PREPARATION OF CELLULOSE TRIACETATE (CTA) – ALIQUAT 336 ELECTROSPUN FIBERS FOR REMOVAL OF METHYL ORANGE FROM AQUEOUS SOLUTION

by

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DECLARATION

I declare that this thesis entitled "Preparation of Cellulose Triacetate (CTA) – Aliquat 336 Electrospun Fibers for Removal of Methyl Orange from Aqueous Solution" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :

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Preparation of Cellulose Triacetate (CTA) – Aliquat 336 Electrospun Fibers for Removal of Methyl Orange from Aqueous Solution

ABSTRACT

Textile wastewater is classified as the most polluting sector compared to all other industrial sectors due to the discharge of dye pollutants. Dye-containing effluents from this industry can affect environmental health as well as human health. Today, there have been many studies conducted about removal of heavy metals from aqueous solution using electrospun fibers. However, the study and research about electrospun fibers on dye removal is scarcely reported. This research aimed to investigate the removal efficiency of methyl orange from aqueous solution using electrospun fibers made from cellulose triacetate (CTA) as the base polymer and Aliquat 336 as an extractant. A solvent of dichloromethane (DCM) and methanol (MeOH) with a ratio of 8:2 was used to dissolve the extractant and base polymer followed by electrospinning process for the preparation of electrospun fibers. Parameters such as different Aliquat 336 concentration (5, 10, 15, 35 and 40 w.t%), pH of methyl orange (2, 4, 6, 7 and 10) and methyl orange initial concentration (10, 20, 30, 40 and 50 ppm) that affect extraction efficiency were also studied to determine the best parameters for optimum extraction condition to happen. Based on the results, the removal efficiency for CTA-Aliquat 336 electropun fibers of methyl orange increased with the increasing of Aliquat 336 content up to 10 wt.%. Highest methyl orange removal percentage achieved was 99.86% with concentration of 10 wt.% of Aliquat 336 within 24 hours. Under an optimized condition (10 wt.% Aliquat 336, pH 2 of methyl orange, and 10 ppm of methyl orange), 99.93% of methyl orange was successfully removed by CTA-Aliquat 336 electrospun fibers after 24 hours. The characterization study of membranes using Fourier-transform infrared spectroscopy (FTIR) found the presence of positively charged ammonium groups of Aliquat 336 and some covalent bondings such as C-O and C=O which indicated the presence of base polymer.

Penyediaan *Cellulose Triacetate (CTA)* – Aliquat 336 *Electrospun Fibers* untuk Pengekstrakan Methyl Oren dari Larutan

ABSTRAK

Air buangan sisa tekstil diklasifikasikan sebagai sektor pencemaran yang paling tinggi berbanding dengan semua sektor perindustrian lain disebabkan oleh pencemaran bahan pencemar pewarna. Pengaliran keluar yang mengandungi pewarna dari industri ini boleh menjejaskan kesihatan alam sekitar serta kesihatan manusia. Hari ini, banyak kajian telah dilakukan mengenai penyingkiran logam berat dari larutan menggunakan *electrospun fibers*. Walau bagaimanapun, kajian dan penyelidikan tentang *electrospun fibers* pada penyingkiran penyelup pewarna jarang dilaporkan. Penyelidikan ini bertujuan untuk mengkaji kecekapan penyingkiran methyl oren dari larutan menggunakan *electrospun fibers* yang dibuat daripada *cellulose triacetate* (CTA) sebagai polimer asas dan Aliquat 336 sebagai pengekstrut. Pelarut dikhlorometane (DCM) dan metanol (MeOH) dengan nisbah 8:2 digunakan untuk melarutkan pengekstrut dan polimer asas diikuti dengan proses pemintalan elektro untuk menghasilkan *electrospun fibers*. Pelbagai parameter seperti kepekatan Aliquat 336 yang berlainan (5, 10, 15, 35 dan 40% berat), pH methyl oren (2, 4, 6, 7 dan 10) dan kepekatan awal methyl oren (10, 20, 30, 40 dan 50 ppm) yang mempengaruhi kecekapan pengekstrakan juga dikaji untuk menentukan parameter terbaik untuk keadaan pengekstrakan optimum berlaku. Hasil kajian menunjukkan kecekapan penyingkiran methyl oren dengan CTA-Aliquat 336 *electrospun fibers* meningkat dengan peningkatan kandungan Aliquat 336 hingga 10%. Peratusan penyingkiran methyl oren paling tinggi dicapai adalah 99.86% dengan kepekatan 10% berat Aliquat 336 dalam tempoh 24 jam. Di bawah keadaan yang dioptimumkan (10 wt. Aliquat 336, pH 2 methyl oren, dan 10 ppm methyl oren), 99.93% methyl oren telah berjaya disingkirkan oleh CTA-Aliquat 336 *electrospun fibers* selepas 24 jam. Kajian pencirian membran yang menggunakan spektroskopi infra merah (FTIR) mendapati kehadiran kumpulan ammonium positif Aliquat 336 dan beberapa ikatan kovalen seperti C-O dan C=O yang menunjukkan kehadiran polimer asas.

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LIST OF ABBREVIATIONS

CTA	Cellulose triacetate
DCM	Dichloromethane
FTIR	Fourier-transform infrared spectroscopy
MeOH	Methanol
mg/L	Milligram per Litre
mL	Milliliter
mm	Millimetre
nm	Nanometer
ppm	Parts Per Million
PVC	Poly (vinyl chloride)
PVDF	Polyvinylidene difluoride

CHAPTER 1

INTRODUCTION

1.1 Background of study

During recent years, water pollution has become increasingly serious due to the presence of dyes in the water bodies. Dyes are one of the major water pollution contributors which are widely used in industries such as dyeing, coatings, pigments and textiles. These industries have progressively increased the use of dyes as a colouring agent in their products due to the increasing demand of the population. From the statistics, it is estimated that 700,000 tonnes of colouring varieties is produced each year (Abdi et al., 2017; Holkar et al., 2016). Arora (2014) claimed that about 20 % of the dye usage from manufacturing operation is discharged to the environment directly. The effluent from these industries remains concentrated in colour as large quantities of dyes stay unfixed during colouring and washing (Santos & Boaventura, 2008). The wastewater produced during its manufacturing processes is identified as the most polluting of all the industrial sectors, taking account the amount created and the composition of effluent (Mansour et al., 2012). Overwhelming industrial dye discharge such as methyl orange, congo red and malachite green are difficult to be removed in wastewater as they are refractory organic substances in water (Segneanu et al., 2013). Dye wastewater can cause harm to the environment and living things even the amount of dye is minute (Arora, 2014). As a result, presence of dye in water bodies has become a main concern to the researchers and environmentalists. It is important to select an effective water treatment for industrial wastewater when considering the wastewater pollutants.

Clean and safe water is of utmost importance to all living things and the proper role playing of ecosystems, communities and economics. Water purification can be accomplished by using conventional methods including chemical coagulation/ flocculation, ozonation, reverse osmosis, and adsorption (Gonçalves, 2013). Each method has its own pros and cons. For example, chemical coagulation is one of the most practised technologies but it will cause large amount of sludge (Verma, Das & Bhunia, 2012). Ozonation for instance, has some limitation factors such as a suitable pH range for its operation and is possibly toxic while reverse osmosis can cause undesired deposition of suspended solids on the membrane (Gonçalves, 2013). Another popular practice is by adsorption however, the adsorption process is affected by physical and chemical factors such as dye-adsorbent interactions, surface area of adsorbent, particle size, temperature, pH and contact time (Anjaneyulu et al., 2005; Patel and Vashi, 2010). In most situations, usually a combination of two or three methods is needed in order to achieve complete water purification especially when wastewater contains dye which is hard to be eliminated.

Recently, electrospinning has become an outstanding method in producing electrospun fibers with fibers with diameters in the range of 10 nanometers to few micrometers (Jian et al., 2018), which is favourable in many applications such as biotechnology and environmental engineering applications (Ramakrishna, Fujihara, Teo, Yong, & Ramaseshan, 2006). The produced electrospun fibrous membranes have few fascinating features such as high porosity, larger surface-to-volume ratio, and excellent functionalities. These features make them ideal for many applications (Dougan, Tych, & Hughes, 2013). Moreover, the binding of specific functional groups on the membranes of electrospun fibers has proven them as potential substances in adsorption of pollutants. Thamer, El-Hamshary, Al-Deyab, & El-Newehy (2018) have concluded in their research that functionalization of electrospun carbon nanofibers can remove cationic dye from aqueous solutions effectively. In addition, Feng, Wang, Zhang, Yin, & Bai (2016) mentioned about the combined electrospinning and hydrothermal reaction to form hierarchical SiO2@-AlOOH (Boehmite) core/shell fibers for water remediation.

The recent studies showed that electrospun fibers incorporated with functional groups can facilitate dye removal efficiency as they modified the membrane surface (Klein et al., 2008). Therefore, this research aimed to prepare CTA-electrospun fibers from electrospinning process for the removal of dye in aqueous solution. The electrospun fibers were produced at different Aliquat 336 concentration in order to determine the best extractant content that affect the removal efficiency of methyl orange.

