pH was adjusted by adding HCl and NaOH into the dye solution. The initial dye concentration, stirring speed and temperature were set to the control setting. After that, it followed by the effect of initial dye concentrations. In order to identify the optimum initial dye concentrations, the optimum Aliquat 336 and pH found out from earlier experiment were used in extracting different initial MO concentration which are 10 ppm, 20 ppm, 30 ppm, 40 ppm and 50 ppm. The stirring speed were set at 150 rpm and it was conducted at room temperature.

Then, the effect stirring speed was studied. The experiment was conducted at different stirring speed (100, 150, 200, 250 and 300 rpm) to determine the best stirring speed by using the optimum Aliquat 336, pH and initial dye concentration which have been identified in previous experiment. Lastly, to study the effect of temperature on the removal rate of MO, different temperature (25, 35, 45 and 55 and 65 °C) were used accompanied with all the optimized parameters. All the optimum parameters were identified by using Equation 3.1 and then the line graphs representing the percentage of MO removal at certain hours were tabulated. The optimum parameters chosen were based on the highest percentage of MO removal shown in the line graph.

3.5 Study on facilitated transport of methyl orange

For transport experiment, it was conducted under the optimum parameter which have been identified in the extraction study. This experiment used transport cell consist of feeding and receiving solutions which is separated by a membrane in the middle as illustrated in Figure 3.1. The PVC PIMs was put in the middle of the transport cell while the feeding and receiving compartments contain 120 mL of 10 ppm MO and 120 mL of 1.0 M NaOH respectively. Each of the solution in the transport cell was stirred using magnetic stirrer continuously and 2 mL of aliquot samples from both phase solution was taken for 6 times within 24 hours to measure the dye concentration using UV-vis spectrophotometer at 464 nm (Azami et al., 2012). Then, this experiment was repeated using different receiving solution, KCl. The transport rate of MO can be calculated from the differences of absorbance value in both feeding and receiving solution respectively as shown in Equation 3.1.

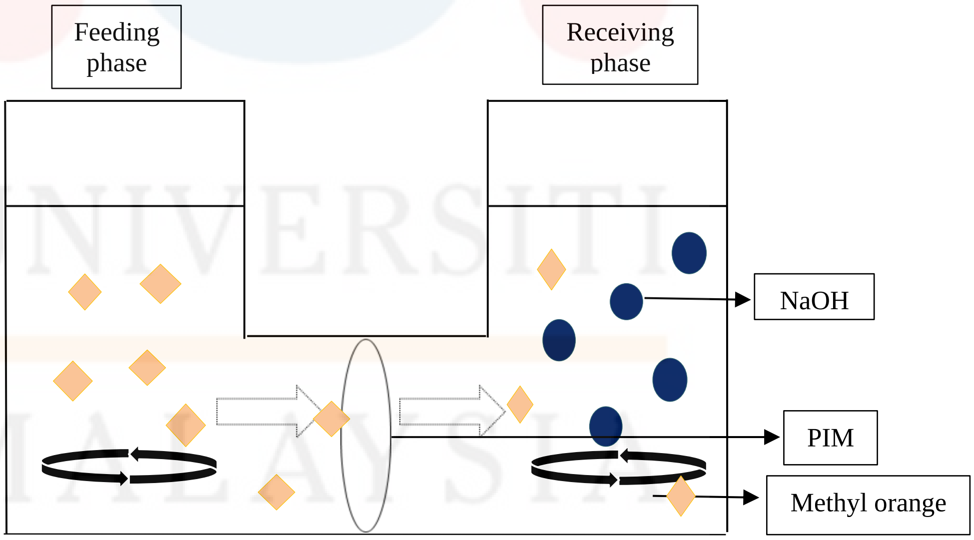

Figure 3.1: Schematic diagram of PIM transport cell

3.6 Characterization of PIM

The PVC PIM with different concentration of Aliquat 336 were characterized using Fourier Transform Infrared Spectroscopy (FTIR) in order to detect a range of functional groups of a sample from the obtained spectrum. The information of the component present on the membrane surface were provided directly (Amir & Anjum, 2013). In this experiment, the components of PIMs were observed prior to extraction studies. FTIR spectra were obtained using FTIR-8400S of Shimadzu spectrophotometer; measures were taken in the range 4000-400 cm^{-1} with 4 cm^{-1} resolution (Salima et al., 2012).

CHAPTER 4

RESULT AND DISCUSSION

4.1 Effect of parameters on extraction of MO

4.1.1 Effect of Aliquat 336 concentration

First, PVC PIM with different Aliquat 336 concentration was studied to determine the best carrier content in the PVC PIM for the removal of MO and the result was presented in Figure 4.1. As explain in Chapter 2, the removal of MO depends on the carrier. Without carrier, there will be no removal. This is clearly seen in PVC 0 (without Aliquat 336) where the removal of MO was not significant.

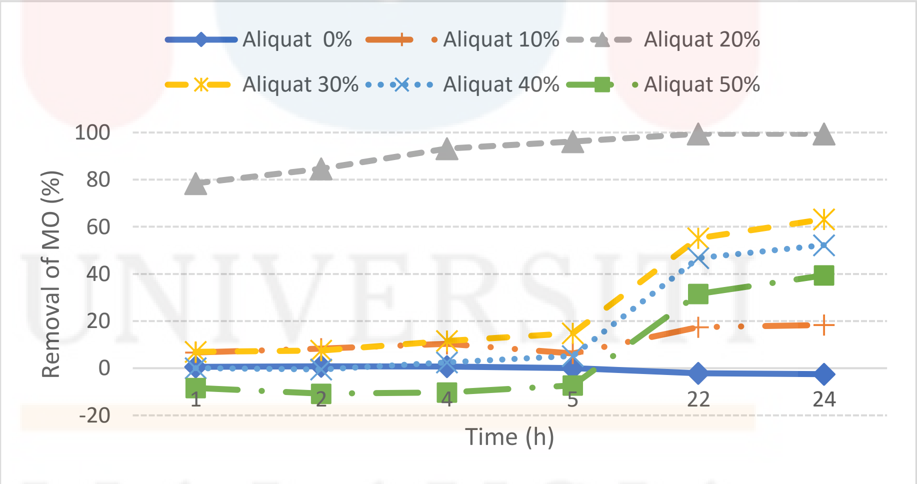

Figure 4.1: Effect of Aliquat 336 concentration on the removal efficiency of MO.

