PREPARATION OF CTA ALIQUAT 336 POLYMER INCLUSION MEMBRANE FOR CONGO RED REMOVAL

By

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DECLARATION

I declare that this thesis entitled Preparation of CTA Aliquat 336 Polymer Inclusion Membrane for Congo red Removal 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:
Name: TOU YIT GUI
Date:

ACKNOWLEDGEMENT

It is with great pride that I hereby present my bachelor thesis. I have gain a lot of knowledge from this project during these two semester. These knowledge and experiences gained would be very useful for my future career and studies.

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ABSTRACT

Polymer Inclusion Membrane (PIM) has been widely used to remove heavy metal from aqueous solution. However, application of PIMs on dye removal is scarcely reported. The potential of CTA PIMs with Aliquat 336 to remove dye was discovered recently and this have attract researcher attention. In this study, CTA PIMs with Aliquat 336 was used to extract an anionic dye, Congo red from aqueous solution. The CTA Aliquat 336 PIM consists of cellulose triacetate (CTA) as base polymer and Aliquat 336 as carrier. The CTA PIMs was characterize by Fourier Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), water uptake and Ion Exchange Capacity (IEC). Important parameters that affect extraction capacity were studied such as Aliquat 336 concentration (0, 20, 30, 40 and 50 wt. %) pH of Congo red (2, 4, 6, 8 and 10), Congo red initial concentration (2, 4, 6, 8 and 10 ppm), temperature (27, 30, 40, 50 and 60°C) and stirring speed (150, 200, 250,300 and 350 rpm). Under an optimized condition (50 wt. % Aliquat 336, pH 2 of Congo red, 2 ppm of Congo red, 30°C and 150 rpm), 87 % of Congo red was successfully to remove by CTA Aliquat 336 PIM after 24H.

ABSTRAK

Membran Termasuk Polimer (PIM) telah digunakan secara meluas untuk meyingkirkan logam berat daripada larutan, walau bagaimanapun penggunaan PIM untuk penyingkiran penyelup jarang dilaporkan. Potensi PIM dengan Aliquat 336 untuk menyingkirkan penyelup pewarna daripada air telah ditemui baru-baru ini dan ini telah menarik perhatian penyelidik. Dalam kajian ini, PIM CTA Aliquat 336 digunakan untuk memindahkan pewarna anionik, Congo merah daripada larutan akueus. CTA Aliquat 336 PIM terdiri daripada selulosa asetat (CTA) sebagai polimer asas dan Aliquat 336 sebagai pembawa. PIM CTA dicirikan oleh specktrometer infra-merah (FTIR), mikroskop elektron pengimbas (SEM), pengambilan air dan Kapasiti Pertukaran Ion (IEC). Parameter penting yang mempengaruhi kapasiti pengekstrakan seperti kepekatan Aliquat 336 (0, 20, 30, 40 dan 50 wt. %) pH Congo merah (2, 4, 6, 8 dan 10), kepekatan awal merah Congo (2, 4, 6, 8 dan 10 ppm), suhu (27, 30, 40, 50 dan 60 ℃) dan kelajuan kacau (150, 200, 250,300 dan 350 rpm). Dikaji dalam keadaan dioptimum (50% Aliquat 336, pH 2 merah Congo, 2 ppm merah Congo, 30 ℃ dan 150 rpm), 87% daripada merah Congo berjaya disingjirkan oleh CTA Aliquat 336 PIM selepas 24jam.

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
BLM	Bulk Liquid Membrane
BOD	Biochemical Oxidation Demand
Cd(II)	Cadmium (II)
Cr(II)	Chromium (II)
Co(II)	Cobalt (II)
COD	Chemical Oxygen Demand
CTA	Cellulose Triacetate
$CuFeO_2$	Copper Iron Oxide
Cu(II)	Copper (II)
DCM	Dichloromethane
D2EHPA	Di-(2-ethylhexyl)phosphoric acid
FTIR	Fourier-transform infrared spectroscopy
JEA	Yellow Erionyl
LM	Liquid Membrane
MB	Methylene Blue
MeOH	Methanol
Mg/L	Milligram per Litre
Mm	Millimetre
2-NPOE	2-nitrophenyloctyl ether
2-NPPE	2-nitrophenyl ether
NaCl	Sodium Chloride
Na_2CO_3	Sodium Carbonate

Ni(II)	Nickel (II)
$(NH_4)_2SO_4$	Ammonium Sulphate
NPOE	1-(2-Nitrophenoxy)octane
PIM	Polymer Inclusion Membrane
PVC	Poly (vinyl chloride)
Pb (II)	Lead (II)
RBA	Red Bor-Deaux acid
SCN^-	Thiocyanate
SLM	Supported Liquid Membrane
TBP	Tri-n-butyl phosphate
TBPO	Tri-n-butyl phosphine
TEHP	Tris(2-ethylhexyl)phosphate
TOPO	Tri-n-octylphosphine oxide
TiO_2	Titanium Dioxide
TSS	Total Suspended Solid
Zn (II)	Zinc (II)

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Dye is a coloured substance that has an affinity to give the product colour. There are more than 10,000 dyes available commercially which widely used in textiles, cosmetic, plastic, leather and food industrial. Varieties of synthetic dyes including azo dyes which are mostly toxic, mutagenic and carcinogenic in nature present in coloured industrial effluent. Dyes are classified as anionic, cationic and non-ionic dyes (Kandisa,Saibaba & Khasim Shaik, 2016). It has been estimated that textile and manufacturing factories use more than 10,000 commercial available dyes and the consumption of dyes in textile industry is more than 1000 tonnes per year. 10 to 50% of these dyes were lost to the environment during the dyeing process (Kandisa et.al. 2016).

Congo red is an azo dye which is used in textile, paper, plastic and others products. It is a benzidine based anionic diazo dye. Congo red can cause allergic reaction to human and it becomes carcinogen when it is metabolized into benzidine (Nagapadma & Rao, 2015). Besides, these coloured wastewaters will damage the aquatic ecosystem and also affect the water quality and pose threat to microbial

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populations and mammalian animals. It will affect the aquatic life by decreasing light penetration and photosynthesis activity, causing oxygen deficiency which lead to mortality of aquatic life. Furthermore, water pollution by dyes will affect downstream beneficial use such as recreation, drinking water and irrigation activity (Mostafavi, Mirmajlessi & Fathollahi, 2009).

Different separation technique have been used in the removal of dyes from aqueous solution, such as physical, chemical and biological method (Kandisa et. al, 2016). Coagulation and flocculation is the example of physical method used. Adsorption, ion-exchange, oxidation process and irradiation are the example of chemical method which commonly used for treating wastewater. Bioremediation which can be one of the example of biological method also can be used to remove dye from textile effluent with lower cost and optimum operating time. Biological material such as bacteria and fungi have an ability to disintegrate and absorb varieties of dye. However, Bhatia, Sharma, Singh, & Kanwar (2017) gave the insight that biological process is efficient in reducing the COD and turbidity but inefficient in removing the colour.

Adsorption using activated carbon is the most frequent method used to treat dyes. Activated carbon is used due to its simplicity, low cost and availability of adsorbents (Nagapadma & Rao, 2015). Besides, structural characteristics and porosity of activated carbon make it more suitable for adsorbing dyes. However, activated carbon is a non-selective and the cost of activated carbon increase if the quality increase. Regeneration of activated carbon also expensive as chemical and thermal

procedure used in regeneration process is expensive, difficult and high risk of loss of absorbent (Nagapadma & Rao, 2015).

Membrane filtration is gaining acceptance as it is more cost-effective solution than many conventional methods. Pressure driven technology with pore size ranging from 100 molecular weight to 5 microns is used in membrane filtration (Minnesota Rural Water Association, 2001) such as membrane filtration are reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). RO and NF are used to remove impurities from water or other liquids (Munir, 2006). Membrane are basically filters with very small "opening" that prevent contaminants from passing through when the liquid that is being purified is pushed through the membrane. Membrane technology is mighty used to remove pollutants in the wastewater due to its energy-efficient, low cost, greater flexibility, high permeability and high selectivity (Lee & Nikraz, 2015). Membrane technology has a good ability to reduce chemical oxidation demand(COD), biological oxidation demand (BOD), total suspended solid (TSS), pH, and conductivity (Jianhong & Sufang, 2017).

Polymer inclusion membrane (PIM) is one of the liquid membrane type which contains a base polymer, carrier and plasticizer. The base polymer provides mechanical strength for the membrane, plasticizer provides elasticity and carrier enables the diffuse of constitutes liquid (Yildiz, Manzak, Aydin, & Tutkun, O, 2014). PIM is formed by casting a solution to form a thin, flexible and stable film (Yildiz et al., 2014). The base normally used to form PIM are cellulose triacetate (CTA) and Poly (vinyl chloride) (PVC).

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PIMs were mainly used to extract and remove heavy metal such as Cu (II), Pb(II) Cd(II) (Kebiche-Senhadji, Mansouri, Tingry, Seta, & Benamor, 2008) and others. However, recently PIM shown potential removing cationic dye (methylene blue) (Salima, Ounissa, Lynda, & Mohamed, 2012). This study used CTA polymer with incorporated with Di-(2-ethylhexyl) phosphoric acid (D2EHPA) as carrier and 2-nitrophenyloctyl ether (2-NPOE) as plasticizer to remove methylene blue and 93 % of methylene blue was extracted.

But study on PIMs for dye removal is new and scarcely reported. Therefore this research focuses on the application of Aliquat 336 as an ion carrier in CTA PIM to remove Congo red from aqueous solution. Condition such as concentration of Aliquat 336, pH of Congo red, initial Congo red concentration, stirring speed and temperature for CTA PIMs to remove Congo red were optimized in this study.

1.2   Problem Statement

Dyes are widely used in manufacturing industrial such as textiles, papers, plastics, cosmetic and others manufacturing process. This colour is directly excreted from the industrial into the water stream without being treated properly. This colour affects the water quality which makes the water undesired to use by human and aquatic life. For example, Congo red, it is commonly used in silk clothing manufacture are notoriously difficult to dispose of in an environmentally benign way. Congo red is a suspended carcinogen and mutagen (Sistla & Chintalapati, 2008). It is banned in many countries due to health concerns. Congo red is highly resistant to biodegradation due

to its structural stability, and its bright colour and toxicity cause to the surrounding make it undesirable in environment (Sistla & Chintalapati, 2008). Biological treatment and chemical method such as flocculation–coagulation and activated carbon are normally used to remove these dyes from water. But, these technologies is not cost-effective and will produce side product which is another environmental problem (Salima, Ounissa, Lynda & Mohamed 2012). Therefore, PIM which is more cost-effective, easy to prepare and high degree of reusability is more suitable used to remove these large amounts of dyes in coloured wastewater without living side-product (Salima, Ounissa, Lynda & Mohamed 2012).

1.3 Objective

The objectives of this study are:

a) To determine the optimum concentration of Aliquat 336, initial dye concentration, pH of dye, stirring speed and temperature that affect dye removal using CTA Aliquat 336 PIM.

b) To characterise the CTA Aliquat 336 PIMs in term of its morphology, functional group, water uptake and ion exchange capacity.

c) To study the transport of dye using CTA Aliquat 336 PIMs with static batch cell.

1.4   Scope of Study

In this study, concentration of Aliquat 336, initial Congo red concentration, pH of Congo red, stirring speed and temperature were optimised to extract Congo red. CTA PIM was first prepared with different Aliquat 336 concentration (0, 20, 30, 40 and 50 wt. %) for Congo red removal. CTA PIM with optimum Aliquat 336 was used to remove Congo red and the pH was varied from 2 to 8. Next, the optimized of pH of Congo red and CTA PIM with optimum Aliquat 336 concentration was used to remove Congo red with different concentration (2, 4, 6, 8 and 10 ppm). Stirring speed was adjusted from 150 to 350 rpm to investigate the stirring effect on dye removal. Lastly, the temperature of Congo red was varied from 25, 30, 40, 50, and 60 ℃ to study the effect of temperature on the Congo red extraction. Each previous condition which has been optimized is used in the transport cell to study the removal efficiency.