1.2 Problem Statement

Nowadays, the presence of dyes in wastewater causes environmental pollution that can affect the balance of natural environment. The treatment of wastewater is complicated by the existence of various dye effluents where most of them are not easily biodegradable (Patel & Vashi, 2015). The dye toxicity and its difficulty in biodegradation can cause the pollutant concentration and environmental risk to increase if the dye effluent is discharged into the water bodies. Commonly known as a dyestuff, methyl orange is an orange, azoic dye. The discharge of methyl orange into the environment is critical due to colour, toxicity, mutagenicity and carcinogenicity of the dye. Therefore, proper treatment of methyl orange is crucial.

The advancement of membrane technology has been gaining trust as an approach to treat wastewater productively. Statistics have indicated that membrane technologies accounting up to 53 percent of the total world processes for clean water production (Mezher, Fath, Abbas, & Khaled, 2011). The elevating market value in membrane advancement is primarily due to their characteristics itself as well as the feasibility to practise sustainable approaches in industries. Many types of substances are capable for the fabrication of membranes. Generally, they can be categorized into ceramic-based and polymeric-based membranes.

Cellulose triacetate (CTA) is known as a polymer with good hydrolytic stability and outstanding inert nature to free chlorine and biodegradation and its utilization as a membrane material has been attempted over the last thirty years (Sata Murayama & Shimamoto, 2004). According to O'Rourke et al. (2009), the specific groups from CTA such as hydroxyl and acetyl groups can form highly orientated hydrogen bonds, giving CTA a crystalline structure. To date, researches on electrospun fibers incorporated with extractant are limited to poly(vinyl chloride) (PVC) and polyvinylidene difluoride (PVDF) polymer only (Zhang et al., 2013). So far, there was only one study conducted on CTA electrospun fibers incorporated with Aliquat 336 and the electrospun fibers showed better removal efficiency on heavy metals compared to polymer inclusion membrane (Zulkefeli, Soo, & Abdul-Halim, 2018). However, the removal of dyes using electrospun fibers is scarcely reported.

Hence, this study investigates the potential of CTA electrospun fibers incorporated with Aliquat 336 for methyl orange removal in aqueous solution.

1.3 Objectives

The objectives of this study are:

a) to determine the best Aliquat 336 concentration, pH and dye concentration, that affect the removal efficiency of methyl orange.
b) to characterize the functional group of CTA-Aliquat 336 electrospun fibers at different Aliquat 336 concentrations using Fourier-transform infrared spectroscopy (FTIR).

1.4 Scope of study

The scope of this study was to extract methyl orange using CTA electrospun fibers incorporated with Aliquat 336 as an extractant. The CTA-Aliquat 336 electrospun fibers were prepared using electrospinning process. A range of concentrations of Aliquat 336 (5, 10, 15, 35, 40 wt.%) in CTA electrospun fibers were tested to determine the best extraction of methyl orange. Then, CTA-Aliquat 336 electrospun fibers with the best Aliquat 336 concentration was further used to study on the effect of pH (2, 4, 6, 7, 10) and initial dye concentration (10, 20, 30, 40, 50 ppm) on the removal of methyl orange. Lastly, the morphology structures of CTA- Aliquat electrospun fibers at different Aliquat 336 concentrations (5, 10, 15, 35, 40 wt.%) were characterised by using Fourier-transform infrared spectroscopy (FTIR).

1.5 Significance of study

The deterioration of water quality is a critical issue in the world today. Many countries are confronting issues with access to clean drinking water source and it is predicted that almost 1 billion people are already drinking unclean water (Sarkheil, Noormohammadi, Rezaei, & Borujeni, 2014). In addition, about 8 million people die every year because of various diseases caused by drinking contaminated water. Thus, making the most from safe water sources to deal with water scarcity has been a global challenge.

Therefore, treatments of wastewater for harmful contaminants removal have gathered much attention of the world. Recently, electrospun fibers have been in the spotlight due to their outstanding characteristics displayed in wastewater treatment application (Ramakrishna, Fujihara, Teo, Yong, & Ramaseshan, 2006). The advancement of new composite nanofibers shows even greater capability and the investigation aimed at enhancing both their properties in terms of physical and chemical aspects has attracted massive interest.

When compared to conventional wastewater treatments, electrospun fibers offer a wide range of benefits such as high surface to volume ratio, high pervious structure and improved physico-mechanical properties as in this process, manipulation of the solution and process parameters can be done with ease to obtain the required fiber morphology and mechanical strength (Bhardwaj & Kundu, 2010). Besides, the electrospun fibers are required in a small quantity and the electrospinning process itself is a versatile process as fibers can be spun into any shape using a wide range of polymers (Doshi & Reneker, 1995). The applications of electrospun nanofibers are broad such as biomedical field, as tissue engineering scaffolds, in injury recovering, drug delivery, filtration, as affinity membrane, in immobilization of enzymes, small diameter vascular graft implants, healthcare, biotechnology, environmental engineering, defense and security, and energy storage and generation and in various researches that are ongoing (Gopal et al., 2006).

CTA has numerous advantages such as it is a polar polymer with a number of hydroxyl and acetyl group that are capable of making highly oriented hydrogen bonding (Matamá Cavaco-Paulo, 2010). Not only that, CTA is highly crystalline and infusible. These characteristics strengthen the mechanical ability of CTA (Matamá & Cavaco-Paulo, 2010). Moreover, the addition of Aliquat 336 into CTA electrospun fibers will functionalise the membranes.

Due to the limited number of studies regarding the application of electrospun fibers on the wastewater treatment particularly in dye removal, this research will characterize CTA electrospun fibers incorporated with Aliquat 336. It is expected that CTA-Aliquat electrospun fibers have the potential for dye removal from aqueous solution. Also, it will benefit the various industries and also secure the environment as dye in water can be harmful.

CHAPTER 2

LITERATURE REVIEW

2.1 Dyes

Dyes are a class of organic compounds that give other substances a distinct and firm colour. Since the pigments used today are synthetic, they are also called synthetic dyes. Dyes and pigments are self-coloured which provide a clear and strong colour to other substances in a molecular state or in a dispersed state. There are few ways to classify dyes. For example, they may be classified by fiber type, such as dyes for nylon, dyes for cotton, dyes for polyester, and so on. Dyes may also be classified by their method of application to the substrate such as direct dyes, reactive dyes, vat dyes, disperse dyes, azoic dyes, and several more types. Azoic dyes, which are dye intermediates, have been classified as suspected carcinogens by government agencies in some countries. Among them, the ethylamine of benzidine has been identified as the most potent carcinogen in humans (Department of Health and Human Services, 2011). Therefore, in all countries of the world, focusing on dye production and emphasizing environmental protection has become a top priority.

2.1.1 Methyl orange

Methyl orange (MO), its molecular formula is $C_{14}H_{14}N_3NaO_3S$ and has a formula weight of 327.34. Its structure is shown in Figure 2.1. It is a popular dye with acidic/ anionic characteristics (negative charge) and classified as an azo dye. Usually, the azo group of dyes has nitrogen in molecule. The existence of azo group

(N=N) on methyl orange and low biodegradability makes it a worrying issue to environmentalists as it makes the structures difficult to break (Mittal, Malviya, Kaur, Mittal & Kurup, 2007). Non- biodegradable methyl orange can release carcinogenic and mutagenic components, thus complete degradation of methyl orange in wastewater is necessary. Methyl orange is generally considered to be very stable to light and difficult to oxidize (Dvininov et al., 2011). Methyl orange has the property to colour alkaline and neutral water yellow. If the water becomes acidic, it turns red immediately. The point of change is at ± pH 4.3 (Eumann & Schaeberle, 2016). Methyl orange is able to show different colours at different wavelengths since it acts as indicator of a chemical equilibrium (Pradeep & Dave, 2013). Often, methyl orange is used in medical field and research sector which indicates its importance in science developments (Mittal et al., 2007). Ito & Yamamoto (2015) discovered some findings that can support the development of a dye-binding method that enables accurate measurements, and of a novel tissue-staining method involving the use of a newly synthesized dye.

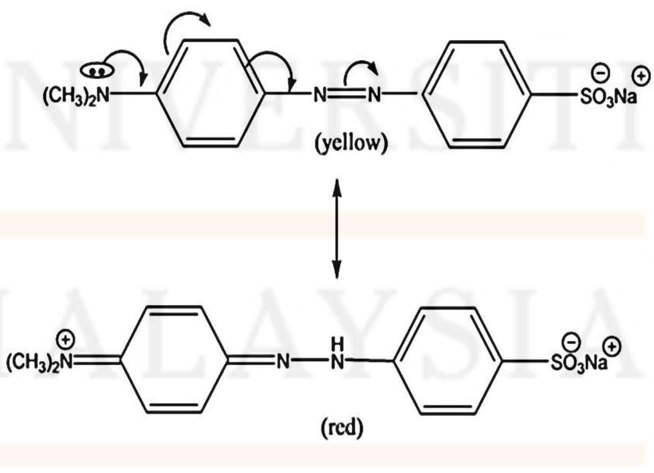

Figure 2.1.: Structures of methyl orange in different pH condition (acid= red, base= yellow).