In most study, the increased in carrier content will increased the removal efficiency of targeted ions but then will stabilized at higher carrier concentration (Salima et al., 2012). However, based on the figure, PVC 20-Aliquat 336 show the highest removal efficiency of MO compared to PVC 30-Aliquat 336, PVC 40-Aliquat

336 and PVC 50-Aliquat 336. This mean that the low amount of Aliquat 336 is already effective to extract MO. Taylor et al., (2014) stated that higher Aliquat 336 concentration may result in the membrane saturation of the Co(II)–Aliquat 336 complex, because the Co(II)–Aliquat 336 complex creation was enhanced when the carrier concentration increased.

When the membrane become saturated with the carrier, the carrier is possibly to be deposited on the membrane surface, which may reduce the removal activity and slow down the transport characteristics of the membrane by destroying the homogeneous structure of the membrane (Taylor et al., 2014). They also mentioned the high concentration of carrier also will cause high viscosities in the membrane which might stop the transfer of the ion-carrier complex in the membrane. This also might be the reason why PVC 20-Aliquat 336 is the optimum concentration as the higher concentration lead to declining of removal activity. This can be supported by a study by Taylor, Karayünlü, & Boz (2015) which reported the highest percentage of MO removal was obtained when the amount of adsorbent (activated carbon) is 0.1 mg/L. It can be assumed that lower amount/concentration of adsorbent or carrier is effective to extract MO.

4.1.2 Effect of pH

The pH plays an important role to control the removal process of dye. This is because the pH can affect the charge or ions of the adsorbent, degree of ionization of different contaminants, splitting of functional groups on the active sites of the adsorbent as well as the structure of dye molecule (Bazrafshan, Zarei, Nadi, & Zazouli, 2014). Suitable pH will ensure the extraction process is effective. To study the effect of pH on the removal efficiency of dye from the aqueous solution, pH is varied between 2 to 9. The correlation between the pH and removal efficiency is given in Figure 4.2.

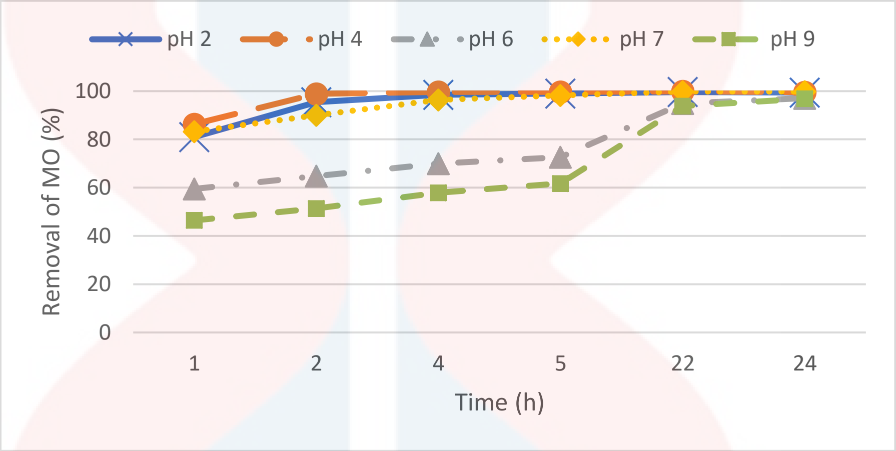

Figure 4.2: Effect of pH on the removal efficiency of MO

The results show that the extraction of MO is the highest at pH 4 with 99.92%. pH 2 showed the second highest reading of removal percentage which is 99.62%. Only small degree of differences distinguished in term of extraction percentage between pH 4 and 2. It can be proven by a study by Taylor et al., (2015) when the finding showed the highest percentage removal of MO was obtained at a dye solution pH of 2. Hence, it can be said that MO can be extracted successfully in acidic medium.

When MO become acidic, SO_3Na part of the dye molecule will become SO_3^- after it loses one positive charged atom (Na^+) which cause it to change to negatively charged ions. The positively charged ion on Aliquat 336 due to the presence of amine group will interact with the dye molecules (SO_3^-) thus, gets adsorbed due to the different charge will attract to each other (Iqbal & Datta, 2019).

For the pH 9, the percentage of removal is the lowest among other pH therefore it can be assumed that the efficiency to extract MO in alkaline solution is less effective in short period. If the rate of extraction is considered after 24 hours, it also showed high percentage of MO removal (96.84%). pH 7 (neutral) also show good extraction efficiency, which the rate of removal is 99% but if compared with pH 2 and 4, acidic pH is more ideal to extract MO. From the results, it can be assumed that MO can be extracted in wide range of pH. Iqbal & Datta (2019) stated that Aliquat 336 are effectively used in anionic dye separation because it has many organic cation associated with chloride ion, $[R_3NCH_3]^+Cl^-$ which is responsible for the formation of a stable cation-anion pair over a wide range of pH.

4.1.3 Effect of initial dye concentration

To study the effect of the initial dye concentration, the concentration was varied from 10 ppm to 50 ppm. Figure 4.3 represents the relationship between the removal rate of MO with the initial dye concentration. The removal efficiency for 10 ppm is 99.02% after 4 hours and is the highest compared to other initial dye concentration. Other study conducted to remove MO using activated carbon showed 20 ppm of MO solution is the optimum parameter for initial dye concentration (Taylor et al., 2015). The finding is quite different as the materials used to remove MO was different. In this study, 20 ppm of MO showed the second highest percentage of removal which is 82.67% after 24 hours. The result of this study is still comparable to previous study as 20 ppm of MO in this study also show promising removal efficiency. The concentration of 10 ppm and 20 ppm also are not hugely different. It can be concluded that the lower initial dye concentration, the higher the rate of dye removal.

This can be attributed to the fact that at lower concentrations, the availability of extraction sites increased; thus, extraction of dyes occurred immediately (Badri et al., 2018). As for 10 ppm, the removal percentage is remained constant after 22 hours of extraction time. The reason is the membrane probably become saturated and there are no or less effective area of the membrane (Salima et al., 2012). Iqbal & Datta (2019) reported that for a fixed mass of adsorbent, the free site available will be limited if the concentration of dye is increase thus lead to the decline in the removal efficiency of MO.

After 5 hours, the rate of removal remained constant as almost all of the MO have been extracted. For the initial dye concentration higher than 10 ppm, the extraction efficiency is lower as the reason is the membrane probably become saturated and there are no or less effective area of membrane (Salima et al., 2012). However, initial dye concentration with 40 ppm showed the second highest of removal (75.53%) at the first five hours of extraction. This might be due to changes of laboratory temperature or the problems with laboratory instrument that interfere the accuracy of the result.