1.5   Significance of Study

Congo red is an anionic dye. It contains benzidine which is a carcinogenic compound (Hernández-Zamora, Martínez-Jerónimo, Cristiani-Urbina, & Cañizares-Villanueva, 2016), it affect human health by causing Huntington's disease (Jennifer Couzin-Frankel, 2003). Besides threat to human health, it also affect the aquatic life by reducing the dissolved oxygen in the water. Therefore, Congo red is one of the dyes which affect human and the environment. Absorption by using activated carbon is one of the method used to treat water pollution by Congo red. However, due to its high cost and high energy consumption, alternative method is investigated.

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CTA Aliquat 336 PIMs is one of the new technology that have the potential treat water pollution by Congo red. It is easy to prepare compare to activated carbon. It is form by casting a solution which contain carrier, base and plasticizer to form a thin layer. The process is easy and use less energy (Johansen, 2011). Besides, it can be regenerate after the treating process, therefore it is environmental friendly. As this method is easy and low initial cost, it will bring a lot of benefits to the researchers and textiles industrials if extraction of dye by using CTA Aliquat 336 PIM is applicable. Therefore, it will become another option for the textiles industrial to choose which is more cost effective and environmental friendly.

However, study on dye removal especially Congo red by using CTA Aliquat 336 PIMs is new and scarcely reported. Therefore this study is important to show the capability of CTA Aliquat 336 PIMs in removing Congo red. This can be a source of valuable up to date information which can be act as a guide for others similar study. Besides, this research determine the optimum condition such as Aliquat 336 concentration, pH of Congo red, initial concentration of Congo red, stirring speed and temperature that able to remove Congo red efficiently.

CHAPTER 2

LITERATURE REVIEW

2.1   Congo Red

Congo red is introduced in 1884 as a synthetic dye. It is one of the example of anionic dye. Congo red is used to test for amyloidosis and test for hydrochloric acid in gastric contents. Congo red is a sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid as it is made by coupling 4-sulfo-1-1-naphthylamine with bis-diazotized benzidine (Ch & Changes, 2010). It is the first dye to be known as direct dye. Direct dye is a class of coloured, water-soluble compound that has an affinity for fibre and are taken up directly. Direct dye is cheap, easily applied and they are bight in colour, therefore it is widely used in manufacturing industrial especially textile and paper industries (Pubchem, 2011). The structure of Congo red is shown in Figure 2.1.
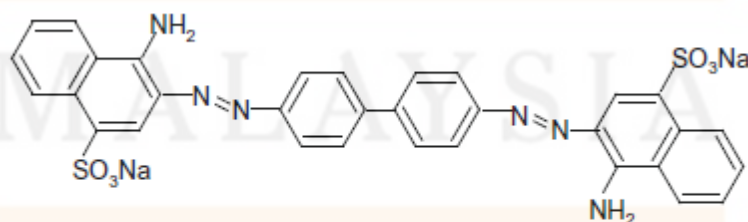
Figure 2.1: Structure of Congo red.

Congo red is used in the laboratory aid in the diagnosis of amyloidosis and indicators as Congo red shows blue in pH 3 and red in pH 5 (Congo red shows red in alkaline solution and appears as blue in acid solution) (Steensma, 2001). Besides, Congo red is used for diagnostic purpose. Amyloid in tissues of patients with Alzheimer's disease can be identify by using Congo red. For example, the tissues of patients with Alzheimer's disease show "apple green" birefringence of amyloid plaques was explained by Belgian neuropathologist and Paul Divry when stained with Congo red and examined under polarized light (Pubchem, 2011).

However, Congo red will affect the environment if it is released into the surrounding without proper treatment. Congo red affect the photosynthetic activity in an aquatic ecosystem as this azo dye modifies light quality and decrease underwater light penetration, therefore reduce the dissolved oxygen in the water. Congo red is also a carcinogenic agent as it is manufactured with benzidine which is a carcinogenic compound (Hernández-Zamora, Martinez-Jeronimo & Cristiani- Urbina, 2016). If consume water contaminated by Congo red, it will cause Huntington's disease as Congo red will break the hallmark protein clumps in the brain (Jennifer Couzin-Frankel, 2003).

Physio-chemical treatment such as adsorption, oxidation and chemical precipitation method is used to remove Congo red from coloured wastewater. Among these adsorption is one of the most frequent methods used. Adsorption method always uses activated carbon as treatment such as chitosan, sawdust and Maize Seed Powder

(MSP) (Hernández-Zamora et al., 2016). Recently, PIM also shows the potential in treatment of remove Congo red from aqueous solution.

2.2   Liquid Membrane (LM)

The liquid membrane is a homogeneous, porous thin film of liquid interspersed between feed and strip phase of the different composition. The feed and strip phase is miscible while the LM phase is immiscible with both (Johansen, 2011). LM is widely used in the fields of industrial, biomedical, analytical and also wastewater treatment. LM has a lot of advantages which allow it widely used in industrial application. The advantages of LM including high selectivity of target substances, mobile carrier enhance the mass transfer rate and its capability of treating a variety of element and compound in the laboratory and selected industrial at great speed with high degree of effectiveness (Johansen, 2011).

LM is divided into two main categories, non-supported membrane (non-SLMs) and supported liquid membrane (SLMs) (Johansen, 2011). Emulsion liquid membrane (ELM) and bulk liquid membrane (BLM) are the example for non-SLMs whereas flat sheet SLM, spiral wound SLM are the example for SLMs (Johansen, 2011).

2.3 Polymer Inclusion Membrane (PIM)

2.3.1 Base of PIMs

Polymer-based liquid membrane concept have been introduced since 50 years ago. PIMs also is known as polymer liquid, gelled liquid, polymer plasticized, fixed site carrier or solvent polymeric membrane (Johansen, 2011). PIMs are composed of base polymers, plasticizer and a carrier (Johansen, 2011).

The base polymer that most often uses in preparing polymer membrane is CTA and PVC. The base polymer plays an important role to provide mechanical strength for the membrane. The structure of CTA and PVC are shown in the Figure 2.2 and Figure 2.3. Cellulose-based polymers are useful for PIM application due to its highly infusible. CTA is a polar polymer with a number of hydroxyl and acetyl groups that are capable of forming highly orientated hydrogen bonding (Gherasim, Bourceanu, Olariu, & Arsene, 2011a). CTA and other cellulose derivatives are prone to hydrolysis, particularly in an acidic environment due to hydration characteristics of CTA. Furthermore, CTA is highly crystalline (Johansen, 2011). The mechanical strength of CTA is attributed to its crystalline domain. However, crystalline nature of CTA polymer made it incompatible with high concentrations of hydrophobic non-polar carriers. As a result, metal ion transport at such a high carrier concentration becomes ineffective (Nghiem, Mornane, Potter, Perera, Cattral, Kolev, 2006).

PVC polymer, it is an amorphous polymer with a small degree of crystallinity compare to CTA which is highly crystalline (Gherasim, Bourceanu, Olariu, & Arsene,

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2011b). However, PVC cannot hydrated as compare to CTA. Due CTA is always used to prepare base polymer compare to PVC.
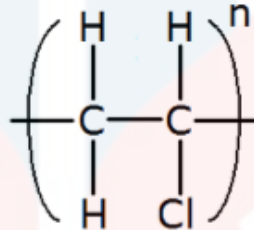
Figure 2.2: Structure of polyvinylchloride (PVC).
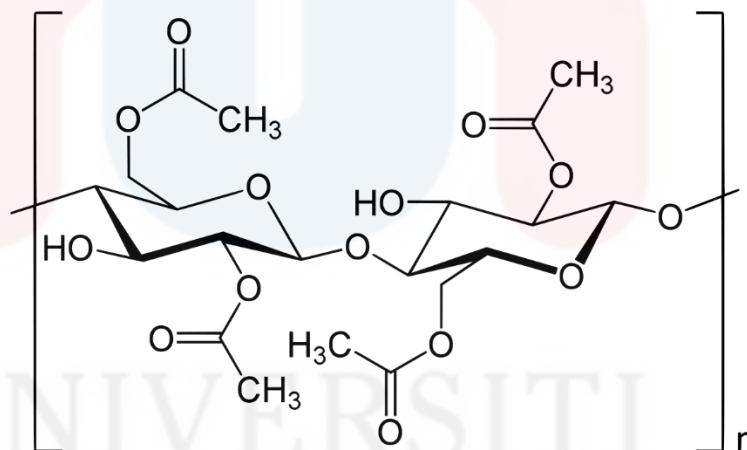
Figure 2.3: Structure of Cellulose Triacetate (CTA).

PIMs is widely accepted as it is high selectivity, low energy consumption and operating cost (Johansen, 2011). In addition, PIMs can be used as an alternative way to remove the heavy metal from the aqueous solution, for example, Cu (III), Pb (II) and Ni (II) ions as it is easier to manage as compared to others hydrometallurgical method (Konczyk, Kozlowski, Walkowiak, 2010).

2.3.2   Carrier of PIMs

PIMs also consist of a carrier which is responsible for the binding site of complexation or ion-pair formation. According to Nghiem (2006), the distribution of carrier in the membrane determine the transport efficiency. There are 4 types of carriers in PIMs which are classified as acidic carrier, neutral or solving carrier, basic carrier and macrocyclic and macromolecular carriers (Johansen, 2011; Nghiem, 2006). Each carrier is used to transport different kinds of target ions.

An uncharged complex is formed when an acidic carrier is combined with anion in order to extract cation from aqueous solution. An acidic carrier will exchange the proton for the cation when it is used to separate cations (Johansen, 2011). Hydrogen ion is used to generate the driving force for the solute permeation across the membrane. Acidic carrier is further classified into chelating extractants and alkyphosphorous compound. A chelating extractant is a compound that contains a group with easily dissociating proton near an atom with a free electron pair, whereas alkyphosphorous compound are more soluble in the organic solvent than metal chelates (Johansen, 2011).

Neutral extractants are used to extract uncharged metal complexes. Organo-phosphoryl compound such as tri-n-butyl phosphate (TBP), tri-n-butyl phosphine oxide (TBPO), and tri-n-octylphosphine oxide (TOPO) are the example of neutral extractants (Johansen, 2011). Transport of lead and cadmium ions in two different membrane systems PIM and Supported Liquid Membrane (SLM) using TBP as carrier and 2nitro phenyl octyl ether (NPOE) or Trisethylhexylphosphate (TEHP) as

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plasticizer has been investigated by Arous et al., (2010), and the results showed that for Pb^{2+} ion, the concentrations of strip phase increases using synthesized membranes.

Basic carrier is a long chain organic compounds containing primary, secondary and tertiary amino functions. Basic carrier enables the forming of anionic complexes in aqueous solution (Johansen, 2011). Amine which is one of the basic carriers can be stripped with a wide variety of inorganic salt solution such as NaCl, Na_2Co_3 and $(NH_4)_2SO_4$ (Johansen, 2011). The quaternary alkyl ammonium salts such as Aliquat 336 is also one the example of basic carrier even it does not have a lone electron pair at the nitrogen atom. Aliquat 336 was used in this study because of its ion exchange properties, which is release counter ion through these exchange.