(Sources: Aziztyana et al., 2019)

2.2 Conventional techniques for dye removal

Traditionally, many technologies are available for dye removal, including chemical coagulation, biological method, adsorption method, and oxidation but these are frequently inefficient when applied for the removal of dye ions in low concentrations and usually require costly equipment and high cost of operation and energy (Verma et al., 2012).

Chemical coagulation involves low concentration dye wastewater containing acid, alkali, salt and organic matter, first homogenized and precipitated, added with an appropriate amount of alkali or acid to neutralize, and then coagulated with a coagulant. The treatment effect of flocculation and sedimentation of dye wastewater depends on the choice and dosage of coagulant, pH of wastewater and hydraulic conditions of coagulation. The chemical coagulation method generally removes chromaticity of about 70 to 90 % and 50 to 80 % of chemical oxygen demand (COD) (Verma et al., 2012). The main disadvantage will result in sludge production due to the addition of lime in the process.

Commonly used biological methods include activated sludge method, biofilm method, oxidation pond method and anaerobic biological method. Biological methods can handle most dye wastewater. The wastewater contains amines, phenols, etc., and has good effects by biological treatment. For acidic and alkaline wastewater, it can be treated by biological treatment after neutralization treatment; the azo dye and sulphur dye wastewater can be treated by reduction and oxidation treatment to reduce its toxicity and then treated by biological method. However, longer duration of treatment, toxicity of dyes and its low biodegradability are the major limitations (Verma et al., 2012).

For adsorption method, the commonly used adsorbents include activated carbon, activated diatomaceous earth, activated coal, activated clay, lignite and polymeric adsorbents. It is influenced by physical and chemical factors such as dye-adsorbent interactions, surface area of adsorbent, particle size, temperature, pH and contact time (Anjaneyulu, Sreedhara Chary, & Samuel Suman Raj, 2005; Patel & Vashi, 2010). The main requirement for determination of adsorbents is based on the characteristics like high affinity, capacity of target compound and possibility of adsorbent regeneration (Karcher, Kornmüller, & Jekel, 2002). The adsorption method can remove substances that are not easy to be degraded in the wastewater. If the concentration of organic matter in the wastewater is high, it is uneconomical to use activated carbon adsorption treatment.

Oxidation uses strong oxidation to destroy organic matter in the wastewater, thereby achieving a more thorough decolorization, detoxification, deodorization and deodorization (Robinson, McMullan, Marchant, & Nigam, 2001). It is one of the main topics in the research of dye wastewater treatment. The oxidation methods that can be employed include ozone oxidation, chlorination oxidation, radiation oxidation, photo oxidation, electrolytic oxidation, wet air oxidation, combustion, and nitric acid air oxidation (Robinson et al., 2001). In general, ozone has a fast decolorizing effect on hydrophilic dyes (such as direct dyes, acid dyes, basic dyes, reactive dyes, etc.), and is effective for hydrophobic dyes (such as vat dyes, narvic dyes, oxidative dyes, sulphur dyes, disperse dyes, etc. and coatings). However, most of the time two or three methods have to be used so that good percentage level of colour removal can be achieved as there is no single economically and technically viable method to solve wastewater problem (Robinson et al., 2001).

2.3 Electrospinning technology

Electrospinning is a special form of electrostatic atomization of polymer fluids. Electrospinning is a special fiber manufacturing process in which a polymer solution or melt is spun in a strong electric field. Under the action of an electric field, the droplets at the needle change from a spherical shape to a conical shape ("Taylor cone"), and the fiber filaments are extended from the conical tip (Bin & Jianyong, 2015). This way it is possible to produce polymer filaments of nanometer diameter. Electrospinning technology has produced a wide variety of nanofibers, including organic composites and inorganic nanofibers.

Adsorbents based on electrospun nanofibrous membranes offer unique properties such as large surface area, tailored pore structure, flexibility of surface functionalization, and self-standing, which make them ideal candidates to pollutant adsorption (Patel & Vashi, 2015). The large surface area of the fibrous membranes provides abundant active sites for materials to adsorb and consequently improve the absorption capacity, while the tailored pore structures lead the nanofibrous membranes to adsorb different materials selectively (Patel & Vashi, 2015). The functionalized nanofibers could adsorb materials selectively depending on the specific force between adsorbent and adsorbate. In addition, the nanofibrous membrane-based adsorbents are easy to recycle and would not cause secondary pollution which is much more suitable than nanoparticles.

In the field of biomedicine, electrospun fibers have been well applied in drug-controlled release, wound repair, biological tissue engineering and so on. This is because the diameter of nanofibers is smaller than that of cells, which can simulate the structure and biological function of natural extracellular matrix, most tissues and organs of humans are similar in form and structure to nanofibers, which are used for tissue of nanofibers (Bin & Jianyong, 2015). Moreover, the repair of organs provides the possibility, some electrospun raw materials have good biocompatibility and degradability, can enter the human body as a carrier, and are easily absorbed (Bin & Jianyong, 2015).

Therefore, the electrospun fiber material can be used as a template to uniformly disperse, and at the same time, the flexibility and ease of operation of the polymer carrier can be exerted. The surface composition of the catalytic material and the polymer micro-nano size can be used to generate a strong synergistic effect and improve the catalytic efficiency (Patel & Vashi, 2015).

2.3.1 Electrospinning fibers for dye removal

Electrospun nanofibrous membranes have surface area and porosity that make them suitable for the dye removal from wastewaters. The high surface area enables excessive adsorption sites for dye adsorption and the higher porosity leads to smaller driving forces to push the water through the membrane which make the process use lesser energy and effortless (Singh et al., 2010).

Plenty researches were conducted on the use of electrospun nanofibrous membranes for water treatment. The findings of previous researches showed that the functional polyethersulfone (PES) nanofibrous membrane was specifically capable to purify water (Yoon, Hsiao, & Chu, 2009). Outstanding ability to remove particle separation applications was shown by electrospun PAN nanofibrous membrane particularly from water (Bazargan, Keyanpour-rad, Hesari, & Ganji, 2011) while good adsorption capability was manifested by cyclodextrin-functionalized nanofibrous membranes for indigo carmine dye (Teng, Li, Zhang, & Taha, 2011). Also, a micronanostructure poly (ether sulfones)/poly (ethyleneimine) nanofibrous membrane was employed as an adsorbent for anionic dyes (Min et al., 2012). All these findings support that electrospun fibers with its unique properties such as high specific surface area and high porosity with fine pores led for the removal of dye molecules from wastewater.

2.4 Electrospinning fibers incorporated with Aliquat 336

According to Xu, Paimin, Shen, & Wang (2003), Aliquat 336 (trioctylmethyl ammonium chloride) is a quaternary ammonium salt composed of a large organic cation associated with a chloride. It is a mixture of C_8 (octyl) and C_{10} (capryl) chains with C_8 predominating. One of the main uses of Aliquat 336 is as a phase transfer catalyst in the catalytic oxidation of cyclohexene to 1,6-hexanedioic acid. It is also used extensively as an ion extraction agent. Aliquat 336 is a surface-active compound and tends to stay at the surface of the membrane. When the membrane is in contact with the aqueous phase, Aliquat 336 molecules at the surface orientates itself so that the ammonium ion group faces the water and the non-polar hydrocarbon groups face away from the water (Xu, Paimin, Shen, & Wang, 2003).

Recently, different types of membranes particularly polymer inclusion membranes (PIMs) and electrospun fibers incorporated with Aliquat 336 extractant have attracted increasing interests for their effective absorption on wastewater contaminants. To incorporate specific extractant in the membrane can result in larger surface area of polymer fibers which can improve removal efficiency. Vázquez, Romero, Fontàs, Anticó, & Benavente (2014) reported that Aliquat 336 was playing an essential role on the mechanical behavior (high plasticity or brittle) of the membranes for PIMs manufacture, based on the significant reduction in Young modulus associated to Aliquat 336 content in dry AlqCl / CTA membranes. Pospiech (2015) reported that Aliquat 336 has been acting as a carrier in PIMs used in the removal of metal ions such as cadmium and copper or in organic compounds such as antibiotics or water pollutants. On the other hand, the studies from Zulkefeli et al. (2018) showed that electrospun fibers incorporated with Aliquat 336 achieved significant removal of cadmium (II) ion. One recent research actually compared the characteristics and cadmium extraction performance of polyvinyl chloride (PVC)/ Aliquat 336 electrospun fibers with PIMs, the findings showed that that the role of Aliquat 336 in electrospun fibres differ from that in PIMs (Abdul-Halim, Whitten, & Nghiem, 2016). The PVC/Aliquat 336 electrospun fibrous mats exhibited web like structures and were visually opaque while PVC/Aliquat 336 PIMs were homogenous (Abdul-Halim et al., 2016). In addition, the extraction performance improved when used PVC/Aliquat 336 electrospun fibers compared to PVC/Aliquat 336 PIMs even though the reduced amount of carrier was used on fibers. Despite all the applications mentioned, there was no research on dye removal conducted using electrospun fibers incorporated with Aliquat 336 so far.