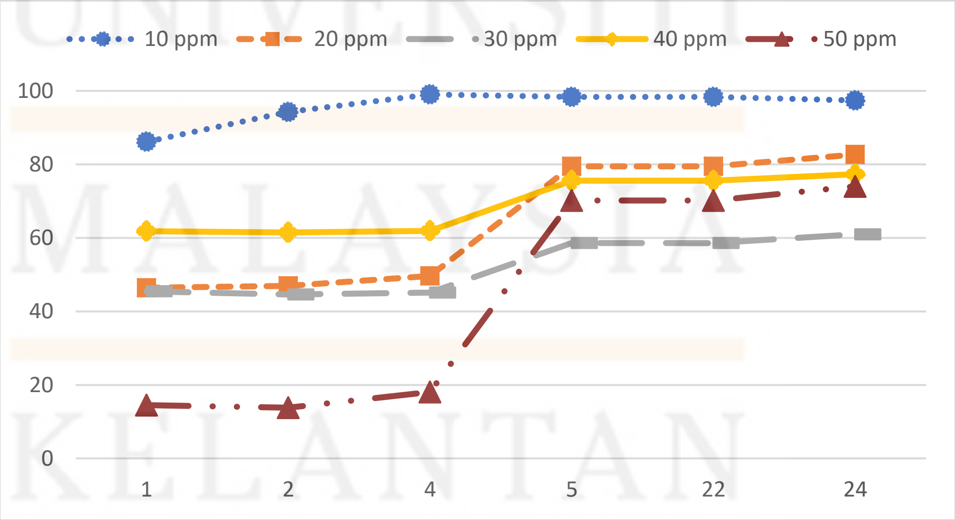

Figure 4.3: Effect of initial dye concentration on the removal efficiency of MO

4.1.4 Effect of stirring speed

To study the influence of stirring speed, the experiments were accomplished at different stirring speed. The stirring speed studied are ranged from 100 to 300 rpm. The stirring speed is assumed to affect the adsorption process. During the stirring, the particles of adsorbent and the molecules of adsorbate will moving and collide to each other in the aqueous solution, enhancing the adsorption process (Eduardo et al., 2019). For this study, the result showed in Figure 4.4 indicates that the slower stirring speed contribute to higher extraction percentage of dye. Stirring speed of 100 rpm is the optimum speed as it showed the highest percentage of extraction which is 99.51%.

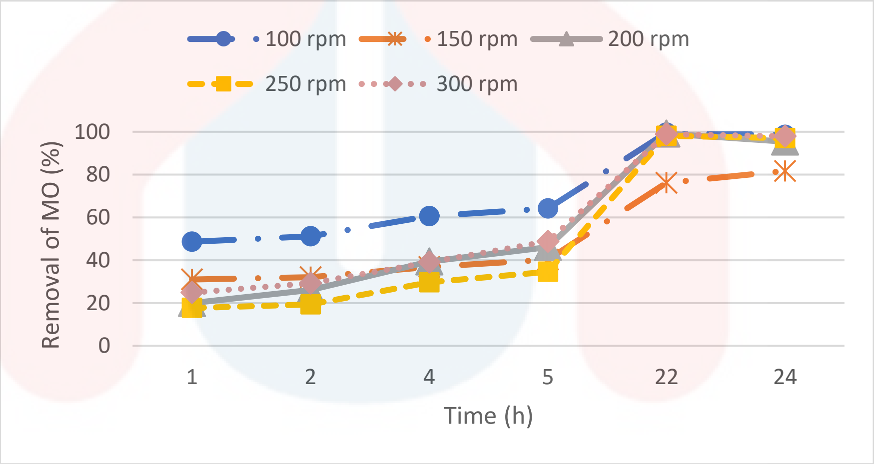

Figure 4.4: Effect of stirring speed on the removal efficiency of MO

This finding can be associated with previous study by Hajarabeevi et al., (2009) which stated that a decreased permeability of membrane when higher stirring speed exerted could be caused by turbulence or unsteady movement while stirring. It also can be supported with a study by Iqbal & Datta (2019) as they stated when reciprocating action (100 rpm) or magnetic stirring was used, nearly 97% removal of MO achieved in 60 min of time. The aqueous boundary thickness might be reduced with increasing of stirring speed. In this case, the boundary layer of membrane is minimal at 100 rpm since the 100 rpm have the highest extraction efficiency. Since that the PVC PIMs used is very thin, it is acceptable that the PVC PIMs cannot withstand the speed higher than 100 rpm which causing the removal efficiency quite dropped. But, the removal efficiency at 300 rpm is opposite from the finding above as it showed the second highest percentage of MO removal (98.92%). It might due to the laboratory instrument error.

4.1.5 Effect of temperature

The temperature also play an important role in influence the removal efficiency. The experiment was conducted at different temperature in range between 25 °C to 65 °C. The interrelation between the removal efficiency and the temperature is given in Figure 4.5.

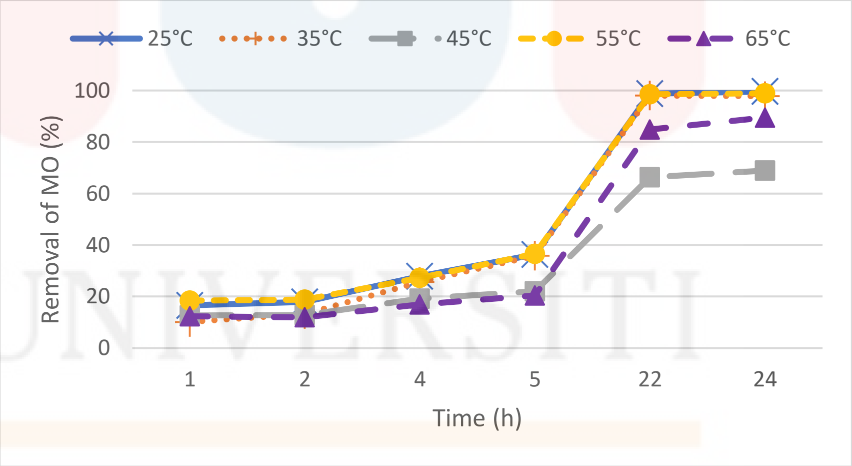

Figure 4.5: Effect of temperature on the removal efficiency of MO

From Figure 4.5, the highest removal efficiency observed at 25ºC is 99.61%. Previous study conducted also showed the removal efficiency of MO is the highest at 25 ºC (Taylor et al., 2015). As the temperature increase beyond 25ºC, the rate of removal started to decrease except at temperature 55ºC. According to Eduardo et al.,

(2019) an increase in temperature leads to a decrease in MB dye adsorption, indicating that adsorption process is desirable at lower temperature. At higher temperature, adsorption forces between the active sites of the adsorbent and the molecules of adsorbate become weaker. So, the attraction of ion-carrier complex become weak and decelerate the removal process. This also can be applied on the membrane surface where the adsorption site at the membrane become weaker with higher temperature. However, at 55ºC, the removal efficiency increased to 98.56% which is contradict with the finding in a study mentioned earlier. It might be due to the changes of temperature when the dye solution was left in the laboratory or influenced by instrument error.