Macrocyclic and macromolecular carriers contain hetero atoms which then capable of forming electron-rich interior cavities. They are high complexing selectively for metal ions due to present of specifically tailored encapsulating coordination sites in their structure (Johansen, 2011). Based on study by Yordanov & Roundhill, (1998) the initial cost of the macrocyclic compounds are very high and their solubility in aqueous phases make them less suitable for use for large-scale process. However, in order to make them more applicable in membrane process, this carrier will modify with a long-chain aliphatic compound. Consumption of these compound in a PIMs is lower compared to solvent extraction. (Johansen, 2011).

2.3.3 Plasticizer of PIMs

Most of the synthetic polymer used was prepared by using a plasticizer. Plasticizer present in the membrane help to reduce brittleness, impart flexibility, increase strength and improve adhesiveness of the film with other surfaces of membranes (Nghiem et al., 2006). Few of the plasticizer such as 2-nitrophenyl octyl ether (2-NPOE) and 2- nitrophenyl pentyl ether (2-NPPE) have been tested and successful in PIMs studies (Nghiem et al., 2006). However, entrapment of a large amount of plasticizer and various other membrane components in the polymer leads to exudation and leaching and the exuded plasticizer is often toxic (Heng & Hall, 2000). The exudation of plasticizer can cause short-term or long-term toxic respond (Heng & Hall, 2000). Therefore many solutions have been developed to resolve problems related to leaching, adhesion, and the photocurability of ion-sensor membranes, including developed the PIMs with self-plasticizer, such as methacrylic-acrylic copolymers which is the new self-plasticizing membrane matrixes for ion-selective electrode (Heng & Hall, 2000).

Tricaprylmethylammonium chloride or known as Aliquat 336 is a quaternary ammonium salt that is commercially available extractant often used in PIMs. According to some research, Aliquat 336 has a plasticizing properties (Gherasim, Bourceanu, Olariu, & Arsene, 2011), and this can act as a plasticizer at the same time. PIMs with Aliquat 336 without plasticizer have been successfully used to extract and transport of heavy metal, such as Cd(II), Co(II), Cr(II), Ni(II) (Konczyk et al., 2010) common anion (SCN^-) and organic compound (amino acid and lactic acid) (Gherasim & Bourceanu, 2013).

2.4 Mechanism of facilitated transport

The transfer phenomenon of a substance through the membrane phase can be achieved either by passive transport or active transport.

2.4.1 Passive transport

Passive transport or simple transport is a process of substrate sharing between the aqueous phase and the membrane phase. Concentration gradient affect the diffusion of substrate in passive transport.

2.4.2 Facilitated Transport

Facilitated transport is used in the membrane phase contains a carrier dissolved in an organic solvent. The transfer of substrate through the membrane phase is done through three main steps, firstly, the target solute was first diffuse through the aqueous stagnant layer at the membrane interface, and react with the carrier to form a complex. This complex then is transported across the interface and replace by another carrier. Secondly, the complex then is diffused across the membrane toward the strip solution. Lastly, the complex dissociated and the target solute is released into the strip solution at the membrane strip solution interface (Eljaddi & Lebrun, 2017).

2.4.2.1 Co-transport

This type of transport is observed when the carrier is neutral in natural, and the feed phase contain a pair of ions (M^{m+} mX^-) (cation and anion) associated and extracted reversibly by carrier L (Eljaddi & Lebrun, 2017). The reaction can be shown in the equilibrium below:

$$M^{m+} (aq) + mX^- (aq) + L \longleftrightarrow (ML^{m+}, mX^-)$$
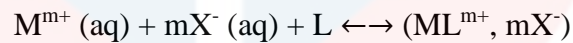
2.4.2.2 Counter Transport

In the counter transport, the carrier can be acidic or basic nature, therefore counter transport can be anions or cations. Counter cation transport occur when the carrier in the membrane is acid, and the process is done by a cation-exchange proton (pH pump), cations move from high pH to low pH (Eljaddi & Lebrun, 2017). The balance in the sources-membrane interface can be written as:

$$M^{m+} (aq) + mHL \longleftrightarrow (ML_m) + mH^+ (aq)$$
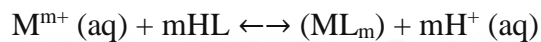
where M^{m+} is the concentration of ion, L is the carrier, MLm is the ion complex with carrier in receiving phase and mH^+ is the ion product.

The counter facilitated transport of anions can occur when the carrier in the membrane phase can exchange an anion by interaction with the substrate at sources phase-membrane interface. The formation of neutral entity can be form in this reaction:

$$A^- (aq) + XL \longleftrightarrow (A^- L^+) + X^-$$
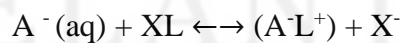
where A^- is the concentration of anion, L is the carrier in PIMs, (A^-L^+) is the ion complex formed in receiving phase. The principle of transfer material, cotransport of cation species and counter transport of a cation species through a PIM is presented in Figure 2.4, 2.5 and 2.6 respectively.
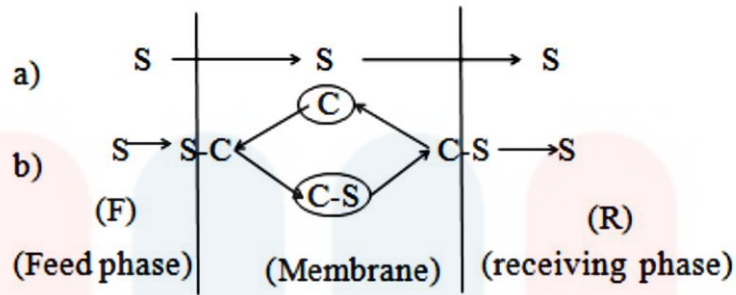
Figure 2.4: Principle of the transfer of material through the membrane, (a) passive transport, (b) facilitated transport. *(Source: Eljaddi et al., Journal of Membrane Science and Research 3 (2017) 199-208)*
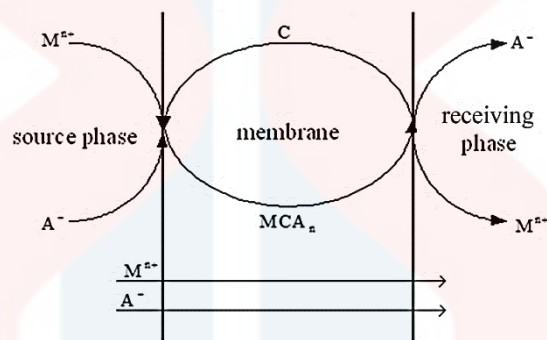
Figure 2.5: Cotransport of a cation species through a PIM. C represent the carrier, $[M^+]$, $[A^-]$ represent the concentration of respective solute in the bulk aqueous phases (Nghiem et., al 2006).
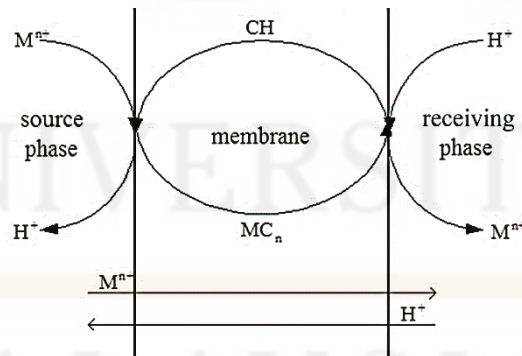
Figure 2.6: Counter transport of a cation species through a PIM. C represent the carrier, $[M^+]$, $[A^-]$ represent the concentration of respective solute in the bulk aqueous phases (Nghiem et., al 2006).

2.5   Application of PIMs

2.5.1   Removal and Recovery of Dyes

PIMs was introduced since 50 years ago and it were used in analytical chemistry. In recent year, PIMs are widely for sample separation, electro-driven extraction, passive sampling and others application due to their high stability and easy to prepare. There are less research study on using PIM to remove dyes due to this technology is still new and need more research to develop its potential. Previous study on using PIMs to remove dyes are shown in the section below.

According to Salima, Ounissa, Mohamed (2016), a study was carried out to investigate the absorption equilibrium, adsorption kinetics and facilitated transport of Methylene Blue (MB) and Rhodamin B (RB) on PIM with carrier Di (2-ethyl hexyl) phosphoric acid (D2EHPA). The PIMs were prepared using CTA as base polymer, plasticized with Nitrophenyl Octyl Ether (2-NPOE) and containing D2EHPA as the carrier. The effect of time, pH, stirring speed, concentration of D2EHPA and dye have been optimized. This research shown that under optimal conditions, about 93 % of MB and 97 % of RB were removed.

Another study used a simple and efficient method for the recovery of a cationic methylene blue (MB) by Salima, Ounissa, Fadila, & Mohamed (2016). The investigation of PIMs consisting of plasticizer, CTA and Di (2- ethyl) phosphoric acid (D2EHPA) as the carrier, which transfers quantitatively MB species from an aqueous feed phase into a solid organic phase (PIM) has been carried out. The effects of time, pH, the stirring speed, concentration of the D2EHPA and dyes have been optimized in

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the research. More than 93 % extraction of MB have been reached under optimized condition (Salima et al., 2016).

Furthermore, Salima, Ounissa, Fadila, Mohamed (2014) use the application of PIMs consisting of plasticizer CTA , tricaprylmethylammonium chloride (Aliquat 336) as the carrier for removing the anionic dyes (red bor- Deaux acid (RBA) (acid violet 90) and yellow erionyl (JEA) (acid yellow 127)) from aqueous solution have been done. The condition such as pH (2-9) of the aqueous solution, the stirring speed (250 - 400 rpm), and concentration of the extractant in the membrane (5-30 μ mol/cm^2) and initial dye concentration (50-250 ppm). The result of this study proves that PIM can be used to extract anionic dye with a result of 99% of acid dyes were extracted under optimized experimental condition.

Yeoh Ling and Mohd Suah (2017) carried out a study to extract a basic dye, Malachite Green (MG) from wastewater by using PIM. The PIM consists of PVC -as base polymer, bis-(2-ethylhexyl) phosphate (B2EHP) as extractant and dioctyl phthalate (DOP) as plasticizer. The composition of the components were varied to determine the optimum composition of membrane with better extraction efficiency. The research showed that more than 98 % for MG concentration of 20 to 80 mg/L was extract efficiency by using PIM under optimized condition(Ling & Mohd Suah, 2017)

According to Ozmen and Yilmaz (2007) two starch-based and a β-cyclodextrin ($\beta -$ CD) based polymers were synthesized using 4,4'-methylene-bis-phenyldiisocyanate (MDI) or hex- amethylenediisocyanate (HMDI) as a cross linking

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agent in dry dimethylformamide and used as a sorbent for the removal of Congo red from aqueous solutions. Parameters such as pH of aqueous solution, initial dye concentration and contact time were investigated in his study. Elif Yilmaz Ozmen, Mustafa Yilmaz proof that the polymers has relatively high sorption capacity for Congo red compared to activated carbon (Ozmen & Yilmaz, 2007).

2.6   Factors that Affect the Dye Removal

2.6.1   Effect of Extractant

Carrier concentration play an important role on dye removal. Aliquat 336 is act as a carrier in this research. It is used to extract the anionic dye, Congo red from strip phase to received phase. The effect of carrier concentration was investigated by Aitali Salima et al., (2012) by using CTA PIM with Di-(-Ethyl hexyl)phosphoric acid (D2EHPA) as carrier to remove methylene blue. It showed that the extraction efficiency of methylene blue increase as the concentration of D2EHPA increase. Increase concentration of extractant will increase the formation of ion pair complex between extractant and dye (Ling & Mohd Suah, 2017), hence extraction efficiency also increase.