CHAPTER 3

MATERIALS AND METHODS

3.1 Reagents

CTA and Aliquat 336 are from Sigma Aldrich (Australia) while DCM is from R&M Chemicals and MeOH is from HmbG® Chemicals. All chemicals were of analytical grade and used without further purification. Methyl orange dye was obtained from Bendosen and was selected as a model industrial wastewater. The dye solution was prepared by dissolving the dye in distilled water. Distilled water (UMK laboratory) was used for the preparation of all aqueous solutions.

3.2 Preparation of CTA-Aliquat 336 fibers

CTA-Aliquat 336 electrospun fibers at different Aliquat 336 concentrations (5, 10, 15, 35 and 40 wt.%) were prepared from respective CTA-Aliquat 336 solutions. For electrospinning process, apparatus involved a high voltage power supply (Gamma Model ES30P-5W/DAM, Gamma High Voltage Research Inc.), a 5 mL Terumo® syringe barrel with a 23 gauge needle tip syringe pump and a metal collector.

A series of polymer solution at different Aliquat 336 concentrations was prepared by dissolving the Aliquat 336 (5, 10, 15, 35 and 40 wt.%) and CTA in a solvent mixture of DCM and MeOH with a ratio of 8:2 respectively. The total volume of DCM/ MeOH used was 10 mL. Each mixture contained CTA polymer and Aliquat 336 weight of 500 mg. The mixtures were stirred continuously and vigorously until the solution became clear or homogenous. To start the electrospinning process, 5 mL of the polymer solution was placed in a 5 mL plastic syringe attached with 23-gauge needle tip as shown in Figure 3.1. The polymer solution was electrospun for 8 hours at 20 kV with a flow rate of 1 mL/h and 140 mm of distance from needle tip to metal collector. After 8 hours of electrospinning, the CTA-Aliquat 336 electrospun fibers were collected and kept under dry condition for further extraction experiments. All CTA-Aliquat 336 electrospun fibers were prepared using the same electrospinning conditions with different concentrations of Aliquat 336.

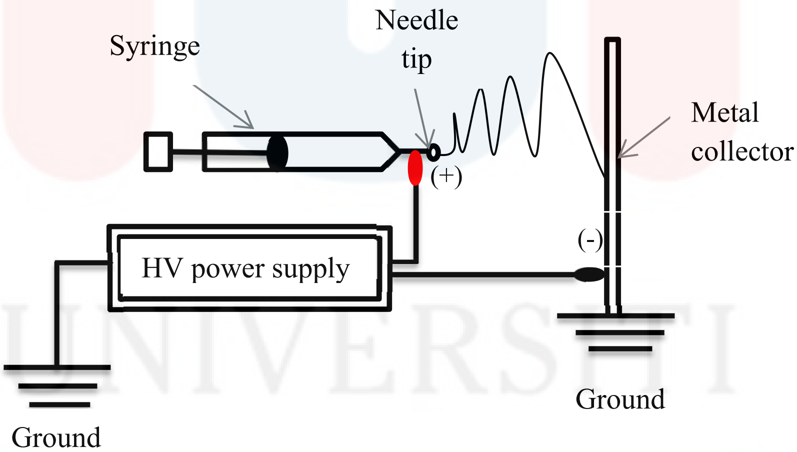

Figure 3.1: Schematic diagram of electrospinning process.

3.3 Preparation of Methyl Orange Solution

1000 mL of stock solution (100 mg/L) of methyl orange ($C_{14}H_{14}N_3NaO_3S$) was prepared by dissolving 1 g of methyl orange powder with distilled water. For calibration curve purpose, a series of methyl orange at different concentrations (10, 20, 30, 40 and 50 ppm) were prepared in volumetric flasks. The linear regression coefficient is also called R-squared (R^2) for all calibration curves achieved values of $0.995 \leq R^2 \leq 0.999$. Then, the amount of stock solution needed for the dilution was determined next and Equation 3.1 was used.

$$M_1 V_1 = M_2 V_2 \tag{3.1}$$

Where;

M_1= Concentration of stock solution (mg/L)

V_1= Volume of stock solution needed for dilution (mL)

M_2= Concentration needed (mg/L)

V_2= Volume of volumetric flask used for dilution (mL)

3.4 Study on Methyl Orange Extraction

Extraction experiments were conducted in a batch mode. In order to determine the removal efficiency of methyl orange, CTA-Aliquat 336 electrospun fibers with different Aliquat 336 concentration (5, 10, 15, 35 and 40 wt.%), followed by different initial concentrations of methyl orange dye solution (10, 20, 30, 40 and 50 ppm) and then different pH values (2, 4, 6, 7 and 10) were optimized in sequence. For all the extractions, the amount of electrospun fibers used was ±0.1 g, the amount of extraction solution used was 150 mL, the stirring speed was set at 150 rotations per minute (rpm) and temperature was 25 ºC in the incubation shaker. At predetermined time intervals (0, 20, 40, 120, 180, 300 and 1440 minutes), about 1.5 mL sample of extraction solution was collected from each conical flask for analysis by using UV-Vis spectrophotometer (DR6000 brand) at 464 nm wavelength. The concentration at different time interval can be determined by using equation from calibration curves obtained. Then, the removal efficiency was calculated using Equation 3.2. The efficiency of methyl orange removal was investigated by first optimising the parameter of Aliquat concentration (5, 10, 15, 35 and 40 wt. %), followed by pH of methyl orange (2, 4, 6, 7, and 10) and then initial methyl orange concentration (10, 20, 30, 40 and 50 ppm).

$$\text{Extraction efficiency, } E(\%) = \frac{C0 - Cf}{C0} \times 100\% \quad (3.2)$$

Where C_0 is the initial concentration and C_f is the final concentration.

3.4.1 Effect of Aliquat 336 Concentration

To determine the optimum Aliquat 336 concentration on methyl orange removal, pH of methyl orange solution was set at pH 7 and concentration of methyl orange aqueous solution was set at 10 ppm for all extractions. Electrospun fibers with different Aliquat 336 content were cut into smaller pieces and put into five different conical flasks containing 150 mL of 10 ppm methyl orange solution. Temperature of 25 ºC and stirring speed of 150 rpm remained the same in incubation shaker throughout the extraction study. At predetermined time intervals (0, 20, 40, 120, 180, 300 and 1440 minutes), about 1.5 mL of samples were withdrawn from respective conical flask for dye ion analysis by UV-Vis spectrophotometer. The highest removal efficiency achieved within the predetermined time intervals among five different Aliquat 336 concentrations should be the optimized Aliquat 336 concentration.

3.4.2 Effect from pH of Methyl Orange

To determine the optimum pH for methyl orange removal, the optimized CTA-Aliquat 336 concentration electrospun fiber was used and concentration of methyl orange aqueous solution was set at 10 ppm for all extractions. The electrospun fibers with optimised Aliquat 336 content were cut into smaller pieces and put into five different conical flasks containing 150 mL of 10 ppm methyl orange solution. The pH of the solution was varied from values 2 to 10. At predetermined time intervals (0, 20, 40, 120, 180, 300 and 1440 minutes), about 1.5 mL of samples were withdrawn from respective conical flask for dye ion analysis by UV-Vis spectrophotometer. The highest extraction efficiency achieved within the predetermined time intervals among five different pH solutions should be the optimized pH for the removal of methyl orange.

3.4.3 Effect of Initial Dye Concentration

To determine the optimum initial dye concentration for methyl orange removal, the optimized CTA-Aliquat 336 concentration electrospun fiber and optimized pH of methyl orange solution were used. The electrospun fibers with optimised Aliquat 336 content were cut into smaller pieces and were put into five different conical flasks containing 150 mL of methyl orange in optimised pH solution. At predetermined time intervals (0, 20, 40, 120, 180, 300 and 1440 minutes), about 1.5 mL of samples were withdrawn from respective conical flask for dye ion analysis by UV-Vis spectrophotometer. The highest extraction efficiency achieved within the predetermined time intervals among five different initial dye concentrations should be the optimized condition for the removal of methyl orange.

3.5 Fourier-transform infrared spectroscopy (FTIR) Analysis

FTIR (8400S of Shimadzu) was used to study the chemical structure of CTA-Aliquat 336 electrospun fibers. Generally, FTIR is used to identify the types of bond and number of functional group present in the electrospun fibers before and after the extraction. Infrared light is used to scan sample and observe chemical properties. The reactions undergone would affect types of bonds and functional group. So, the fiber sheets absorbed infrared radiation at specific wavelengths (500 cm^{-1} – 4000 cm^{-1}). Thus, different peaks were shown in the analysis.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Overview

The removal efficiency of methyl orange dye was studied using CTA-Aliquat 336 electrospun fibers with different Aliquat 336 composition as shown in Table 4.1. The weight of each electrospun fiber sheet is ±0.1 g. Three parameters including Aliquat 336 concentration (5, 10, 15, 35 and 40 wt.%), pH (2, 4, 6, 7 and 10) and initial concentration of methyl orange (10, 20, 30, 40 and 50 ppm) were tested to determine the optimized methyl orange extraction. The feed extraction was set at 25 ºC, 150 rpm and remained constant throughout the extraction study. Batch experiments were carried out for 24 hours continuously and each parameter was repeated for three times to get an average reading. For each parameter, the extraction solutions were collected every 0, 20, 40, 120, 180, 300 and 1440 minutes for Ultraviolet-visible (UV-Vis) spectrophotometer analysis. In addition, the CTA-Aliquat 336 electrospun fibers at different Aliquat 336 concentrations were characterized by Fourier-transform infrared spectroscopy (FTIR).