4.2 Transport cell removal

This experiment have been conducted using MO as the feeding solution and NaOH and KCl as the receiving solution respectively. Figure 4.6 and 4.7 show the removal rate of MO using NaOH and KCl as the feeding solution respectively. The finding showed that the transfer of MO to the NaOH solution did not occur as there is no colour changes observed in receiving solution. The initial colour MO (bright orange) in the feeding compartment change to yellow as some of the dye are attached to the membrane placed at the middle of transport cell, however it does not successfully being transported across the membrane to the receiving solution. The clear solution of NaOH remained unchanged after 24 hours. The UV-Vis reading also indicate that there is no significant changes from the sample taken in receiving solution. After 5 hours, the PIM was found out to break into pieces. This may be due to the PIM is too thin and the stability of PIM decreased over period of time.

Then, the transport experiment were repeated using different receiving solution which is KCl. During the observation, the initial colour of (MO) (orange colour) is gradually change into yellow colour and the reduction in absorbance value of MO in feeding solution was recorded. But MO was not transferred to the KCl solution, as it is only attached or adsorb by the PIM placed at the middle of transport cell. The transport of dye into KCl solution is not successfully performed because chloride, Cl^- may interfere with transfer of the dye. It may be preferable to work with a chloride free system. In these cases, it may be desirable to exchange the chloride anion for some other anion such as bisulfate (BASF, 2015). The PIM structure is still in good condition after 24 hours unlike the PIM used along with NaOH as feeding solution. This is probably because NaOH is not suitable with Aliquat 336.

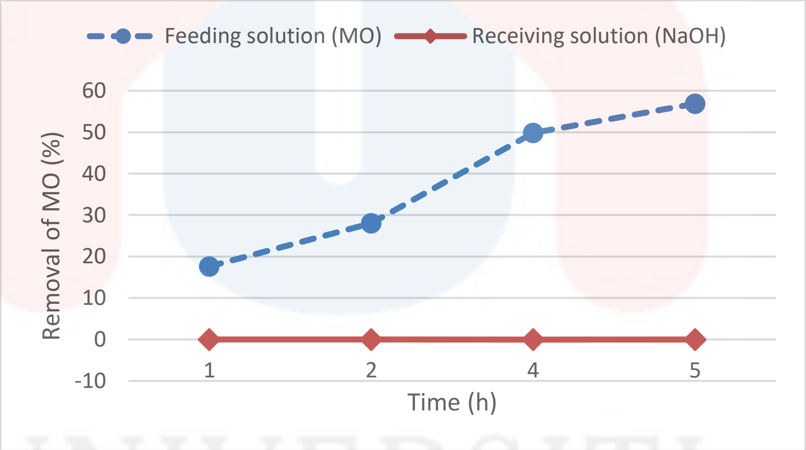

Figure 4.6: The removal rate of MO using NaOH as receiving solution in transport cell

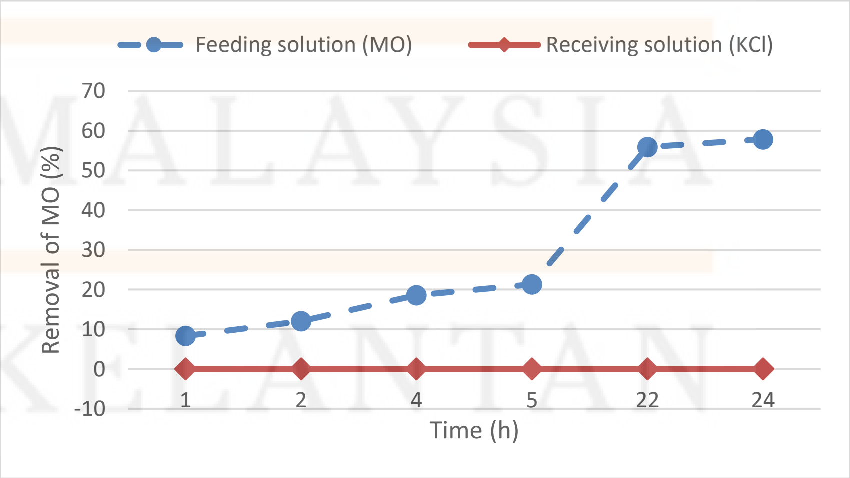

Figure 4.7: The removal rate of MO using KCl as feeding solution in transport cell

4.3 Characterization of Membrane

The functional groups present in an adsorbent material is notably influence the adsorption process; therefore it is essential to find out which type of functional group is present in it. The FTIR spectrum is useful to predict the sort and properties of functional group present in an adsorbent material. Figure 4.8 show the FT-IR spectra of Aliquat 336, PVC, PIM with PVC-0 Aliquat 336 and PIM with PVC-20 Aliquat 336.

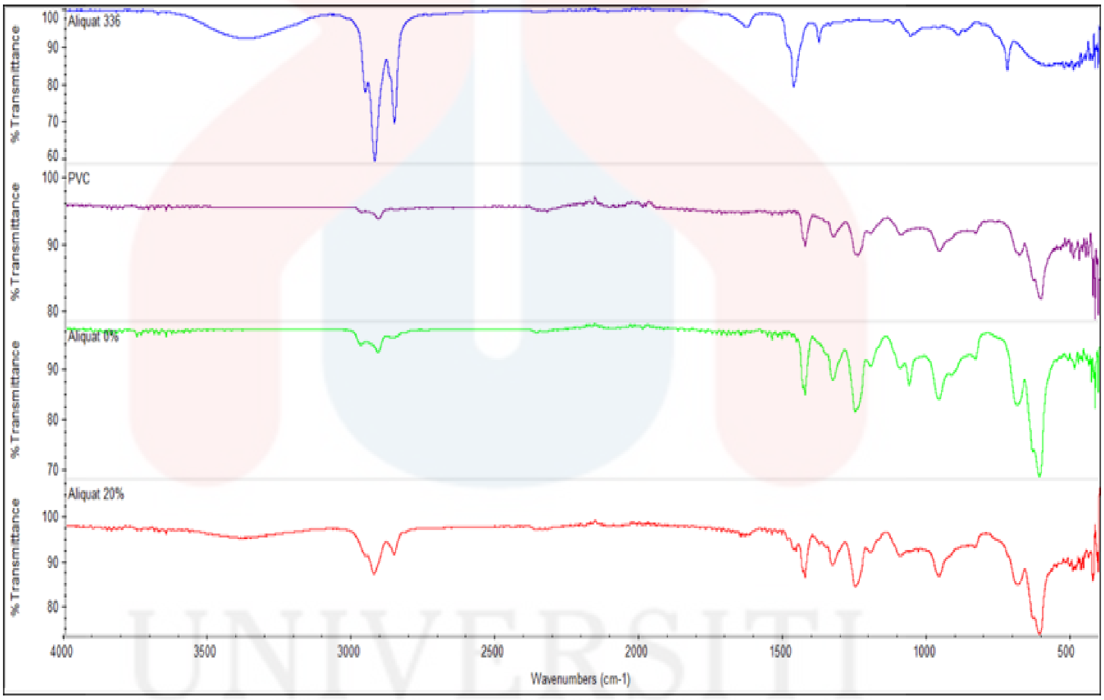

Figure 4.8: FT-IR spectra of Aliquat 336, PVC, PIM with PVC-0 and PIM with PVC-20 Aliquat 336.