2.6.2   Effect of pH

pH of dye is an important parameter that will affect the extraction of dye. pH affect the concentration of H^+ or OH^- present in the dye aqueous solution, this is because the adsorptive process is affected by pH through dissociation of functional group on the adsorbent surface active site (Muhammad Imran Khan, Shahbaz Akhtar,

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Shagufta Zafar, Aqeela Shaheen,Muhammad Ali Khan, Rafael Luque & Aziz Rehman, 2015) Anionic dye or cationic dye will be affected by acidic and cationic condition respectively, the adsorption of anion decrease while cation increase with the increase in pH. For example, research have been done by Yeoh Ling and Mohd Suah (2017) showed that Malachite Green (cationic dye) which is a cationic dye show high removal percentage higher pH.

2.6.3 Effect of Initial Dye Concentration

Initial dye concentration play an important role in dye removal experiment. As the concentration of Congo red increase, the molecule present in the dye will increase. The molecule present in the Congo red will react with the active site of PIMs. Therefore, increase initial Congo red concentration will decrease the extraction efficiency of PIMs as the membrane active site will become saturate with dye molecule after certain time interval. Similar evidence have been prove by Saliman et al., (2012) which use CTA PIM with 2-Nitrophenyl octyl ether (2-NPOE) as the plasticizer and Di-(- Ethyl hexyl) phosphoric acid (D2EHPA) as the carrier to remove methylene blue. It showed that the extraction of cationic dye is decrease with the increase of dye concentration.

2.6.4 Effect of Temperature

Adsorption is also controlled by temperature. Adsorption is an exothermic process and the rate of absorption will decrease with an increase in temperature in nature (Khan et al., 2015). Studied shown by Khan et al., (2015) on the removal of

Congo red from aqueous solution by Anion Exchange Membrane (EBTAC) showed a decrease in extraction efficiency when temperature increase. However, in some condition, the extraction efficiency will increase with increasing temperature, this is caused by the increase of reactive site due to breaking some of the internal bond in the active surface site of adsorbents (Khan et al., 2015). Therefore the extraction rate will increase with the increase of temperature (Foroughi-Dahr, Abolghasemi, Esmaili, Shojamoradi, & Fatoorehchi, 2015).

2.6.5 Effect of Stirring Speed

Agitation ensure proper contact between the extractant and dye. As the stirring speed increase, more molecule is collide with each other and attract to the surface of carrier, thus increase the extraction rate (Salima et al., 2012). At lower agitation speed, mass transfer is controlled as stationary fluid film is thicker around the particle. However, this condition is reverse when agitation speed is increase and the process become intra particle diffusion controlled (Dâas & Hamdaoui, 2010). Therefore, increase in stirring speed can increase the dye removal efficiency as shown in study Saliman et al., (2012), the extraction of cationic dye increase as stirring speed increase to an optimum speed at 350 rpm. However, some studies showed a decrease in dye extraction efficiency as the stirring speed increase, Attef Daas, Oualid Hamdaoui (2012) which studied the extraction of anionic dye from aqueous solutions by emulsion liquid membrane show that increase in speed from 200 to 400 rpm caused a reduction in extraction efficiency. They explain this condition is result from the unstable of emulsion liquid membrane at higher stirring speed.

2.7   Membrane Characterization

2.7.1   Fourier Transform Infrared Analysis (FTIR)

FTIR is an infrared spectroscopy method used to identify organic and functional group of sample. Chemical properties of sample can be scan and observed by using the infrared light. Chemical bonds and molecular structure of the sample can be shown in a profile in the form of absorbance spectra. The functional group (ketones, alkanes) which is present in the sample will show in a peak in these profile (Naseska, 2016).

Different types of bonds, functional group absorb different wavelength of infrared radiation, therefore showing different wavelength number as shown in Figure 2.7. FTIR analysis can be classified into 2 main region, functional group region (more than $1450\,cm^{-1}$) and fingerprint region (less than $1450\,cm^{-1}$). A functional group region provide information about functional group present in a sample whereas a fingerprint region provide information about variation characteristics of molecule (Naseska, 2016).
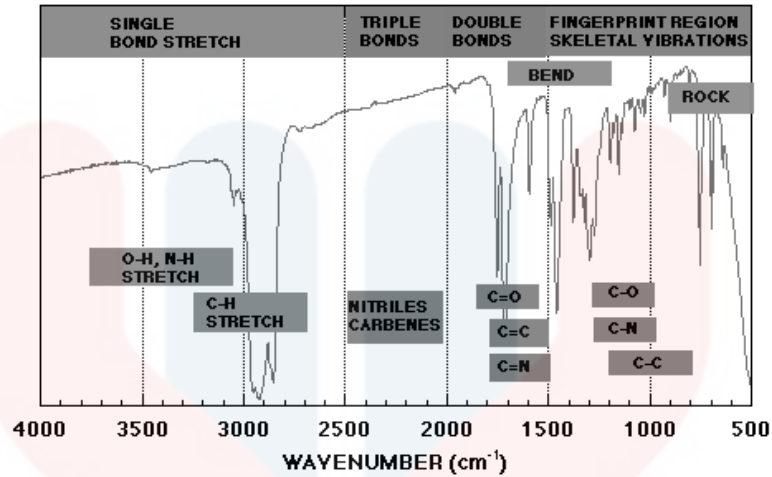
Figure 2.7: FTIR analysis showing a sample with different types of bonds and functional group absorbed at different wavelength *(source: the material characterization lab)*

2.7.2 Energy Dispersive X-ray (EDX) and Scanning Electron Microscopy (SEM)

SEM produce 2D mage, reveal information about the sample including external morphology and chemical composition. SEM is effective in microanalysis and failure analysis of solid inorganic materials. It helps to study the morphology of sample by generating high resolution image at high magnification.

EDX in SEM involve two steps. Firstly, the electron beam hits the sample and the energy is transfer to the atoms of sample. Electrons then use the energy to 'jumps' to an energy shell with higher energy or be knocked-off from the atom (Hafner, 2006). A positive charged hole is left after transition occurred. Secondly, the positively charged hole will attract the negatively-charged electrons from higher energy shell. The energy difference of this transition can be released in the form of an X-ray (Hafner, 2006).

CHAPTER 3

MATERIALS AND METHODS

3.1   Reagents

Cellulose triacetate (CTA) and Aliquat 336 purchased from Aldrich were used as base polymer and carrier respectively. Dichloromethane (DCM) and methanol (MeOH) supplied by R&M, Bendosen were used as solvent. Congo red purchased from Aldrich was used to prepare stock solution with concentration of 10 ppm.

3.1.1   Apparatus

DR6000 UV- VIS Spectrophotometer were used to analyse sample, Jeol scanning electron microscopic were used to study the morphology of CTA PIMs, Hot Plate Stirrer SP-88850107 from thermo fisher scientific were used to mix the polymer solution, Incubator Shaker KS 4000i from thermos fisher scientific were use in batch adsoption process, Petri Dish, Micropipette 1000µ brandTech, Static Batch Cell were used in transport experiment.

3.2 Preparation of CTA/Aliquat 336 Solution

CTA/Aliquat 336 solution was prepared by dissolving CTA and Aliquat 336 in 10 mL of DCM and MeOH with a ratio of 8:2. Different Aliquat 336 concentrations (0, 20, 30, 40 and 50 wt. %), each mixture contained a combined CTA and Aliquat 336 weight of 500 mg. The mixture was stir until the solution become homogenous. Then, the solution was poured into petri dish and covered with filter paper for overnight. The solvent were allowed to evaporate forming a transparent membrane. Later, the membrane was peeled and stored in dry condition for further experiment.

3.3 Preparation of Congo red

0.1 g of Congo red is dissolved in a 100 ml volumetric flask to prepare 1000 ppm Congo red stock solution. Then, 1.0 mL of stock solution was pipette and diluted with deionized water in a 100 mL volumetric flask to prepare 10 ppm of Congo red which is used as extraction solution as stated in section 3.4.

A calibration curve was constructed by preparing five sets of Congo red solution with concentration of 2, 4, 6, 8 and 10 mg/L from stock solution. The volume of Congo red solution needed for dilution was calculated by using the formula shown in Equation 3.1. Then, the absorbance values for each prepared solution were measure by using UV-Vis spectrophotometer for calibration curve purpose.

$$m_1 v_1 = m_2 v_2. \qquad (3.1)$$

where,

m_1 = Molarity of Congo red stock solution

v_1 = Volume of Congo red stock solution

m_3 = Molarity of working solution

v_2 = Volume of working solution

3.4 Batch Adsorption

CTA PIMs with different Aliquat 336 concentration (0, 20, 30, 40 and 50 wt. %) were cut into smaller pieces and put into 100 mL conical flask containing 50 mL of 10 ppm Congo red. The mixture was stirred continuously in incubator shaker and 1.5 mL of sample was taken at specific time interval for Congo red analysis using UV-Vis spectrophotometer. The efficiency of Congo red removal was investigated by optimising the parameters such as the Aliquat concentration (0, 10, 20, 30, 40 and 50 wt. %), pH of Congo red (2, 4, 6, 8 and 10), initial Congo red concentration (2, 4, 6, 8 and10 ppm), stirring speed (150, 200, 250, 300 and 350 rpm) and temperature (27, 30, 40, 50 and 60 ℃).

3.4.1 Effect of Aliquat 336 Concentration

CTA PIMs with different Aliquat 336 concentration (0, 20, 30, 40, 50 wt. %) were cut into small pieces and put into the 100 mL conical flask containing 50 mL of 10 ppm of Congo red. The pH of Congo red was kept at pH 7 and stirring speed was kept at 150 rpm. 5 conical flask contain PIMs with different Aliquat 336 concentration

were put into 10 ppm of Congo red solution and stirred for 360 minutes. The sample were withdrawn from the shaker at predetermined time intervals and analysed by using UV-Vis spectrophotometer.

3.4.2 pH of Congo red

Five conical flask were filled with 50 mL of 2 ppm of Congo red. CTA PIMs with optimise Aliquat 336 concentration was cut into smaller pieces and put into the 100 mL conical flask and was stirred at speed 150 rpm. 0.1 mole of HCl and NaOH were used to adjust the pH of the Congo red. pH meter was used to measure the pH of Congo red. The pH of Congo red were varying from 2, 4, 6, 8 and 10 ± 0.1. The conical flask were put into the incubator shaker with speed 150 rpm at 30 ℃ for 360 minutes. 1.5 ml of sample were withdrawn at predetermined time intervals and analysed by using UV-Vis spectrophotometer.

3.4.3 Initial Dye Concentration

The variation of dye concentration has been done over the range of 2 to 10 ppm. The CTA PIMs with optimise Aliquat 336 was put into different concentration of Congo red, the pH of the Congo red was optimise as previous and stirred in the incubator shaker with 150 rpm at 30 ℃ for 360 minutes. 1.5 ml of sample was withdrawn at predetermined time interval and analysed by using UV-Vis spectrophotometer. Molecule present in the Congo red increase with the increase of concentration. Therefore, different concentration of Congo red was used to study the effect of concentration on the extraction efficiency.

3.4.4 Temperature

The extraction temperature of Congo red was varied at 27, 30, 40, 50 and 60℃. CTA PIMs with optimise Aliquat 336 concentration, pH and optimise initial Congo red concentration was put into shaker and stirred at 150 rpm. 1.5 ml of sample were withdrawn at predetermined time intervals and analysed by using UV-Vis spectrophotometer.

3.4.5 Stirring speed

Different stirring speed (150, 200, 250, 300 and 350 rpm) were varying to test the effect of kinetic on the removal of Congo red. CTA PIMs with optimise Aliquat 336 concentration, pH, initial Congo red concentration and temperature was stirred at different speed for 360 minutes. 1.5 ml of sample were withdrawn from the shaker at predetermined time intervals and analysed by using UV-Vis spectrophotometer.

