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The Removal of Methyl Orange Using CTA-Aliquat 336 Electrospun Fibers From Aqueous Solution

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Abstract. Electrospinning is a versatile method in producing electrospun fibers with fascinating features such as high porosity, larger surface to volume ratio and excellent functionalities. The binding of specific functional group to the electrospun fibers has proven them as potential substances in adsorption of pollutants. Thus, this research aimed to investigate the extraction of methyl orange from aqueous solution using electrospun fibers made from cellulose triacetate (CTA) as the base polymer and Aliquat 336 as extractant. The effect of extractant (5-40 wt.%), pH of aqueous solutions (2, 4, 6, 7, 10) and initial dye concentrations (10- 50 ppm) were examined to determine the optimal extraction of methyl orange. Fourier transform infrared spectroscopy (FTIR) was performed to investigate the functional group of the CTA-Aliquat 336 electrospun fibers at various Aliquat 336 concentration. The presence of positively charged ammonium groups and some C-O and C=O bonding are believed from the interactions of Aliquat 336 and CTA. Based on the results, the optimal extraction for methyl orange achieved was 98 % with CTA electrospun fibers containing 10 wt.% at pH 2 and 10 ppm of initial concentration. Thus, it can be concluded that this electrospun has potential to remove dye from wastewater.

1. Introduction

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 [1]. 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 [2]. 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 resistance to free chlorine and biodegradation and its utilization as a membrane material has been



attempted over the last thirty years [3]. According to [4] CTA with its 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. 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 [5]. However, the removal of dyes using electrospun fibers is scarcely reported. Hence, this study will investigate the potential of CTA electrospun fibers incorporated with Aliquat 336 for the removal of methyl orange in aqueous solution.

2. Materials and method

2.1 Preparation of CTA-Aliquat 336 electrospun fibers

A total mixture of 600 mg 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 dichloromethane (DCM) and methanol (MeOH) with a ratio of 8:2 respectively. The total volume of solvent used was 10 mL. The mixtures were stirred continuously and vigorously until the solution became clear or homogenous. To start the electrospinning process, the polymer solution was placed in a plastic syringe attached with 23-gauge needle tip as shown in Figure 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.

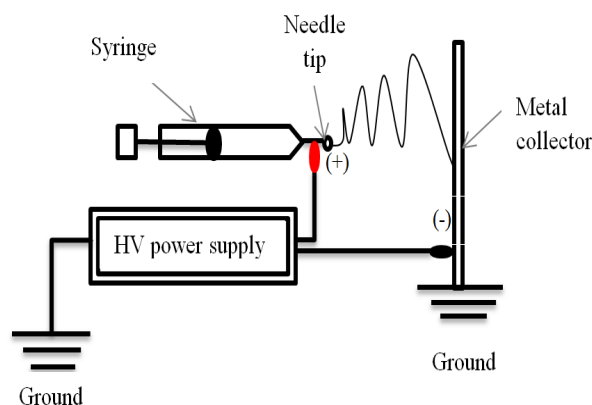


Figure 1. Schematic diagram of electrospinning process.

2.2 Extraction experiment

The extraction of methyl orange was 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. The electrospun fibers weighing 0.1 g, were put into the extraction solution containing 150 mL of 10 ppm methyl orange. The solution was stirred at 150 rpm at room temperature. At predetermined time intervals (0, 20 mins, 40 mins, 2 hrs, 3 hrs, 5 hrs and 24 hrs), 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 1; where C_i is the initial concentration and C_f is the final concentration.

$$\text{Extraction removal, } R (\%) = \frac{c_i - c_f}{c_i} \times 100\% \quad (1)$$

2.3 Membrane characterization

2.3.1 Fourier-transform infrared spectroscopy (FTIR) Analysis

The scanning for fourier transform infrared spectra (FTIR) analysis of the desired electrospun fibers were carried out in the range of 500 to 4000 cm^{-1} (8400S of Shimadzu). The FTIR was used to study the existence of functional group in CTA-Aliquat 336 electrospun fibers. Thus, different peaks were shown in the analysis.

3. Results and discussion

3.1 Effect of Aliquat 336 content

Generally, the extraction of methyl orange by Aliquat 336 is based on an ion exchange mechanism. The complex or ion-pair formed between the ion and the extractant was solubilized in the membrane and facilitates ion transport across the membrane. In aqueous solution, methyl orange becomes negatively charged (SO_3^-) after losing one positively charged atom. Aliquat 336 will then reacts as an ion exchanger forming a neutral ion pair with the methyl orange anion from the aqueous solution as described below:

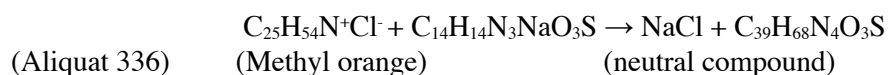


Figure 2 shows the removal of methyl orange using CTA-Aliquat 336 electrospun fibers at different Aliquat 336 compositions (5 to 40 wt.%). Based on Le Châtelier's principle, the increasing of extractant concentration will increase the reaction rate by increasing the rate of collisions [6]. The extraction capacity of membrane should be improved when higher Aliquat 336 content is used. However, as Aliquat 336 concentrations increased up to 15 wt.% (Figure 2), the percentage of extraction decreased. This is because as the extractant concentration increased, the viscosity in the electrospun fibers also increased which caused the limitation in the diffusion of the dye and the extractant complex into the membrane phase. Another possibility could be due to the saturation of extractant in the membrane that resulted a decrease in extraction capability by changing the structure of the membrane surface as reported in [7].