For Aliquat 336, the obtained result showed the absorption peak located at 2922.26 cm^{-1}, which is attributed to stretching vibrational modes of the aliphatic hydrocarbon group. An aliphatic compound is a hydrocarbon compound containing carbon and hydrogen joined together in straight chains, branched trains or non-aromatic rings (Helmenstine, 2019). The IR spectra of the Aliquat 336 display the -CH deformation modes around 1466 cm^{-1} and 1377 cm^{-1}. The CH_3 asymmetric stretching vibration occurs at 2975-2950 cm^{-1} while the CH_2 absorption occurs at 2922.26 cm^{-1}. The symmetric CH_3 vibration occurs at 2885-2865 cm^{-1} while the CH_2 absorption occurs at about 2870-2840 cm^{-1}. The IR spectrum of PVC exhibited a band around 2900 cm-1, indicating the C-H stretching of the aliphatic CH group. Also, there was a sharp peak at 606.49 cm^{-1} showing the C-Cl stretching. Ling, Bukhari, & Suah, (2017) described that a peak was exhibited at 2912.20 cm^{-1}, showing the stretching of C-H of the aliphatic CH group and there are also a sharp peak at 691.57 cm^{-1} showing the C-Cl stretching.

For PIM with PVC-20 Aliquat 336, IR spectra exhibit both absorption peak which can be seen in IR spectra of both Aliquat 336 and PVC showing that it was successfully fulfilling its feature which contained the functional groups of carrier and base polymer. Lastly, the spectrum of PIM with PVC-0 Aliquat 336 show no obvious absorption peak observed at band 2922 cm^{-1}, thus proved that there is absence of Aliquat 336 in the membrane. The sharp peak is identified at band 610.24 cm^{-1} showing the C-Cl stretching, which also present in IR spectrum of PVC. It indicate that PVC is one of the component in PIM with PVC-0 Aliquat 336.

Then, PIM with PVC-20 Aliquat 336 then was further used in the extraction study. Characterization of this PIM before and after extraction were performed to identify the differences of functional group present on the PIM surface. The FTIR spectra of PIM with PVC-20 Aliquat 336 before and after extraction is shown in Figure 4.9. The absorption peak occur at bands in PIM before and after extraction does not show any significance changes however, the presence olefins functional group is detected on PIM after extraction.

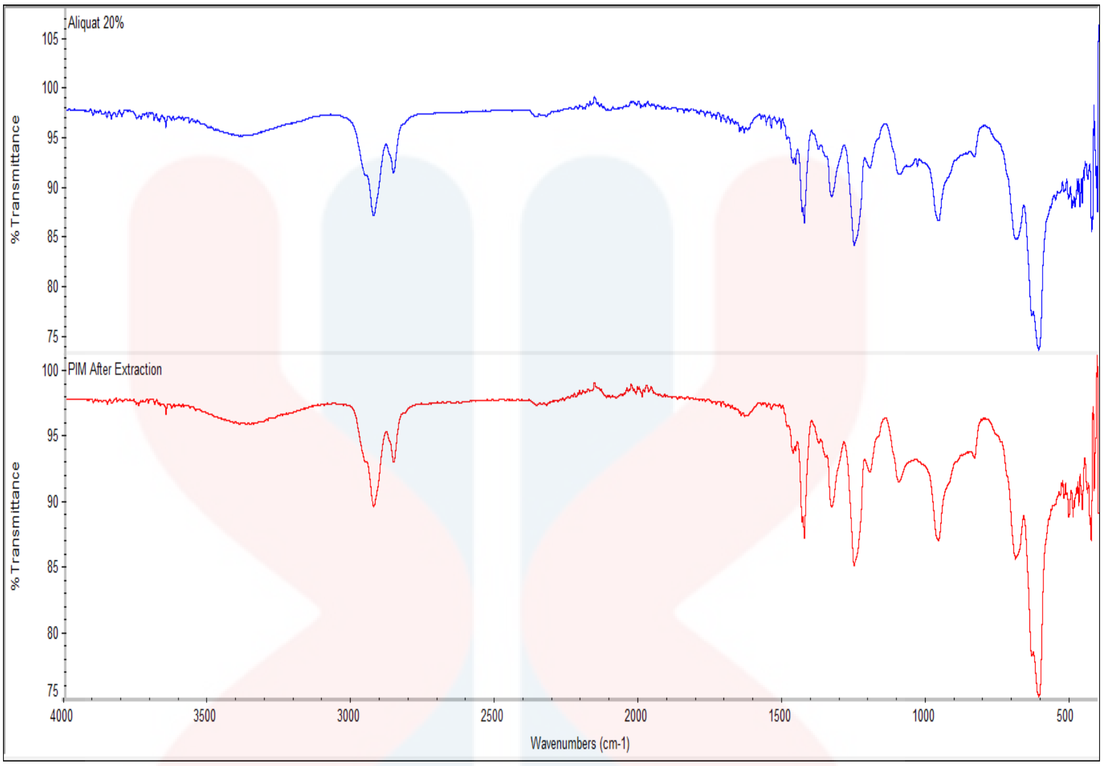

Figure 4.9: FTIR spectra of PIM with PVC-20 Aliquat 336 before and after extraction.

As explained previously, PIM with PVC-20 Aliquat 336 consist of aliphatic hydrocarbon group and it still exist after the this PIM have been in extraction of MO The IR spectrum of this PIM show absorption peak located at 2925 cm^{-1}, which is attributed to stretching vibrational modes of the aliphatic hydrocarbon group. The absorption peak shown in Figure 4.9 for PIM with PVC-20 Aliquat 336 is similar to the absorption peak shown in Figure 4.8. The strectching of C-Cl was also identified when the there is sharp peak at band 609.92 cm^{-1}. This indicate the PVC is still available even after the extraction. Then, the addition of olefins functional group also was spotted. Olefin, also called alkene, compound made up of hydrogen and carbon that contains one or more pairs of carbon atoms linked by a double bond (The Editors of Encyclopaedia Britannica, 2015). The CH-strectching of -CH=CH- (trans) occurs at band 3040-3010 cm^{-1} and non-conjugated C-C carbon stretching vibration occur at band 1634.31 cm^{-1}. Table 4.1 represent the peak values and the corresponding radical in different components.