3.5 Static Batch Cell

A static batch cell was used in transport experiment. Two compartment of static cell was separated by CTA PIMs with optimized Aliquat 336. One of the compartment was labelled as feeding phase while another compartment was labelled as receiving phase. Congo red was put in feeding phase while nitric acid was put in receiving phase. An optimized condition which study in part was used in study the transport experiment. 1.5 ml was extract and analysed by using UV-Vis spectrophotometer in certain interval. Static batch cell was set up as shown in Figure 3.1.
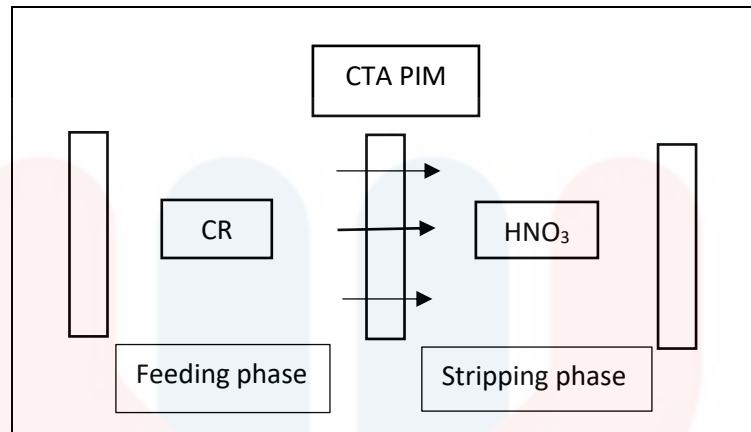
Figure 3.1: The set-up of static batch cell that used in transport experiment.

3.6 Removal efficiency

The removal efficiency of Congo red using CTA Aliquat 336 PIMs was calculated using Equation 3.2.

$$\text{Removal } (\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (3.2)$$

where

C_o = Initial dye concentration (mg/L)

C_e = Final dye concentration (mg/L)

3.7 Characterization of PIM

3.7.1 Fourier-transform infrared spectroscopy (FTIR) Analysis

FTIR was used to study the chemical structure of CTA PIMs with Aliquat 336. FTIR is used to identify the types of bond and functional group present in the CTA PIMs with and without Aliquat 336. Infrared light is used to scan sample and observe chemical properties. Since different types of bond and functional group present in CTA

PIMs will absorb infrared radiation at different wavelength, therefore different peaks were shown in the analysis.

3.7.2 Scanning Electron Microscope (SEM) Analysis

The morphology of CTA PIMs with Aliquat 336 was studied by scanning electron microscope (SEM). The membrane was cut into smaller piece and clips into gold surface. The SEM measurement were performed at an accelerating voltage of 2 kV and 20 kV. The magnification of all SEM image was 500x. Energy dispersive X-ray CTA PIMs also studied to identify the element present in the CTA PIMs.

3.7.3 Water Uptake

Water uptake of CTA PIMs with Aliquat 336 was studied by cutting membranes into small piece. The five CTA PIMs with different Aliquat 336 concentration were immersed in deionized water for 48 hours. After that, dry the membrane in 60 ℃ and weight. The water uptake of CTA PIMs were calculated by using the formula in Equation 3.3 in order to reduce experimental error.

$$WU\% = \frac{w_{wet} - w_{dry}}{w_{dry}} \times 100 \qquad (3.3)$$

where,

w_{wet} = Wet membranes weight

w_{dry} = Dried membranes weight

3.7.4 Ion Exchange Capacity (IEC)

IEC represent the number of exchangeable ionic group present per membrane weight. IEC of CTA PIMs with Aliquat 336 was studied by immerse membrane sample in 1.0 mol NaCl for 48 hours so that all charged site were converted to Cl^- form. Then the membrane sample were washed with deionized water to remove excess amount of NaCl. After t hours. After that, the amount of Cl^- ions liberated was estimated by titration with mole $AgNO_3$ by using K_2CrO_4 as indicator. The IEC of the membrane was calculated using the Equation shown in 3.4 and 3.5

$$IEC = \frac{a}{W_{dry}} \qquad (3.4)$$

Where;

a = the miliequivalent of ion exchange group in membrane

W_{dry} = the weight of dry membrane (g)

The fixed ion concentration (FIC) can be obtained by the equation below:

$$FIC = \frac{IEC}{Water\ content} \qquad (3.5)$$

CHAPTER 4

RESULTS AND DISCUSSION

4.0   Introduction

This chapter discuss about the extraction of Congo red by using CTA PIMs with Aliquat 336 prepared. Five parameters including Aliquat 336 concentration, pH of Congo red, initial concentration of Congo red, stirring speed and temperature were tested to determine the optimise Congo red extraction. Batch experiment were carried out continuously for 6 hours and each parameters was repeated for three times to get an average. A transport of Congo red by using transport cell was also carried out under optimise condition. In addition, the CTA PIMs with Aliquat 336 was characterised in term of its morphology, functional group, water uptake and ion exchange capacity (IEC).

4.1   Congo red Extraction Performance

4.1.1   Effect of Aliquat 336 Concentration

The extraction of Congo red was studied using CTA PIMs with five different Aliquat 336 concentration ranging from 0 to 50 wt. % as shown in Figure 4.1. The condition was first set with pH of Congo red at neutral, 10 ppm Congo red, 30 ℃ and

stirring speed 150 rpm. The presence of Aliquat 336 allow the extraction of Congo red from the aqueous solution. This is because CTA PIM with Aliquat 336 is an anionic membrane. The present of positive charge polyatomic ions of NR_4^+ in Aliquat 336 enable the reaction with the Congo red which is an acid dye. An acid dye is acidic in reaction and usually unite with positively charge ion to form a complex. The negative charge present in the Congo red attract to the positively charge of NR_4^+ Aliquat 336 present in CTA PIM to form CR-NR_4^+ neutral ion pair complex.

The anionic dye forms a neutral ion pair complex with the cationic carrier, and this neutral ion pair complex are extracted across anionic membrane (Ling & Mohd Suah, 2017). The formation of neutral ion pair complex from anionic dye and cationic carrier are shown in the Equation 4.1.

$$Dye^-_{aq} + [\ NR_4^+] \leftrightarrow [\ Dye\ (NR)] + H^+ \tag{4.1}$$

with NR_4^+ is Aliquat 336 and [Dye (NR)] is neutral ion pair complex.

Based on the Figure 4.1, the extraction efficiency of CTA PIM with 50 wt %: Aliquat 336 the highest. PIM with the highest Aliquat 336 concentration has the highest extraction efficiency, therefore CTA PIMs with 50 wt. % Aliquat 336 was used for the next parameter test.
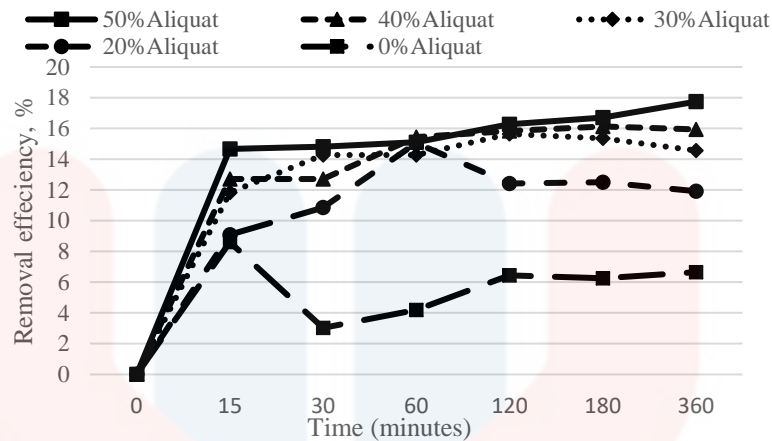
Figure 4.1: Effect of Aliquat 336 concentration on the removal of Congo red on CTA PIMs.

4.1.2 Effect of pH

pH is an important parameter in controlling the Congo red extraction in this experiment. pH of the solution will modify the PIM surface which alter the extraction of Congo red (Shee, 2014). The pH of the feed solution was varied from 2 to 10 in order to study the effect of pH on the Congo red removal. In this study optimum CTA PIM (50 wt. % of Aliquat 336) was used and the initial Congo red concentration was remained at 10ppm, temperature and stirring speed set as previous 30℃ and 150 rpm respectively. The result is shown in Figure 4.2.

Based on the figure, the removal of Congo red increase when the pH of the solution decrease. At pH 2 the removal of Congo red was 28.3 % followed by 23, 18, 17, and 15 % at pH 4, 6, 8 and 10 respectively.

Since Congo red is acid dye with negatively charge, a decrease in pH will increase the concentration of H^+ in the solution, and this increase H^+ concentration will favour the Aliquat 336 with a positive charge functional group (Shee, 2014). The H^+ present in the solution will not compete the active site with the negative charge of Congo red to bind with extractant. In the aqueous solution, the acid dye (Congo red) is first dissolved and the sulfonate group of the acid dye are dissociated and converted to anionic dye ions (Ozmen & Yilmaz, 2007). Congo red is negatively charged at the pH above 5. Therefore, as the pH of the solution increase, more OH^- was present and this OH^- will compete with the dye anions for the adsorption sites. As reported by Ozmen, Yilmaz (2007), the extraction of Congo red by using cyclodextrin and starch based polymers from aqueous solutions increase as the pH decrease due to present of H^+ which will not compete active site with the Congo red.
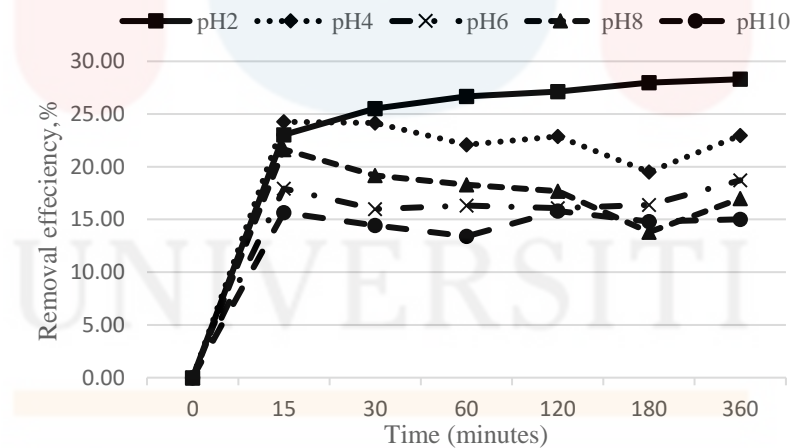

Figure 4.2: Effect of pH on the removal of Congo red on the CTA PIMs with 50 wt. % Aliquat 336.

4.1.3 Effect of Initial Congo red Concentration

In order to study the capacity of CTA PIMs in extracting Congo red, the initial dye concentration was varied between 2 to 10 ppm. Figure 4.3 shows the effect of

initial Congo red concentration on the removal efficiency of CTA PIMs. The feed solution used in this study was at pH 2 using CTA PIM with 50 wt. % Aliquat 336. The stirring speed and extraction temperature were maintained as previously.