Table 4.1: Different composition of CTA-Aliquat 336 electrospun fibers for the extraction of methyl orange.

Membranes	Base polymer	Extractant	Dye ion
CTA-Aliquat 336 electrospun fibers	CTA 95%	Aliquat 5%	Methyl orange
	CTA 90%	Aliquat 10%	
	CTA 85%	Aliquat 15%	
	CTA 65%	Aliquat 35%	
	CTA 60%	Aliquat 40%	

4.2 Methyl Orange Extraction Performance

4.2.1 Effect of Aliquat 336 Concentration

The electrospun fibers at different Aliquat 336 concentrations were investigated ranging from 5 to 40 wt.% and the results were shown in Figure 4.1 and Appendix 1 a. Electrospun fibers with different Aliquat 336 content (5, 10, 15, 35 and 40 wt.%) showed different features when observed under naked eye observations and its figures were displayed in Appendix 2 a, 2 b, 2 c, 2 d and 2 e respectively. Both 35 wt.% and 40 wt.% were harder to be collected at metal plate as they were more fragile due to high Aliquat 336 content. Aliquat 336 is an extractant that allowed the extraction of target ions from the aqueous solution. Due to the structure of Aliquat 336 is of ammonia and carries an existing positive charge (Figure 4.1), it manages to react with methyl orange which carries negative charge. Its structure which composes of a large organic cation together with chloride ion, $[R_3NCH_3]^+Cl^-$ which is in charge for the production of a unbreakable cation-anion pair over different pH values (Iqbal & Datta, 2019).

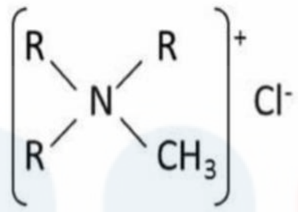

Figure 4.1: Aliquat 336 structure.

Based on Figure 4.2 and Appendix 1 a, the results revealed that the percentage of extraction efficiency increased from 5 wt.% of Aliquat content (98.81 %) until 10 wt.% of Aliquat content (99.86 %) and then gradually decreased from 10 wt.% of Aliquat content (99.86 %) until 40 wt.% of Aliquat content (96.29 %). The highest percentage removal was achieved at 1440 minutes (24th hour) with 10 wt.% of Aliquat content which was 99.86 %. Le Châtelier's principle stated that increasing the concentration of extractant will increase the reaction rate by increasing the rate of collisions (Homsirikamol et al., 2016). The extraction capacity of membrane should be improved when higher Aliquat 336 content is used. However, for 35 wt.% and 40 wt.% of Aliquat concentrations, significant extraction performance were only shown after 300 minutes which were 96.48 % and 96.29 % respectively. This is probably because saturation of extractant in the membrane has resulted a decrease in extraction capability by changing the structure of the membrane surface as reported in another research (Mitiche, Tingry, Seta & Sahmoune, 2008). In another research where the range of extractant concentration used was (0 wt.% to 20 wt.%), Zargar, Parham & Hatamie (2015) reported the optimum Aliquat 336 was found to occur at 10 wt.% which showed maximum reaction where a further increase of the Aliquat 336 reduced the flux of the analyte passing through the membrane. Hence, the highest percentage removal of methyl orange extraction achieved within 24 hours with electrospun fibers at 10 wt % of Aliquat 336 content (99.86 %). Thus, this electrospun fibers was used for further studies.

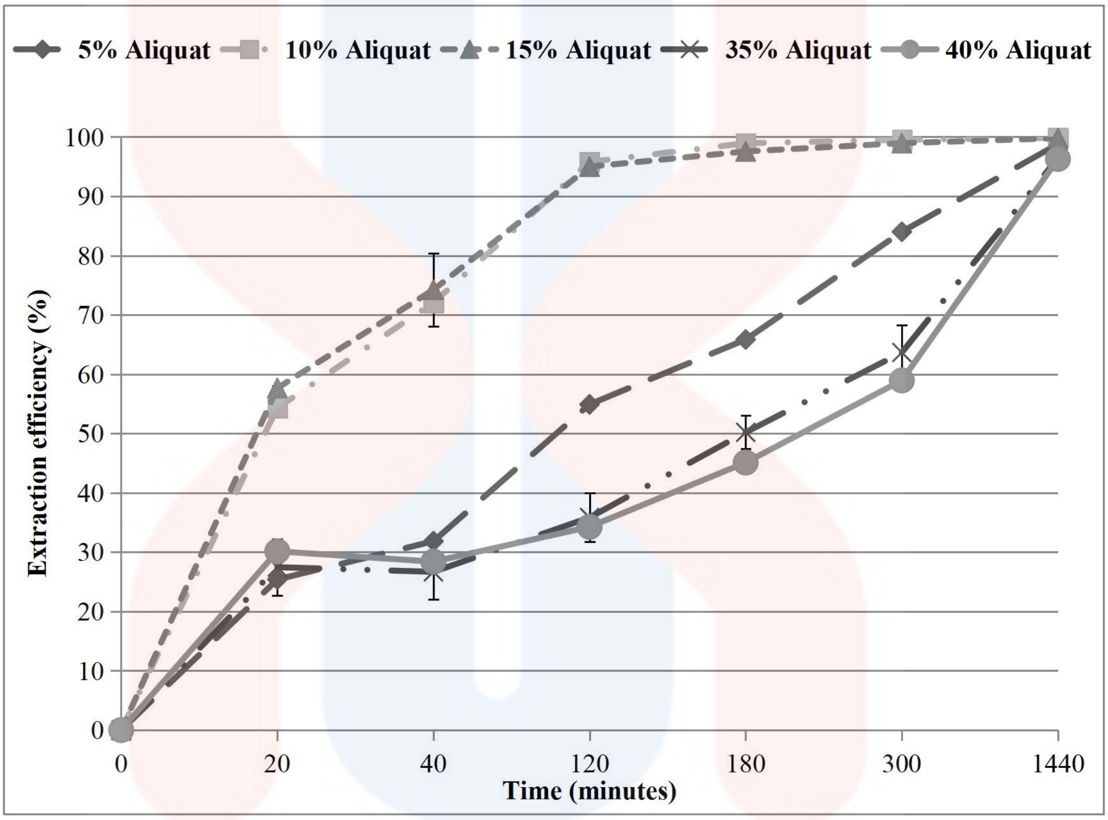

Figure 4.2: Effect of Aliquat 336 concentration on the removal of methyl orange on CTA-Aliquat 336 electrospun fibers.

4.2.2 Effect of pH in aqueous solution

In the aqueous solution, the acid dye (methyl orange) is first dissolved and the sulfonate group (-$SO_3^-Na^+$) of the acid dye are dissociated and converted to anionic dye ions (Ozmen & Yilmaz, 2007). The pH of the aqueous solution has a great impact in the adsorption process, affecting many parameters such as the charge distribution on membrane surface, the ionization yield of the particles in the solution, and the dissociation of functional groups on the active sites of the membrane (Ku, Lee & Wang, 2005). Research by Ghani et al. (2014) showed that the performance of anionic dye extraction is directly connected with solution pH as they reported maximum removal efficiency at lowest pH which was favourable for the condition.

In this study, the pH of the aqueous solution was varied from pH 2, 4, 6, 7 and 10. An optimized CTA-Aliquat 336 electrospun fibers (10 wt. % of Aliquat 336) was used and the initial methyl orange concentration was remained at 10 ppm. Based on Figure 4.3 and Appendix 1 b, it showed that the removal efficiency of methyl orange at pH 2 to pH 7 was better than alkaline solution (pH 10) as the readings achieved above 90 %. As the pH value decreased, the extraction efficiency also increased as period of time increased. The best percentage removal was at pH 2 with 99.93 % removal. Other percentage removals were 99.78 %, 99.85 %, 99.65% and 91.43 % for pH 4, pH 6, pH 7 and pH 10 respectively at 24th hour. The results clearly showed that sorption of methyl orange dye onto electrospun fibers was influenced by the pH value of the solution and acidic pH was more favourable for the adsorption of the dye. This might indicate that at lower pH, H^+ ion particles is relatively high compared to alkaline solutions, so this increment will favour the Aliquat 336 which also has a positively charge functional group to attract negatively charged methyl orange (Shee, 2014). In other words, alkaline pH that showed lower adsorption of methyl orange may be due to the presence of excess OH^- ions racing with dye anions for the adsorption sites. However, at pH 10, significant adsorption of the methyl orange dye still happened (91.43 %). It might be some bonding occurred between Aliquat 336 and methyl orange. In the research of adsorption behavior of methyl orange onto wheat bran, Alzaydien (2015) explained the possible formation of covalent bonding between surface –OH group of wheat bran and negatively charged dye molecules. Overall, the extraction of methyl orange is suitable at wide range of pH solutions.