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

Materials	Peak value (cm^{-1})	Corresponding radical
Aliquat 336	2922.26	CH_2
	1466 and 1377	-CH
	2975-2950	CH_3
PVC	606.49	C-Cl
PVC-0 Aliquat 336 PIM	610.24	C-Cl
PVC-20 Aliquat 336 PIM	2925.36	CH_2
	1466 and 1377	-CH
	2975-2950	CH_3
	610.23	C-Cl
PIM after extraction	2925	CH_2
	1466 and 1377	-CH
	2975-2950	CH_3
	609.92	C-Cl
	3040-3010	-CH=CH- (trans)
	1634.31	non-conjugated C-C

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study use PVC PIM for MO removal from aqueous solution as MO have harmful effects to the environment. The result of the study showed that the extraction of MO using PVC PIM is successful and show promising result. The maximum removal efficiency achieved under optimum condition is 99.61%. There are several parameters studied which are carrier concentration, pH, initial dye concentration, stirring speed and temperature. Optimum parameter is useful in order to maximize the rate of MO removal in shorter period. From the study, the optimum parameters to extract MO from aqueous solution are by using PIM with PVC-20 Aliquat 336, pH 4, 10 ppm of initial dye concentration, stirring speed at 100 rpm and at 25 ℃. This is because the highest of removal efficiency were obtained under these conditions. Then, the colour of MO can be vividly seen attached to the PIM, indicate the removal of MO from aqueous solution was take place.

Meanwhile, study on transport cell for MO using NaOH and KCl in receiving solution was carried out. However, the outcome of this study showed that the MO could not be transferred into both receiving solution; thus there is no recovery. It points out that NaOH and KCl is not suitable to be used as the receiving solution if Aliquat 336 is used as an extractant. Then, the FTIR spectra of Aliquat 336, PVC, PIM with

PVC-0 Aliquat 336 and PIM with PVC-20 Aliquat 336 are obtained and it showed that the PIM with PVC-20 Aliquat 336 fulfill the characteristic of membrane. The PVC used to prepare the PVC PIM in this experiment also have been matched to the other PVC and they are quite similar in term of components in it. After the characterization, PVC PIM used after the extraction exhibit the same absorption peak with the virgin PVC PIM but with addition of olefins functional group. Overall, the removal of MO from aqueous solution is successful and proven by characterization using FT-IR.

5.2 Recommendations

After completing this research, some recommendations are suggested to improve the future study. The application of PVC PIM to real dye effluent can be advocated because the maximum removal of efficiency using 10 ppm of synthetic MO is 99.02% which is outstandigly performed. The ability of PVC PIM in real life application can be identified if it used to treat real dye effluent. Besides, other receiving solution can be used to conduct the transport study. The chemical component in the receiving solution must be able to transport the dye attached to the PVC PIM for the membrane recovery purpose so that the PVC PIM can be reused. Nitric acid, HNO_3 can be suggested to be used as receiving solution as a study by Muthuraman, G., & Ibrahim, M. M. (2013) reported that HNO_3 was found to be suitable for stripping the extracted anionic dye. Next, the characterization of membrane can be enhanced by using other instruments such as SEM and TGA. SEM is useful to illustrate the morphhology of surface membrane while TGA is used to link the specific temperature and height of mass changes to the degradation of a specific compound or fragment of it. Hence, more information on the membrane properties can be obtained.

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APPENDICES

APPENDIX A

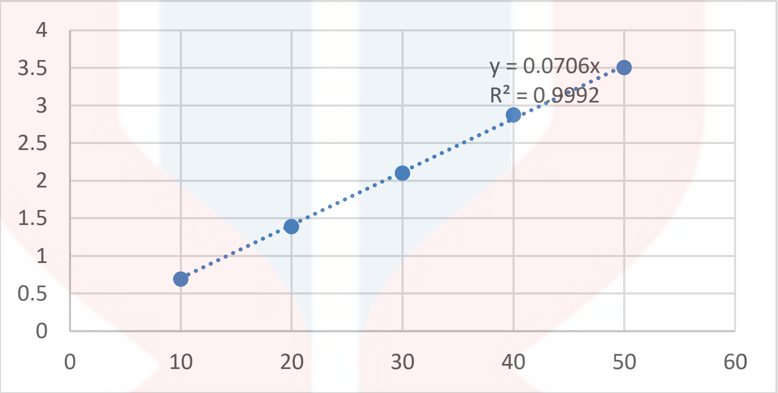

Figure A-1: Calibration curve of MO dye

Time (h)	Absorbance value (Abs)				
	Aliquat 0%	Aliquat 10%	Aliquat 20%	Aliquat 30%	Aliquat 40%	Aliquat 50%
0	1.233	1.374	1.332	1.54	1.476	1.515
1	1.225	1.282	0.287	1.433	1.476	1.641
2	1.223	1.259	0.205	1.424	1.484	1.678
4	1.224	1.231	0.09	1.362	1.44	1.67
5	1.233	1.288	0.05	1.312	1.4	1.626
22	1.259	1.135	0.007	0.691	0.786	1.037
24	1.264	1.122	0.007	0.566	0.705	0.918

Figure A-2: The absorbance value taken from solution with different Aliquat concentration for 24 hours

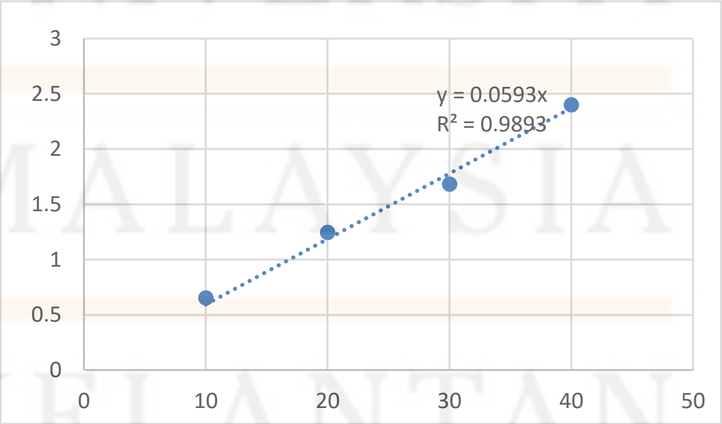

Figure A-3: Calibration curve of MO dye

Time (h)	Absorbance value (Abs)				
	pH 2	pH 4	pH 6	pH 7	pH 9
0	1.052	1.208	1.237	1.225	1.236
1	0.2	0.165	0.501	0.205	0.662
2	0.048	0.014	0.436	0.123	0.6
4	0.016	0.004	0.371	0.044	0.521
5	0.01	0.004	0.338	0.021	0.473
22	0.004	0.001	0.063	0.002	0.076
24	0.006	0.006	0.036	0.002	0.039