Based on the results, the removal of Congo decrease as the dye concentration increase. The highest removal efficiency of Congo red was achieved when the initial dye is 2 ppm whereas at 10 ppm the CTA PIMs has the lowest removal efficiency. This is due to membrane saturation and lower efficiency membrane area (Ling & Mohd Suah, 2017). As reported by Ling and Mohd Suah (2017), the extraction of Malachite Green decrease as the concentration of Malachite green increase from 20 ppm to 100 ppm. The same result was obtained by Salima et al., (2012) which showed that the removal of Methylene blue decrease as the initial concentration of Methylene blue increase from 250 ppm to 800 ppm. It is noteworthy that surface area of CTA PIMs used in this study was less pores present on the extractant which made the surface area easily saturated with dyes. Since 2 ppm of Congo red show highest removal efficiency, hence 2 ppm of Congo red was be used for the next parameter test.
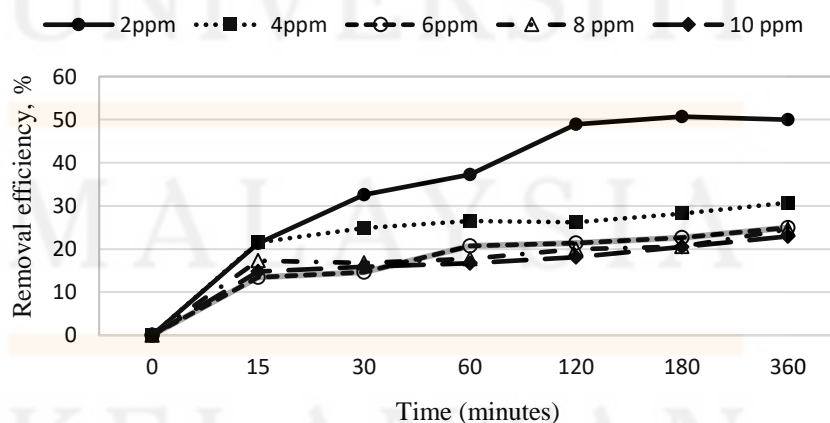

Figure 4.3: Effect of initial dye concentration on the removal of Congo red on CTA PIMs with 50 wt. % Aliquat 336.

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4.1.4 Effect of Temperature

The effect of temperature on the Congo red removal was studied using CTA PIM containing 50 wt. % Aliquat 336 at 2 ppm of Congo red concentration and pH2. The stirring speed was kept at 150 rpm and the temperature was varied from 27 ℃ to 60 ℃. The obtained results are presented in Figure 4.4.

It is shown that as the temperature increase from 40 ℃ to 60 ℃, the extraction efficiency decrease significantly. The adsorption of Congo red into CTA PIMs decrease as the temperature increase, suggesting that the adsorption of Congo red onto CTA PIMs is an exothermic process (Khan et al., 2015). Based on Le Chatelier's principle, exothermic process will reduce the adsorption process in a system because heat is release in the reaction (heat is a product). Hence, increasing temperature will shift the equilibrium to the left (reduce in adsorption). The equation of Le Chatelier's principle is shown in the Equation 4.1.

$$A \leftrightarrow B + heat \qquad \Delta H = - \qquad (4.1)$$

From the result, the optimum temperature for the extraction of Congo red is 30℃ where the extraction percentage reached 50%. The exothermic adsorption can be proof by Khan et al., (2015), which used of anion exchange membrane (EBTAC) on the removal of Congo red from aqueous solution, the extraction of Congo red decrease as the temperature increase from 19 ℃ to 50 ℃ for 25 mg/L and 50 mg/L of Congo red concentrations.
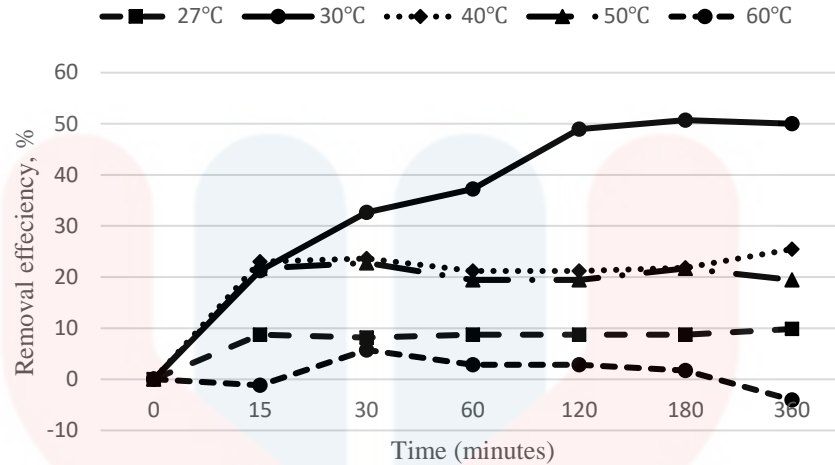
Figure 4.4: Effect of temperature on the extraction percentage of Congo red on CTA PIMs with 50 wt. % Aliquat 336.

4.1.5 Effect of Stirring Speed

Figure 4.5 shows the influence of stirring speed on the extraction of Congo red. In this experiment, stirring speed is varied from 150 rpm to 350 rpm in order to study their effect on Congo red removal. Others parameters such as temperature, pH and initial dye were kept based on optimise data obtained previously. The result indicates that the removal of Congo red decrease as the stirring speed increase from 200 rpm to 350 rpm.

Removal of Congo red increase as stirring speed increase because an increase in the level of mixing would increase interfacial area and mass transfer. However, agitation up to some level will reduce the removal efficiency (Dâas & Hamdaoui, 2010). Therefore, the removal of Congo red by CTA PIMs with 50 wt. % Aliquat 336 decrease as the stirring speed increase from 200 rpm to 350 rpm, as the stability of CTA PIMs was affected when the stirring speed increase above a critical value (Dâas

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& Hamdaoui, 2010). This is most probably due to the CTA PIM used in this study is in the absence of plasticizer. Plasticizer plays an important role in ensuring the stability of the membrane.

Similar condition was reported by Daas and Hamdaoui (2010), which study the extraction of anionic dye from aqueous solutions by emulsion liquid membrane. They found that the removal efficiency decrease as the stirring speed increase from 200 rpm to 400 rpm due to the breakage of emulsion droplets in the membrane. The stability of the emulsion and removal efficiency of the membrane are affected when stirring speed is increase above a critical value. For higher stirring speed (200 rpm to 350 rpm), swelling phenomena is occurred and this lead to greater amount of water to permeate through the membrane causing the internal droplets to swell and coalesce (Dâas & Hamdaoui, 2010). Therefore, 150 rpm is the most suitable stirring speed used in this study.
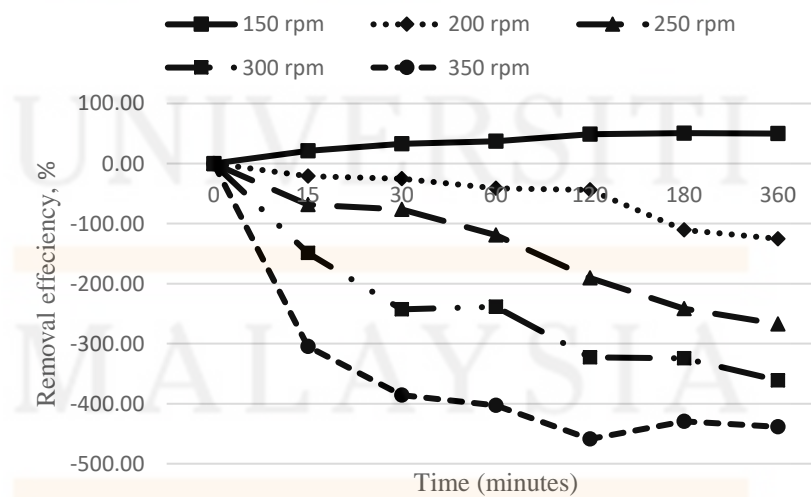
Figure 4.5: Effect of stirring speed on the removal rate of Congo red using CTA PIMs with 50 wt. % Aliquat 336.

4.2   Transport Experiment

Transport experiment was carried out by using a static batch cell which consist two compartment, one of the compartment is labelled as feeding phase while another is stripping phase. The set- up of static batch cell was shown in Figure 3.1.

The feeding solution used was 2 ppm of Congo red in pH 2, whereas stripping phase solution was one mole of nitric acid. The extraction of Congo red using optimized CTA PIM (50% Aliquat 336) which separate the feeding and stripping phase. The extraction experiment was carried out under optimized condition, by using the best CTA PIM with a composition of 50% Aliquat 336, pH 2 of Congo red, 2 ppm of Congo red, 30 ℃ temperature and 150 stirring speed.

Figure 4.6 showed the transport of Congo red under optimized condition. From the graph, the concentration of Congo red decrease with time in feeding phase, whereas the increase in receive phase. This result showed the 87% of Congo red was extract under optimized condition after 24 hour. Similar result was obtained by Ling and Mohd Suah (2017), the extraction of Malachite Green were achieved >98 % and >96 % from wastewater by using PIM which consists of poly(vinyl) chloride (PVC) as base polymer, bis-(2-ethylhexyl) phosphate (B2EHP) as extractant and dioctyl phthalate (DOP) as plasticizer. The graph of feeding phase (Congo red) and receiving phase (nitric acid) against time was shown in Figure 4.6.
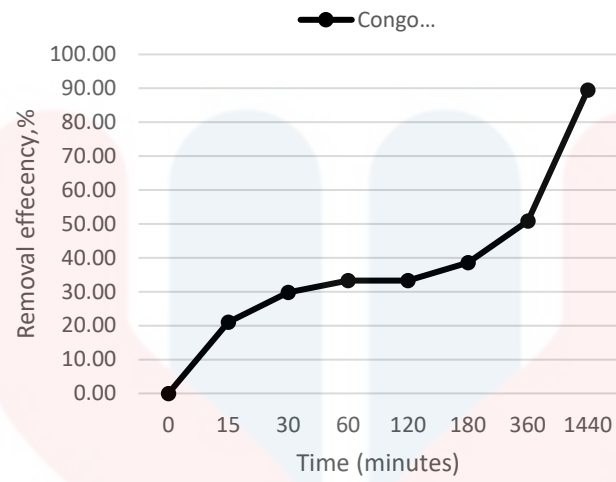
Figure 4.6: Removal of Congo red increase up to 80 % under optimized condition.

4.3   Membrane Characterization

Morphology studies is carried out by using FTIR Analysis, SEM Analysis, water uptake and Ion Exchange Capacity (IEC).

4.3.1   Fourier-transform infrared spectroscopy (FTIR) Analysis

FTIR spectra characterization was used to determine the presence of functional group in CTA Aliquat 336 PIMs. The spectra of CTA PIMs, CTA PIMs with Aliquat 336 and CTA PIMs with 50 wt. % Aliquat 336 after extraction were shown in Figure 4.7 to Figure 4.9 respectively.

According to Figure 4.7, the Infra-red (IR) spectrum of CTA exhibited a band at 1212.53 cm^{-1} and 1031.24 cm^{-1} showing the C-O stretching. The present of ester functional group (carbon atom contains a double bond to an oxygen atom, and a single bond to a second oxygen atom) in CTA is shown with the peak 1732.89 cm^{-1}.

Aliquat 336 act as a carrier in CTA PIM. The present of IR spectrum with a peak between 2924.65 cm^{-1} to 2855.05 cm^{-1} indicating the C-H stretching of the aliphatic CH group in Aliquat 336 (Ling & Mohd Suah, 2017) according to Figure 4.8.

According to Figure 4.9, an IR spectrum band was shown a peak at 3397.64 cm^{-1} after the CTA Aliquat 336 PIM was used to extract Congo red. The peak is due to the present of –OH group. Since –OH group is polar, therefore it allows the

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hydrogen bonding between Aliquat 336 and Congo red. A short peak at 1457.9 cm^{-1} indicate $-CH_3$ asymmetric deformation vibration, these deformation is due to hydrogen bonding between reaction of Aliquat 336 and Congo red.
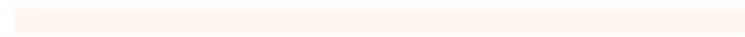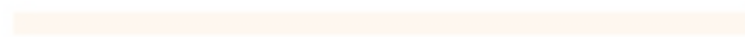
Figure 4.7: FTIR spectrum of CTA PIM without Aliquat 336.

Figure 4.8: FTIR spectrum of CTA PIM with 50 wt. % of Aliquat 336 concentration before extraction of Congo red.

Figure 4.9: FTIR spectrum of CTA PIM with 50 wt. % Aliquat 336 after extraction with Congo red.