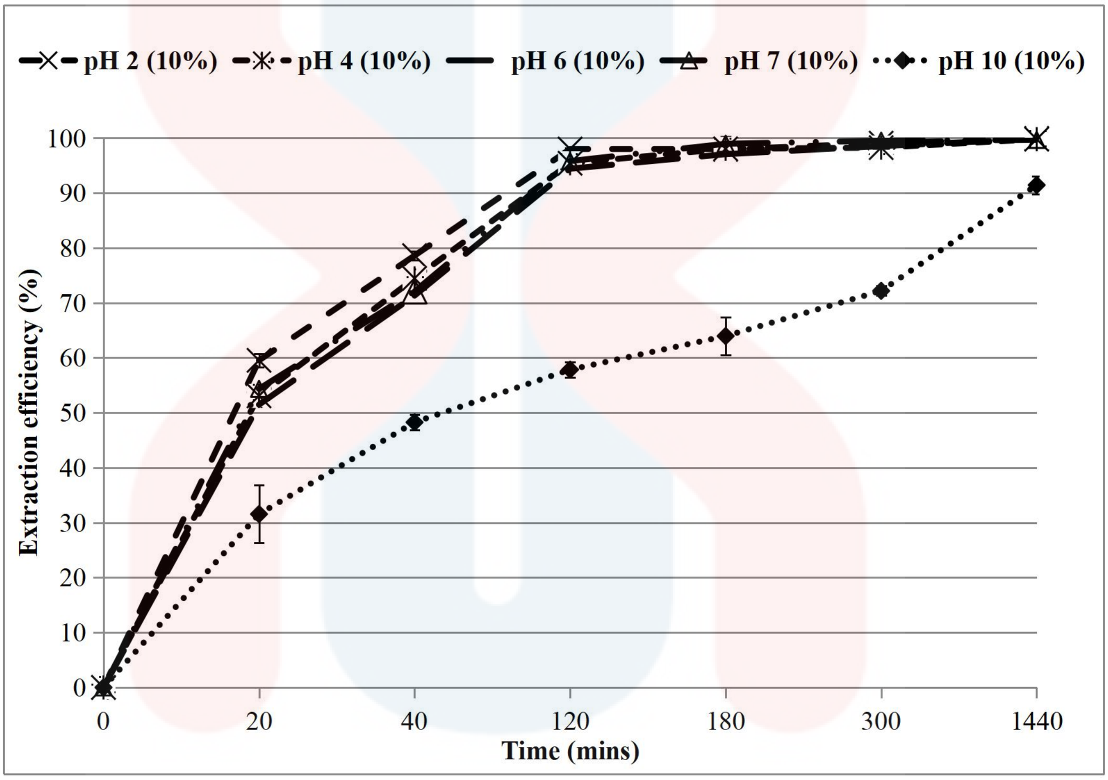

Figure 4.3: Effect of pH on the removal of methyl orange on the CTA- Aliquat 336 electrospun fibers (10 wt. % Aliquat)

4.2.3 Effect of Methyl Orange Concentration

In order to study the capacity of CTA-Aliquat 336 electrospun fibers at 10 wt.% Aliquat 336 in extracting methyl orange, the initial dye concentration was varied between 10 to 50 ppm. Since the extraction of methyl orange was better in acidic solution, the aqueous solution was set at pH 2 and the result of removal efficiency are shown in Figure 4.4 and Appendix 1 c. Based on the results, the removal efficiency of methyl orange decreased as the dye concentration increased. The highest removal efficiency of methyl orange was achieved when the initial dye was 10 ppm (99.93 %) whereas 50 ppm achieved the lowest removal efficiency (98.18 %). This finding is similar with study by Ling and Mohd Suah (2017), where the extraction of malachite green dye decreased as the concentration of malachite green increased from 20 ppm to 100 ppm. This is due to membrane saturation and lower efficiency membrane area. The same result was also obtained by Salima et al., (2012) which showed that the removal of methylene blue decreased as the concentration of the dye increased from 250 ppm to 800 ppm. Although at 10 ppm, the removal rate was the fastest, but other concentrations (20 – 50 ppm) achieved > 98 % of removal rate which was good. This results suggests that higher methyl orange concentration (> 50 ppm), the CTA-Aliquat 336 electrospun fibers can still remove the dye.

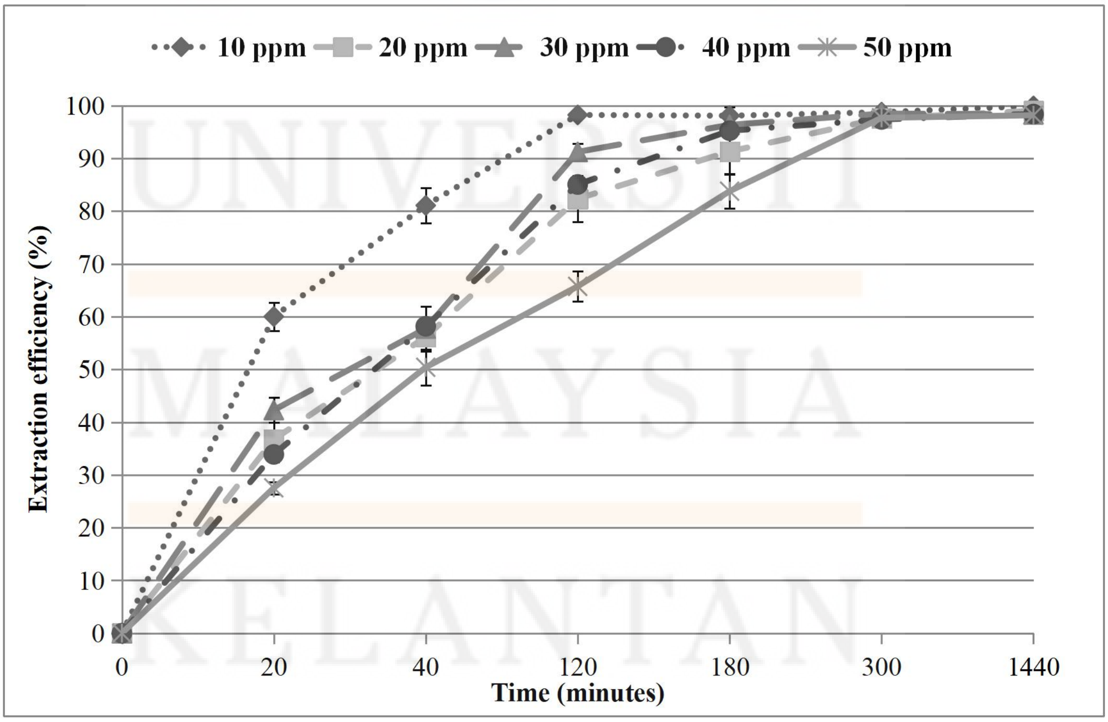

Figure 4.4: Effect of initial dye concentration on the removal of methyl orange on CTA-Aliquat 336 electrospun fibers with 10 wt. % Aliquat 336 at pH 2.

4.3 Membrane Characterization by Fourier-transform infrared spectroscopy (FTIR) Analysis

Morphology studies was carried out by using FTIR analysis to determine the presence of functional group and types of bonds present in CTA-Aliquat 336 electrospun fibers (5, 10, 15, 35 and 40 wt.%) from 500 cm^{-1} – 4000 cm^{-1} wavelength. The spectrum of CTA electrospun fibers with all concentrations of Aliquat 336 was shown in Figure 4.5.