In another research where the range of extractant concentration used was between 0 to 20 wt.%, the optimum Aliquat 336 was found to occur at 10 wt.% which showed maximum reaction where a further increase of the extractant reduced the flux of the analyte passing through the membrane [8]. In this study, the CTA electrospun fibers containing 10 wt.% Aliquat 336 shows the highest percent of extraction (99.5%) after 5 hours. Thus, this electrospun fibers was considered as optimal and selected for further experiment.

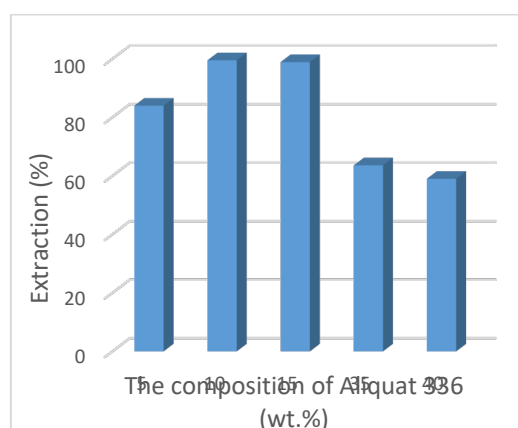


Figure 2. Effect of Aliquat 336 concentrations on the extraction of 10 ppm methyl orange after 5 hours.

3.2 Effect of pH in aqueous solution

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 [9]. In the aqueous solution, the acid dye (methyl orange) is first dissolved and the sulfonate group ($-\text{SO}_3\text{Na}^+$) of the acid dye are dissociated and converted to anionic dye ions [10]. Research by [11] 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 with 10 wt.% of Aliquat 336 was used and the initial methyl orange concentration was remained at 10 ppm. Based on the results in Figure 3, the extraction of methyl orange is more favourable at lower pH 2 than at higher pH. After 2 hours, the extraction of methyl orange reach more than 90% for all pH studied except for pH 10 which is only 57.8%. This is probably because at lower pH, the present of H^+ ion is relatively high. This increment will favour the Aliquat 336 which also has a positively charge functional group to attract negatively charged methyl orange [12]. In other words, alkaline solution showed lower extraction of methyl orange is due to the presence of excess OH^- ions racing with dye anions for the adsorption sites. It can be concluded that extraction of methyl orange dye onto electrospun fibers was influenced by the pH of the solution where acidic pH was more favourable. Thus, pH 2 was chosen for further study.

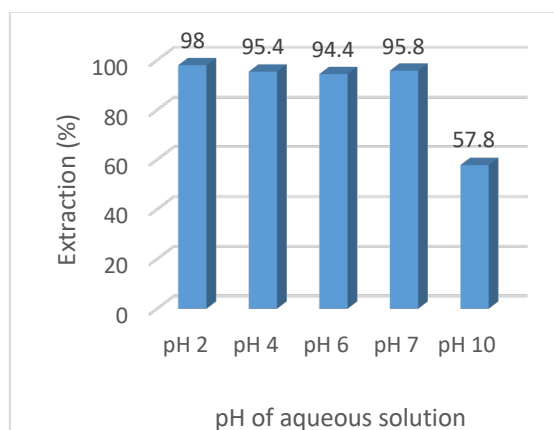


Figure 3. The extraction of methyl orange on the CTA-Aliquat 336 electrospun fibers with 10 wt.% Aliquat after 2 hours.

3.3 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 and the aqueous solution was set at pH 2. Based on Figure 4, the extraction of methyl orange was the fastest at the lowest dye concentration with 98 % of removal in 2 hours. However, after 5 hours, the extraction of methyl orange for all concentrations (10-50 ppm) reached more than 97%. No further increment was observed for 10 ppm as the fibers already saturated with dyes [13]. This result suggests that the CTA-Aliquat 336 electrospun fibers are capable to remove higher methyl orange concentration by increasing the contact time and this trend is similar as reported by [13].