4.3.2 Scanning Electron Microscope (SEM) Analysis

SEM was used to observe the surface morphology of CTA PIMs with different Aliquat 336 concentration as shown in Figure 4.10 (a-f). Figure 4.10 (b-e) showed the CTA PIMs before extraction and Figure 4.10 (f) after extraction of Congo red. In Figure 4.10a, a uniform surface with 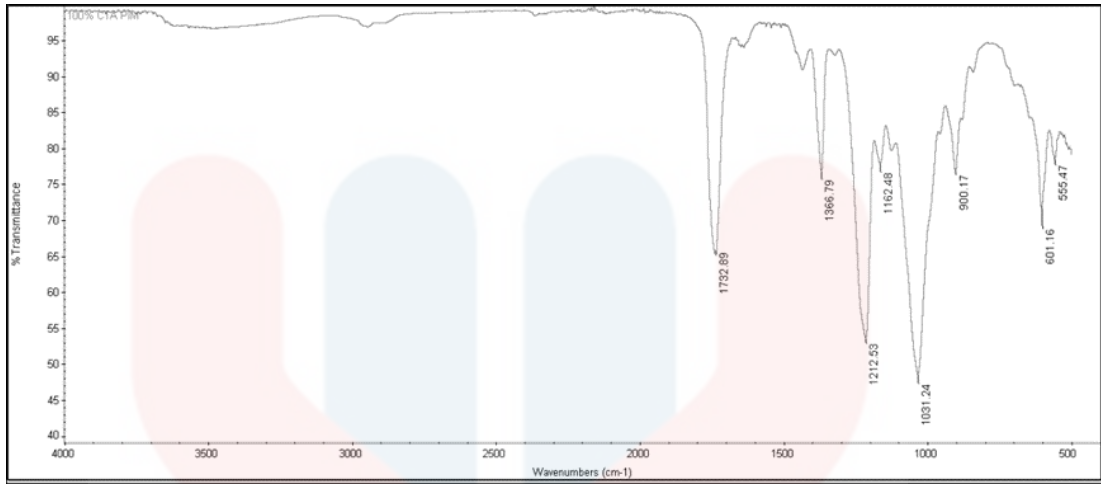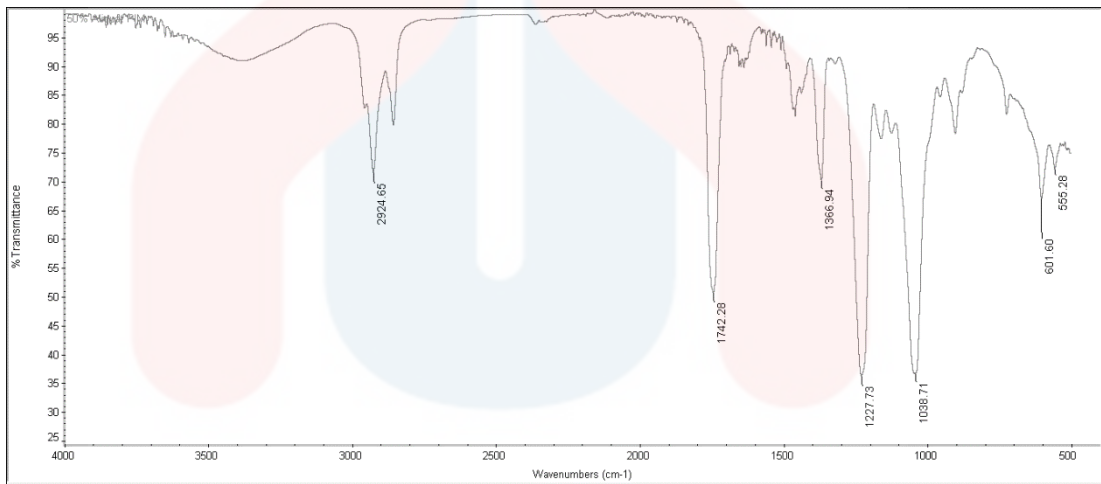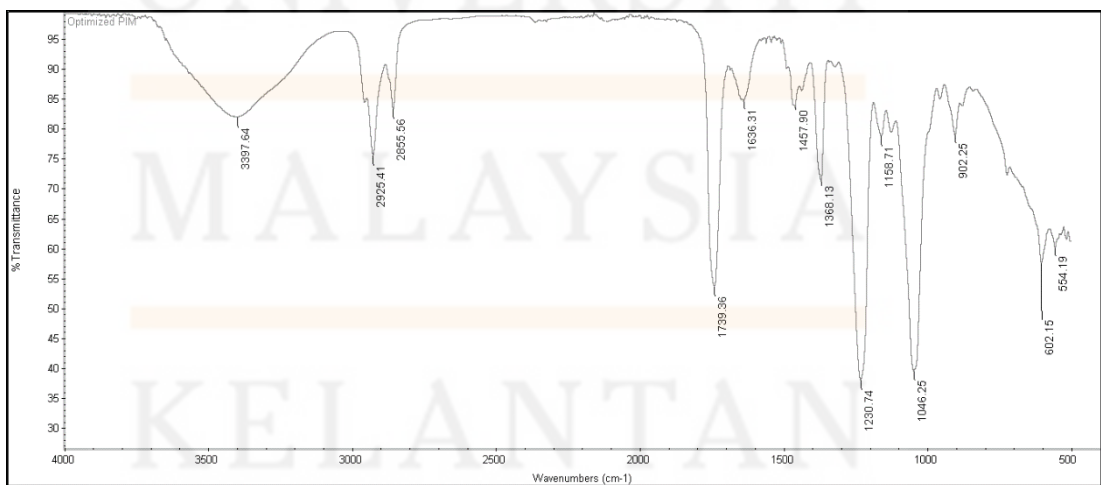no apparent pores was observed for CTA PIM without Aliquat 336. As Aliquat 336 (20-40 wt. %) (Figure 4.10b-d) was added to the CTA PIMs, the surface become rough in the present of Aliquat 336 but no significant pores was observed. Absence of significance pore structure in CTA Aliquat 336 PIM containing Aliquat 336 concentration less than 50% is due to extractant molecules maybe 'entangled' with the polymer chain as report by Xu et al., (2004) where the extractant have low activity and mobility through the polymer matrix.

However, as Aliquat 336 reach 50 wt. % (Figure 4.10e), some pore structure was observed. This is because the excess amount of Aliquat 336 might from micro aggregates, which is prevent the CTA polymer chains to form a complete polymer matrix (Xu, Wang, Shen, Paimin, & Wang, 2004). Meanwhile, the surface of used CTA Aliquat 336 PIM with 50 wt. % of carrier (after extraction with Congo red) was also observed (Figure 4.10f). It can be seen that the surface change with CTA Aliquat 336 PIM before the extraction (Figure 4.10e).

It is noteworthy that, the SEM image do not clearly show sign of Aliquat 336 in the micro pores. SEM image do not show microstructure of Aliquat 336 present in the CTA Aliquat 336 PIM whether micro pore or micro channels, however, it can be confirmed that these microstructures could connected which enable the extraction of

Congo red molecule to diffuse across the membrane film.
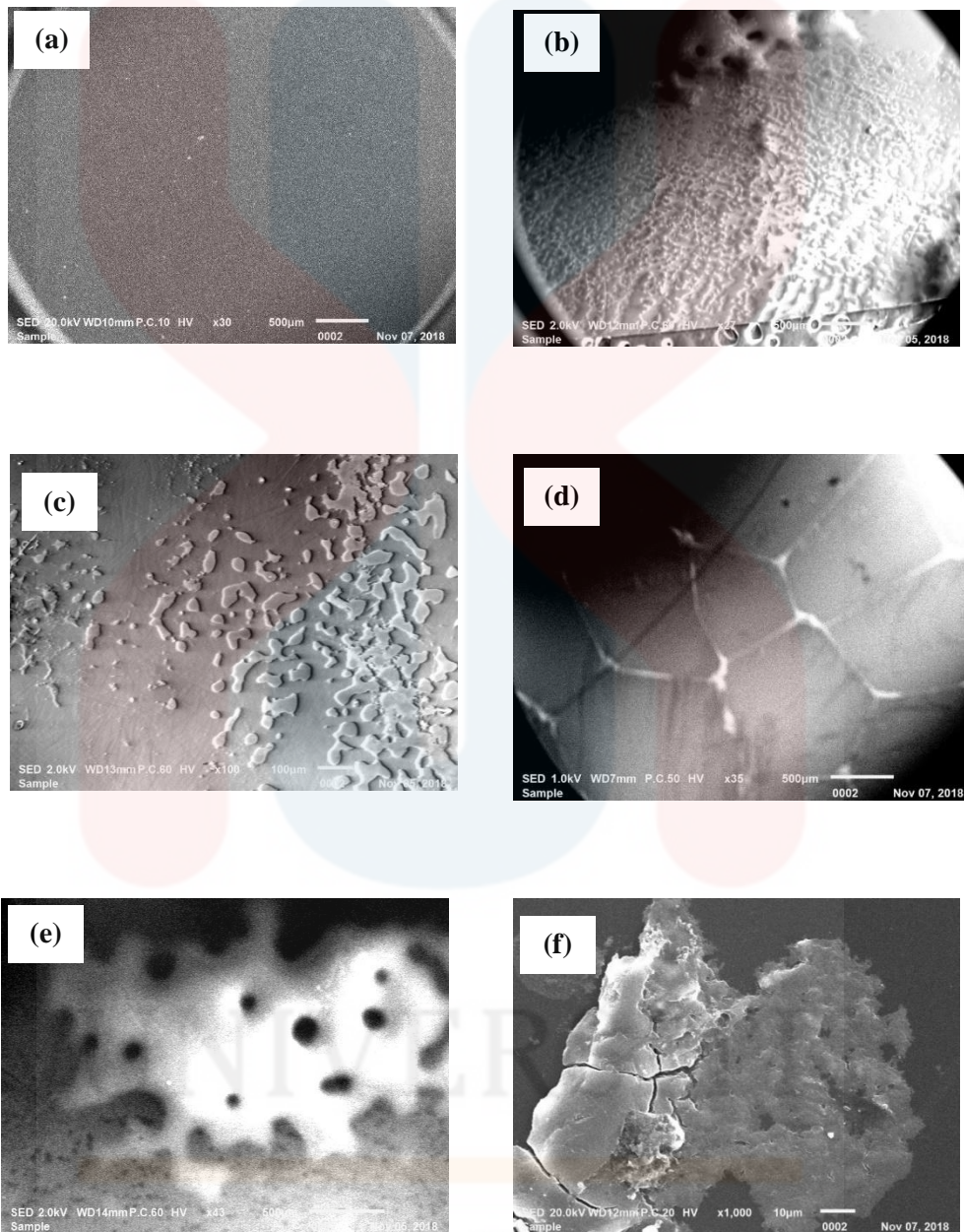
Figure 4.10 : The surface morphology of CTA Aliquat 336 PIMs: (a) without Aiquat 336, (b) with 20 wt. % Aliquat 336, (c) with 30 wt. % Aliquat 336, (d) with 40 wt. % Aliquat 336, (e) with 50 wt. % Aliquat 336 and (f) with 50 wt. % Aliquat 336 after Congo red removal.