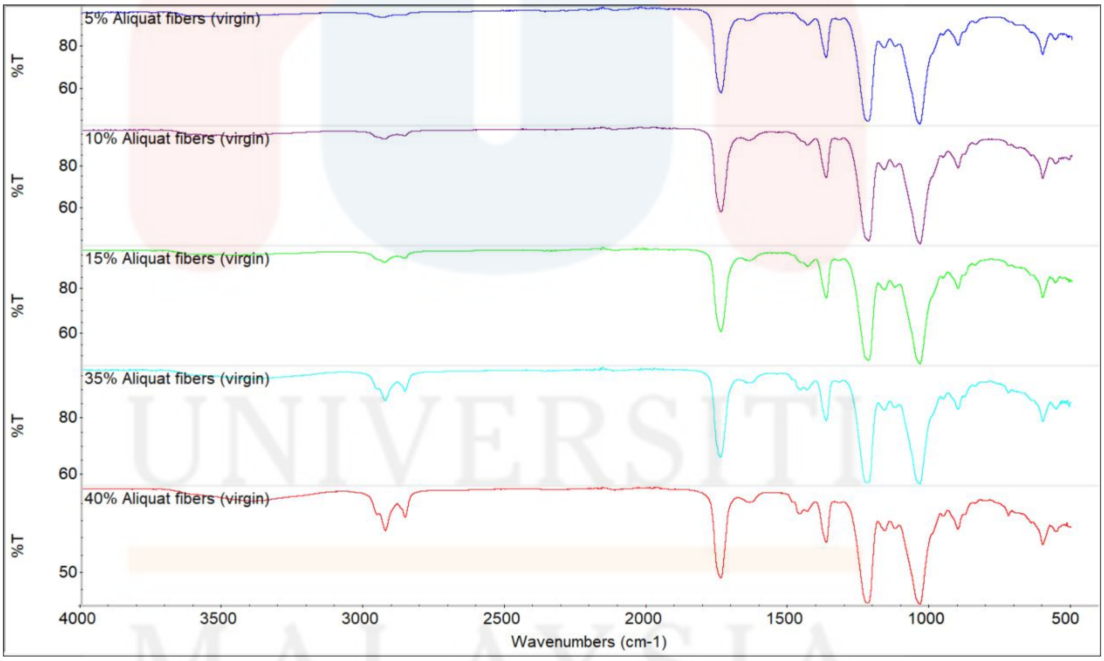

Figure 4.5: FTIR spectra of 5 wt.%, 10 wt.%, 15 wt.%, 35 wt.% and 40 wt.% CTA-Aliquat 336 electrospun fibers.

As it can be observed from the FTIR spectrum of CTA-Aliquat 336 electrospun fibers (Figure 4.5), there are three noticeable infrared absorption ranges located around 1000 cm^{-1} to 2000 cm^{-1} indicating electrospun fibers have the same functional groups. To be specific, at 1738 cm^{-1}, it is assigned to the stretching vibration of the C=O group and the presence of the bands at 1218 cm^{-1} and 1035 cm^{-1} correspond to the stretching vibration of the C-O bonds. Based on these results, the absorption bands showed the ester absorptions from aliphatic acetate esters as cellulose acetate is the acetate ester of cellulose. Furthermore, when the spectrum is carefully observed, it is obvious that the regions of spectrum at 2800 cm^{-1} to 3000 cm^{-1} gradually became broader from 5 wt.% Aliquat 336 content to 40 wt.% Aliquat 336 content. This observation linked that it must have something to do with saturation of the extractant, Aliquat 336.

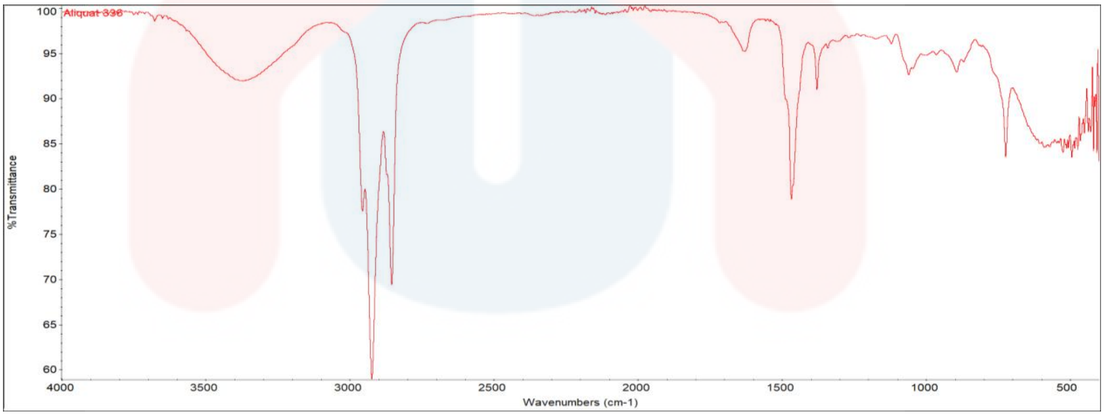

Figure 4.6: FTIR spectra of pure Aliquat 336.

With reference to the pure Aliquat 336 spectra (Figure 4.6), it has the same absorption region but stronger infrared absorption suggesting the presence of Aliquat 336. Reported by Cui et al. (2013), the absorption bands at 2923 cm^{-1} and 2851 cm^{-1} assigned to the -CH_3 groups and at 1467 cm^{-1} and 1378 cm^{-1} attributed to the quaternary ammonium groups are in accordance with the chemical structure of Aliquat 336. The FTIR analysis results revealed the presence of the positively charged ammonium groups of Aliquat 336 and some C-O and C=O bondings that are believed from the interactions of cellulose triacetate. Table 4.2 showed the FTIR peaks at specific wavelength for Aliquat 336 and its respective chemical groups.

Table 4.2: Assignment of FTIR peaks for Aliquat 336. (Sources: St John et al., 2011)

Constituent	**Wavenumber (cm^{-1})**	**Chemical group**
Aliquat 336	2923	C-H (CH_2)
	2851	C-H (CH_3)
CTA	1738	C=O
	1218	C-O
	1035	C-O

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this research, the extraction performance of methyl orange on CTA-Aliquat 336 electrospun fibers was analysed and evaluated on the effects of Aliquat concentration, initial pH of aqueous solution and initial concentration of methyl orange subsequently. The results have shown that an increase in Aliquat concentration does not necessarily increase the extraction efficiency. The 10 w.t% Aliquat 336 concentration electrospun fibers was found more efficient than other fibers (5, 15, 35 and 40 w.t%) with the percentage removal of 99.86 % . Besides, the acidic conditions favour the extraction performance of methyl orange. It can be seen from the trend that when the pH value decreased, the percentage removal of dye also increased. The readings recorded at 99.93 %, 99.78 %, 99.85 %, 99.65 % and 91.43 % at pH 2, 4, 6, 7 and 10 respectively. All the extractions below pH value of 7 showed more than 99 %. Furthermore, initial concentration of methyl orange for highest extraction efficiency to occur was 10 ppm. An increase in initial concentration of methyl orange decreased the extraction efficiency of CTA-Aliquat 336 electrospun fibers. Higher concentration of methyl orange slows down the efficiency of Aliquat 336 extractant.

Then, characterization study was also conducted on all Aliquat concentrations of freshly prepared CTA-Aliquat 336 electrospun fibers using FTIR. The FTIR analysis proved the presence of Aliquat 336 due to the interactions of C-H (CH_2) and C-H (CH_3)

5.2 Recommendations

After completed this research, there are several recommendations that can be carried out in order to obtain significant result for the further research. It would be beneficial if electrospun fibers can be developed in a larger scale that is being applied in a factory wastewater treatment process using actual industrial wastewater. In this way, the knowledge about the optimum conditions for methyl orange extraction by electrospun fibers can have real life applications. Moreover, it is also useful to explore about the functionality of CTA-Aliquat 336 electrospun fibers on cationic dyes that might have useful insights for researchers. In addition, the use of electrospun fibers can be utilized in other applications such as tracing the contaminant of emerging concern (CEC) as the harmful threat caused was still of limited research.

Besides, due to the time constraint of this research, the parameters that were studied in this research is few namely Aliquat 336 concentration, pH of aqueous solution and initial concentration of methyl orange. It is suggested to include stirring speed and temperature. Temperature is known to increase collision rate of particles so it might increase the extraction efficiency of extractant whereas stirring speed might reduce the time needed for efficient extraction. In this way, the study will have greater impact and outcome to the research and society.

During this research, it was found that when higher Aliquat 336 concentration was used to electrospinning fibers, the structure of membrane became denser. When the Aliquat 336 content exceeds 35%, the membrane became fragile which was difficult to collect at metal collector and to be used in extraction (40 wt.% Aliquat 336 electrospun fibers). Therefore, it is important to address the preparation of these electrospun fibers by improving the electrospinning parameters that affect the formation of electrospun fibers such as altering the voltage supply, the distance between the needle tip and metal collector and the solvent composition to dissolve the base polymer and extractant.

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Appendix 1

Table a: The reading of extraction of methyl orange by CTA-Aliquat 336 electrospun fibers with different Aliquat 336 content in 24 hours.