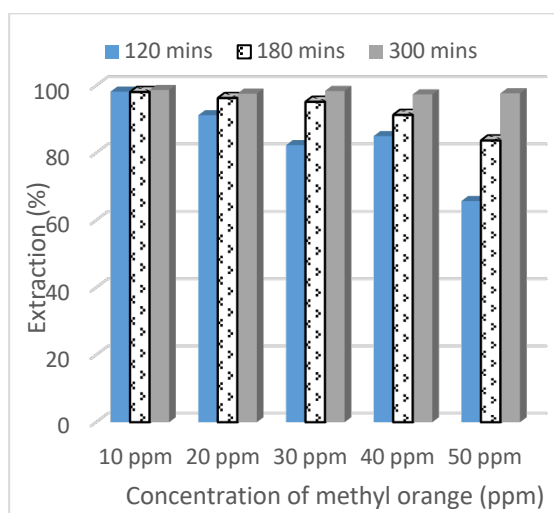


Figure 4. Effect of initial dye concentration on the removal of methyl orange on CTA-Aliquat 336 electrospun fibers with 10 wt. % Aliquat 336 at pH 2.

3.4 Fourier-transform infrared spectroscopy (FTIR) Analysis

The FTIR analysis was conducted from 500 to 4000 cm^{-1} wavelengths in order to determine the presence of functional group in CTA-Aliquat 336 electrospun fibers at different extractant concentrations (5, 10, 15, 35 and 40 wt.%). The spectrum of pure Aliquat 336 and CTA-Aliquat 336 electrospun fibers at various Aliquat 336 content was shown in Figure 5a and 5b respectively. Based on the results, all CTA-Aliquat 336 electrospun fibers showed similar trend of peaks (Figure 5a). The peak at 1738 cm^{-1} , is assigned to the stretching vibration of the C=O group and the presence of the bands at 1218 and 1035 cm^{-1} are correspond to the stretching vibration of the C-O bonds. These absorption bands are corresponding to the aliphatic acetate esters of cellulose. Meanwhile, the absorption band observed between 2800 to 3000 cm^{-1} became gradually broader as Aliquat 336 content increased in the electrospun fibers (Figure 5a). With reference to the pure Aliquat 336 FTIR spectra (Figure 5b), the strong absorption bands at 2923 cm^{-1} and 2851 cm^{-1} are assigned to are attributed to the quaternary ammonium groups which is in accordance with the chemical structure of Aliquat 336 [14]. The FTIR analysis results revealed the presence of the positively charged ammonium groups of Aliquat 336 and some C-O and C=O bonding that are believed from the interactions of cellulose triacetate (CTA). Based on the characterization using FTIR, the presence of quaternary ammonium group is stronger when Aliquat 336 concentration increased in the electrospun fibers.

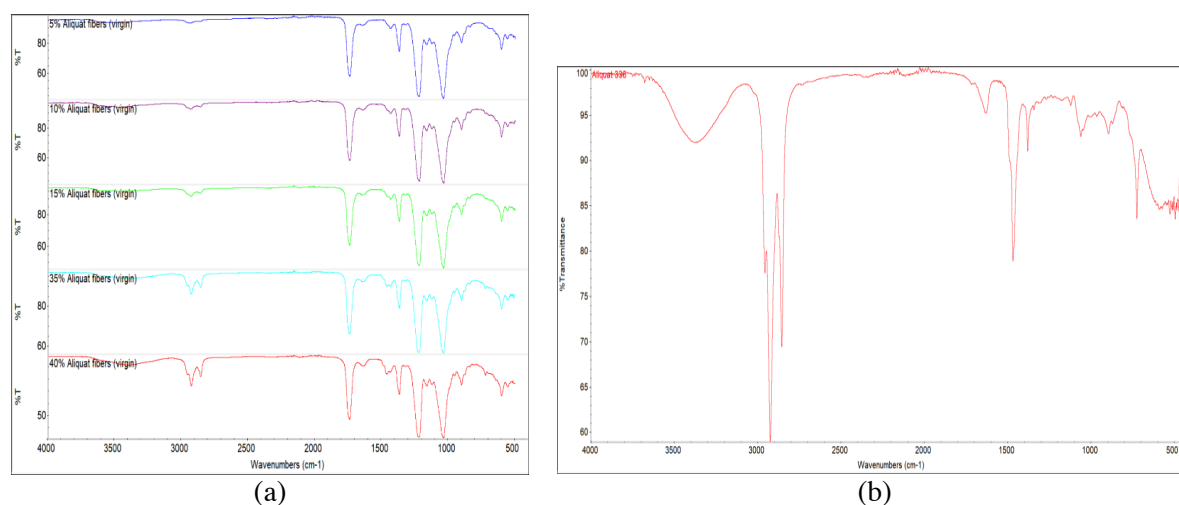


Figure 5. The FTIR spectra of (a) CTA-Aliquat 336 electrospun fibers at various Aliquat 336 content and (b) pure Aliquat 336.

4. Conclusion

In this study, the CTA-Aliquat 336 electrospun fibers were successfully fabricated. Results reported here indicate that extraction performance of methyl orange on CTA-Aliquat 336 electrospun fibers was affected by extractant content, pH of aqueous solution and initial dye concentrations. The optimum methyl orange extraction achieved was 98% at 10 wt.% of Aliquat 336 concentration, in pH 2 solution and 10 ppm of initial dye concentration. Thus, CTA-Aliquat 336 electrospun fibers prepared using electrospinning process has potential to be used as a filter to extract dye from synthetic wastewater.

Acknowledgement

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