4.3.3 Energy Dispersive X-ray (EDX)

In this study, the CTA PIM containing 50 wt. % of Aliquat 336 before and after extraction with Congo red were analysed by SEM-EDX. The results are presented in Figure 4.11 and Figure 4.12 before and after extraction respectively. From Figure 4.11, it can be see that the absence of Na and S atom in the sample. However, these two atom present after the extraction of Congo red. As mention above, the sulfonate group present in the Congo red will first dissolved and convert to anionic dye ions, therefore S molecule is present (Ozmen & Yilmaz, 2007). The present of sodium atom (Na) and sulphur atom (S) indicate the present of Congo red molecule in the sample. Therefore, removal of Congo red by Aliquat 336 PIM is succeed.
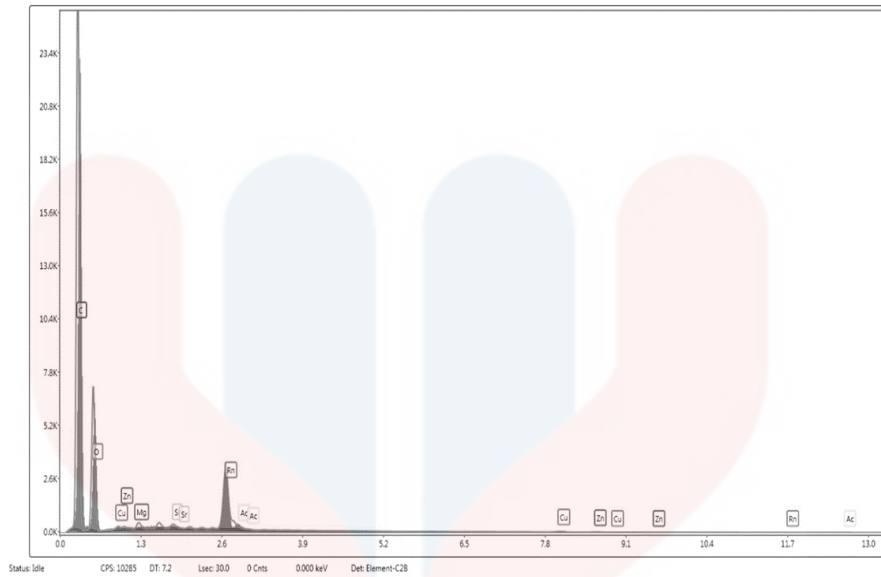
Figure 4.11: The EDX of CTA PIM with 50 wt % Aliquat 336 before Congo red removal.
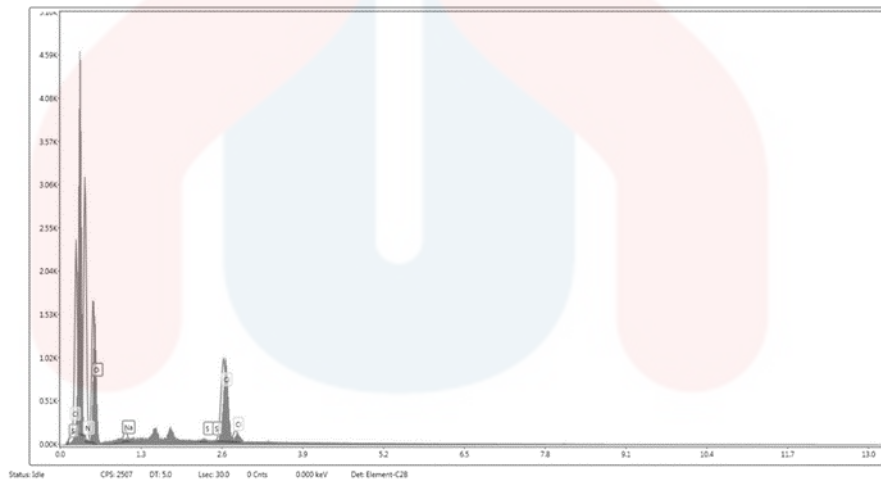
Figure 4.12: The EDX of CTA PIM with 50 wt. % of Aliquat 336 after Congo red extraction.

4.3.4 Water Uptake and Ion Exchange Capacity (IEC)

The average number of water molecules per conducting functional group is defined as water uptake of a membrane. The water uptake and water content of CTA PIMs with Aliquat 336 was presented in Table 4.1. It showed that CTA PIM without Aliquat 336 has the lowest percentage of water content, whereas the water content increase with increasing Aliquat 336 concentration in CTA PIMs. This indicate that

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amination process take place. The amination agent give rise to the quarter amine group functioned as active point, which then increase the hydrophilicity of the polymer (Secutti & Trajano, 2009). Therefore, CTA PIMs become hydrophilic when the concentration of Aliquat 336 (present of quaternary ammonium salt) increases. CTA PIMs with the difference in wettability of CTA PIM without Aliquat 336 and PIM with Aliquat 336 is due to their main chain (polytetrafluoroethylene polymer backbone and hydrocarbon polymer backbone) and side chain (the sulfonic acid group and quaternary ammonium group in the membrane) (Li, Zhao, & Yang, 2010).

Table 4.1: The water uptake of CTA PIMs with different Aliquat 336 concentration.

CTA PIMs	Water uptake (%)
0 wt. % Aliquat 336	60
20 wt. % Aliquat 336	66
30 wt. % Aliquat 336	90.47
40 wt. % Aliquat 336	120.59
50 wt. % Aliquat 336	133.77

IEC is the fundamental characteristics of ion-selective membrane. IEC represent the amount of exchangeable group attached to polymer backbone. It is an important endowment of membranes used in diffusion dialysis process (Khan et al., 2016). Titration is one of the method use in IEC test. Table 4.2 shown the IEC for each membrane which contain 0, 20, 30, 40 and 50 wt. % of Aliquat 336 respectively. From Table 4.2, it can be seen that IEC of membrane increase with concentration of carrier, Aliquat 336. Therefore, CTA PIM with 50 wt. % Aliquat 336 has the highest removal efficiency compare to others Aliquat 336 concentration as higher IEC for 50 wt. % Aliquat 336 indicate more ion can be selectively react with 50 wt. % Aliquat 336.

Table 4.2: The IEC of PIM with different concentration of Aliquat 336.

CTA PIMs	IEC (%)
0 wt. % Aliquat 336	3.64
20 wt. % Aliqaut 336	12.96
30 wt. % Aliquat 336	17.86
40 wt. % Aliquat 336	21.43
50 wt. % Aliquat 336	25

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1   Conclusion

The extraction of Congo red increase with increasing of Aliquat 336 concentration. Aliquat 336 act as a carrier in the CTA PIMs, therefore the concentration of Aliquat 336 affect the extraction of Congo red from aqueous solution. CTA PIMs with 50 wt. % Aliqaut 336 have shown the highest extraction percentage in this research.

The pH value affect the aqueous condition of Congo red. As Congo red appear as blue below pH 3 and appear red above pH 5. Extraction of Congo red increased with at lower pH value. This is due to Congo red is an anionic dye with negative charge. Extraction capacity of PIM decrease with an increase in initial concentration of Congo red. Maybe due to low efficiency of membrane, Aliquat 336 PIM unable to extract higher concentration of Congo red.

Temperature affect the activity of PIM. This research find out that a decrease in extraction percentage when the temperature increase from $40\,℃$ to $60\,℃$. This

indicate that the adsorption in CTA PIMs is an exothermic process. Hence, 30℃ is the best temperature for the removal of Congo red. Stirring speed plays an important role in this research. As the stirring speed increase from 200 rpm to 350 rpm, a significant drop in the extraction of Congo red as the damage of PIM. Hence, 150 rpm is the best stirring speed to extract Congo red by CTA Aliquat 336 PIM in this research. At last, by using the optimized condition, 87 % of Congo red was successfully extract after 24 hour.

5.2   Recommendation

Based on the study conducted, here are some of recommendation which could be useful for further study.

Firstly, adsorption isotherms can be used to study the equilibrium and kinetic modelling of Congo red removal from aqueous solution. Adsorption studies can be described in detail by the models provided in adsorption isotherm. For example the Langmuir, Freundlich and Temkin isotherm model can be used to study the adsorption behaviour of CTA PIMs and Congo red. The mechanism of the adsorption process describes the reaction between adsorbate and adsorbent and when the adsorption process equilibrium is reached, the site of molecule of adsorption between solid phase and liquid phase can be indicate by using these isotherm.

Secondly, the effect of ionic strength can be studied in future as ionic strength is an important parameter that control the interactions between dyes and membrane

surface. Addition different quantities of common salt to Congo red solution in order to study the effect of ionic strength on the Congo red removal.

Thirdly, since removal of dye by using CTA PIM is scarcely reported, therefore another anionic dye can be studied by using CTA PIMs with Aliquat 336. For example, methyl orange (MO). MO is one of the industrial contaminant and non- biodegradable. MO is normally used in titration because it shows red colour in acidic medium and yellow colour in basic medium. Therefore, a comparison can be made between the removal efficiency of Congo red and MO by CTA PIM with Aliquat 336.

Appendix
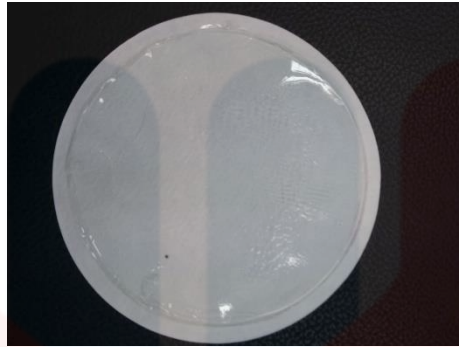
Figure 5: CTA PIM with 50 wt. % Aliquat 336.

Figure 6 : Congo red before extraction (pH in neutral).
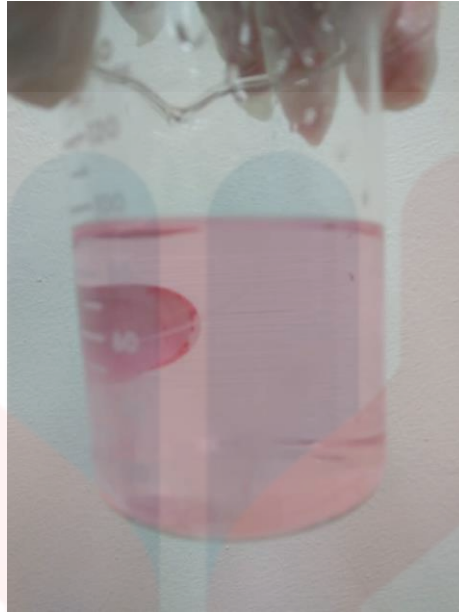
Figure 7 : Congo red before extraction which contain CTA PIMs with 50 wt. % Aliquat 336.

Figure 8 : Congo red before extraction which contain CTA PIMs with40%, 30% and 20% of Aliquat
336 in pH neutal.

Figure 9 : Congo red turn to blue colour in pH 2 with different initial concentration (2ppm, 4ppm,
6ppm and 10ppm) respectively.

Figure 10 : Condition of Congo red after extract under optimized condition (50 wt. % Aliquat 336, 2 ppm of Congo red, Congo red in pH 2, 30℃ and 150 rpm)

Figure 11 : CTA PIM with 50 wt. % Aliquat 336 after extract under optimized condition (2 ppm of Congo red, Congo red in pH 2, 30℃ and 150 rpm)

Figure 12: The set-up of static batch cell.

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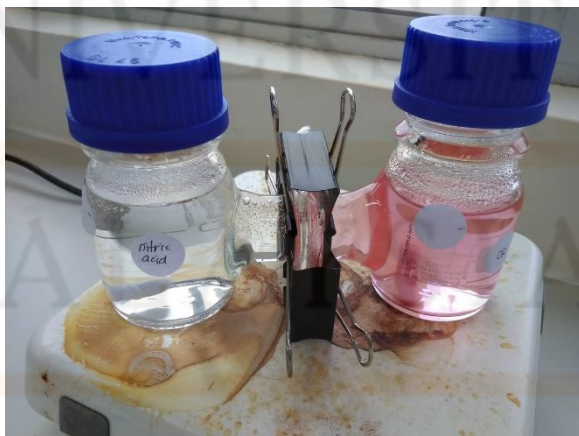
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