Figure A-4: The absorbance value taken from solution different pH for 24 hours

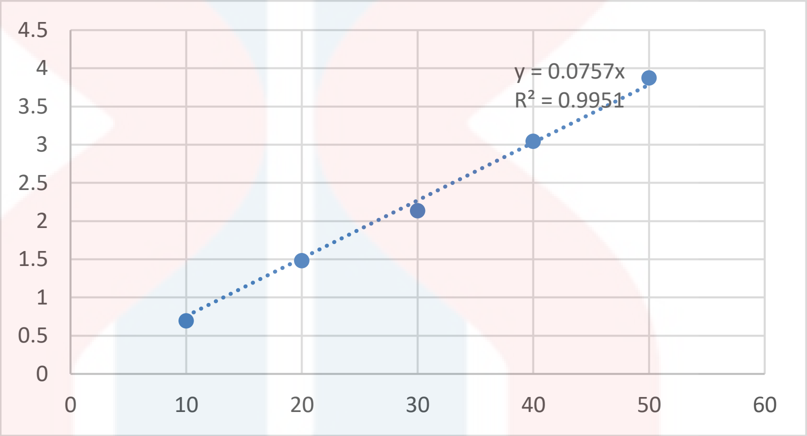

Figure A-5: Calibration curve of MO dye

Time (h)	Absorbance value (Abs)				
	10 ppm	20 ppm	30 ppm	40 ppm	50 ppm
0	0.613	1.385	2.016	2.946	3.698
1	0.085	0.742	1.099	1.125	3.162
2	0.035	0.735	1.117	1.135	3.188
4	0.006	0.698	1.107	1.122	3.029
5	0.013	0.684	1.103	1.101	2.935
22	0.01	0.284	0.834	0.721	1.102
24	0.016	0.24	0.787	0.668	0.961

Figure A-6: The absorbance value taken from solution with different initial dye concentration for 24 hours

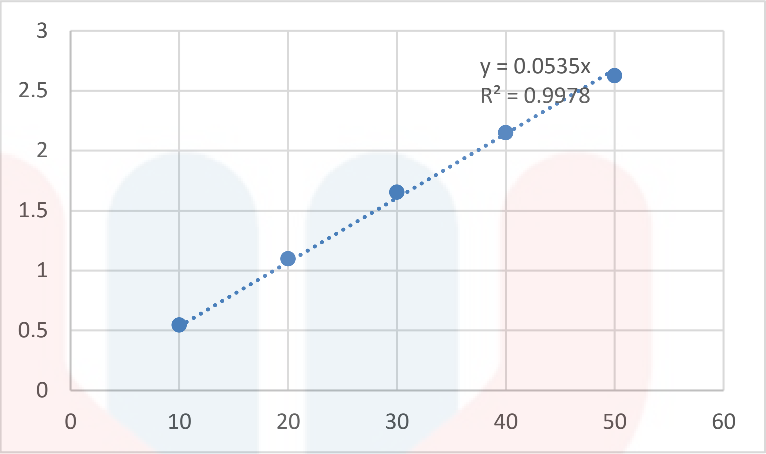

Figure A-7: Calibration curve of MO dye

Time (h)	Absorbance value (Abs)				
	100 rpm	150 rpm	200 rpm	250 rpm	300 rpm
0	0.609	0.568	0.591	0.527	0.519
1	0.313	0.392	0.473	0.434	0.39
2	0.297	0.386	0.437	0.425	0.367
4	0.24	0.359	0.358	0.371	0.316
5	0.218	0.339	0.319	0.345	0.266
22	0.003	0.136	0.005	0.01	0.006
24	0.009	0.104	0.027	0.016	0.011

Figure A-8: The absorbance value taken from solution with different stirring speed for 24 hours

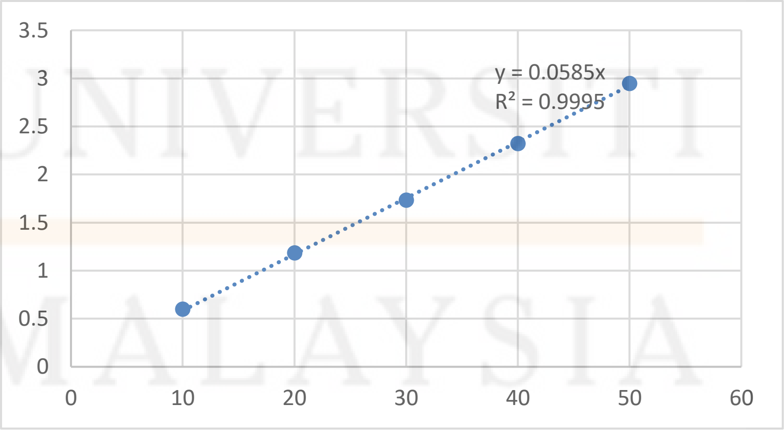

Figure A-9: Calibration curve of MO dye

Time (h)	Absorbance value (Abs)				
	25°C	35°C	45°C	55°C	65°C
0	0.512	0.502	0.553	0.554	0.553
1	0.427	0.451	0.483	0.452	0.485
2	0.42	0.436	0.482	0.45	0.487
4	0.369	0.373	0.447	0.403	0.459
5	0.326	0.322	0.431	0.351	0.44
22	0.006	0.01	0.186	0.008	0.084
24	0.002	0.011	0.172	0.006	0.058

Figure A-10: The absorbance value taken from sample with different temperature for 24 hours

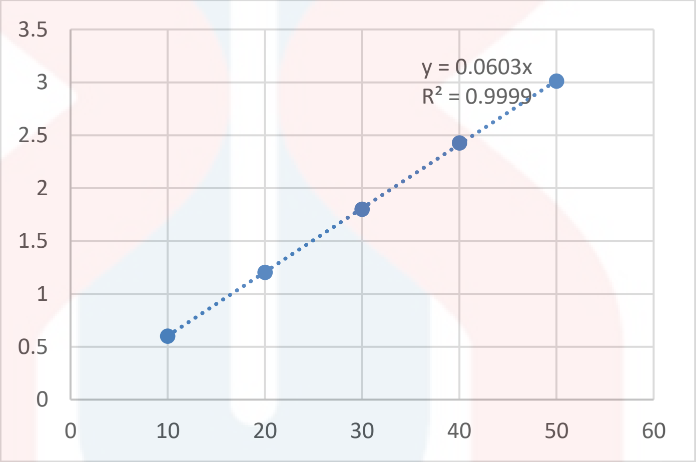

Figure A-11: Calibration curve of MO dye

Time (h)	Absorbance value	
	Feeding solution (MO)	Receiving solution (NaOH)
0	0.596	0.005
1	0.491	-0.003
2	0.429	-0.003
4	0.299	-0.005
5	0.257	-0.008