Aliquat 336	Time (mins)	Percentage removal (%)
5 wt.%	0	0 ± 0.000
	20	25.386 ± 0.252
	40	31.837 ± 0.081
	120	54.909 ± 0.150
	180	65.849 ± 0.041
	300	84.011 ± 0.635
	1440	98.808 ± 0.111
10 wt.%	0	0 ± 0.706
	20	54.342 ± 0.256
	40	72.059 ± 0.907
	120	95.798 ± 1.267
	180	98.950 ± 0.089
	300	99.510 ± 0.201
	1440	99.860 ± 0.201
15 wt.%	0	0 ± 0.000
	20	57.660 ± 0.380
	40	74.234 ± 6.186
	120	94.986 ± 0.650
	180	97.563 ± 0.560
	300	98.955 ± 0.267
	1440	99.791 ± 0.290
35 wt.%	0	0 ± 0.000
	20	27.460 ± 4.737
	40	26.682 ± 4.598
	120	35.835 ± 4.107
	180	50.206 ± 2.807
	300	63.661 ± 4.577
	1440	96.476 ± 1.029
40 wt.%	0	0 ± 0.000
	20	30.140 ± 3.148
	40	28.392 ± 2.427
	120	34.266 ± 4.894
	180	45.105 ± 2.946
	300	58.951 ± 3.801
	1440	96.294 ± 1.821

Table b: The reading of extraction of methyl orange by 10 wt.% CTA-Aliquat 336 electrospun fibers at different pH values in 24 hours.

pH value	Time (mins)	Percentage removal (%)
pH 2	0	0 ± 0.000
	20	59.532 ± 1.228
	40	78.595 ± 0.845
	120	97.993 ± 0.180
	180	97.926 ± 0.842
	300	99.064 ± 0.185
	1440	99.933 ± 0.000
pH 4	0	0 ± 0.000
	20	53.066 ± 0.238
	40	74.453 ± 1.296
	120	95.401 ± 1.295
	180	98.029 ± 0.124
	300	98.248 ± 0.018
	1440	99.781 ± 0.101
pH 6	0	0 ± 0.020
	20	51.471 ± 0.010
	40	71.324 ± 0.034
	120	94.412 ± 0.045
	180	97.059 ± 0.056
	300	98.529 ± 0.012
	1440	99.853 ± 0.043
pH 7	0	0 ± 0.000
	20	54.342 ± 0.706
	40	72.059 ± 0.256
	120	95.798 ± 0.907
	180	98.950 ± 1.267
	300	99.510 ± 0.089
	1440	99.650 ± 0.092
pH 10	0	0 ± 0.000
	20	25.445 ± 5.240
	40	49.958 ± 1.379
	120	57.846 ± 1.420
	180	63.953 ± 3.464
	300	72.180 ± 0.872
	1440	91.433 ± 1.625

Table c: The reading of extraction of methyl orange by 10 wt.% CTA-Aliquat 336 electrospun fibers at pH 2 for different methyl orange concentrations in 24 hours.

Methyl orange concentration	Time (mins)	Percentage removal (%)
10 ppm	0	0 ± 0.000
	20	60.015 ± 2.646
	40	81.075 ± 3.369
	120	98.233 ± 0.026
	180	98.085 ± 1.694
	300	98.748 ± 0.956
	1440	99.926 ± 0.105
20 ppm	0	0 ± 0.000
	20	36.722 ± 4.248
	40	56.173 ± 2.707
	120	82.343 ± 4.404
	180	91.312 ± 4.393
	300	97.608 ± 1.257
	1440	99.015 ± 0.283
30 ppm	0	0 ± 0.000
	20	42.295 ± 2.380
	40	57.752 ± 1.642
	120	91.228 ± 1.600
	180	96.349 ± 0.635
	300	98.483 ± 0.147
	1440	98.340 ± 0.589
40 ppm	0	0 ± 0.000
	20	33.892 ± 1.414
	40	58.176 ± 3.796
	120	85.045 ± 1.310
	180	95.248 ± 2.941
	300	97.379 ± 1.124
	1440	98.393 ± 0.190
50 ppm	0	0 ± 0.000
	20	27.549 ± 1.160
	40	50.401 ± 3.383
	120	65.736 ± 2.885
	180	83.780 ± 3.292
	300	97.679 ± 1.157
	1440	98.176 ± 0.222

Appendix 2

Figure a: The feature of 5 wt.% CTA-Aliquat 336 electrospun fibers.

Figure b: The feature of 10 wt.% CTA-Aliquat 336 electrospun fibers

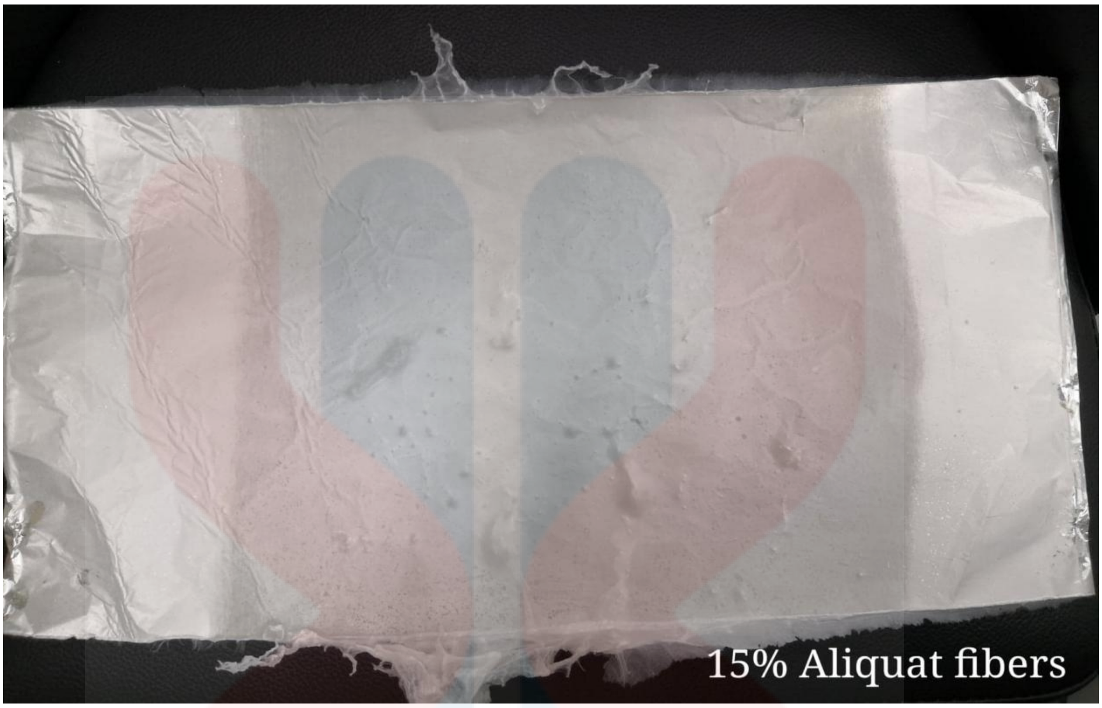

Figure c: The feature of 15 wt.% CTA-Aliquat 336 electrospun fibers.

Figure d: The feature of 35 wt.% CTA-Aliquat 336 electrospun fibers.

Figure e: The feature of 40 wt.% CTA-Aliquat 336 electrospun fibers.

Figure f: The electrospinning process.

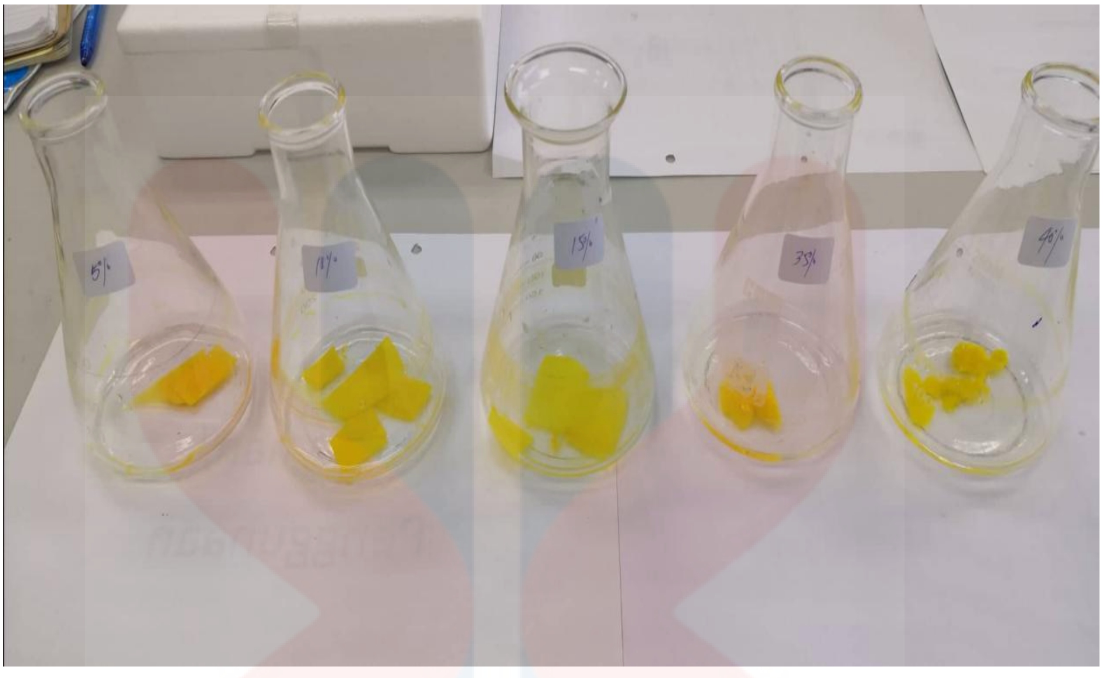

Figure g: The optimum extraction solutions (10 wt.% Aliquat 336, pH 2 and 10 ppm) after 24 hours.