Figure A-12: The absorbance value taken from feeding and receiving solution respectively

Time (h)	Absorbance value	
	Feeding solution (MO)	Receiving solution (KCl)
0	0.614	0.001
1	0.563	0.004
2	0.54	0
4	0.5	0.005
5	0.483	0.001
22	0.271	0.008
24	0.259	0.009

Figure A-13: The absorbance value taken from feeding and receiving solution respectively

APPENDIX B

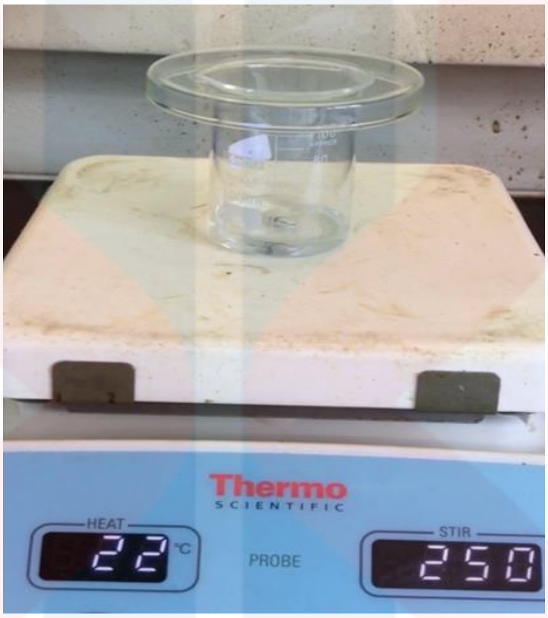

Figure B-1: The PVC PIM preparation process

Figure B-2: The manufactured PVC PIM

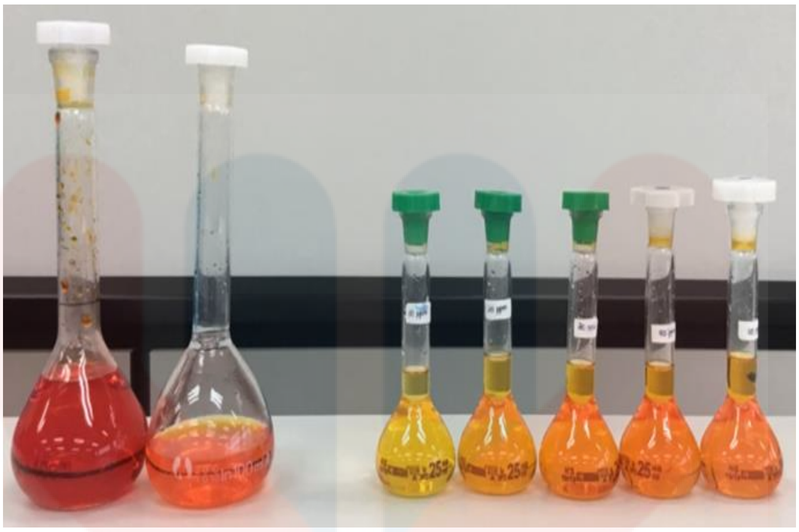

Figure B-3: The dilution of 1000 ppm of MO stock solution into different concentrations

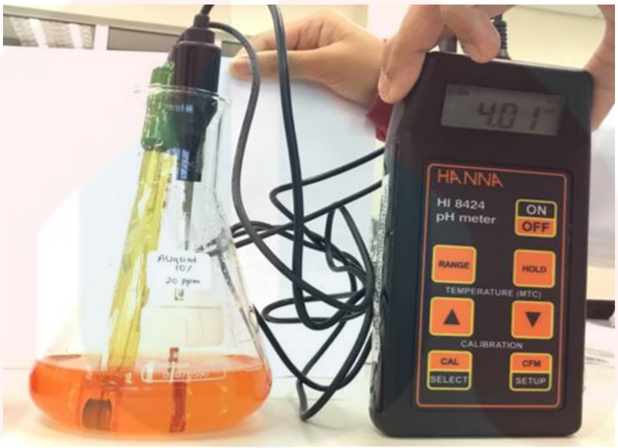

Figure B-4: The pH of dye solution was determined using pH meter

Figure B-5: The solution is ready for the extraction study

Figure B-6: The absorbance value of aliquot sample was obtained using uv-vis spectroscopy

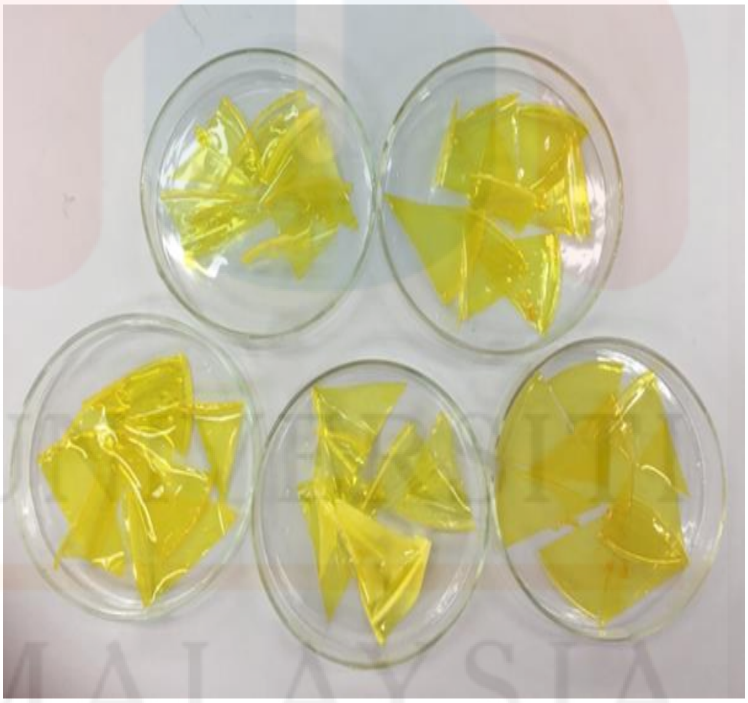

Figure B-7: The PVC PIM after the extraction study

Figure B-8: The initial transport study

Figure B-9: The changes in transport study after 24 hours