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Cellulose triacetate Polymer Inclusion Membrane (PIM) for dye removal

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Abstract. In this study, polymer inclusion membrane (PIM) made from cellulose triacetate (CTA) and Aliquat 336 is used to extract congo red from aqueous solution. Important parameters such as Aliquat 336 concentration (0, 20, 30, 40 and 50 wt. %), pH of extraction solution (2, 4, 6, 8 and 10), concentration of congo red (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) were studied in order to optimize the extraction capacity. The CTA-PIMs was also characterized by Fourier Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) in order to determine the functional group and the morphological structure of the PIMs respectively. From this study, 87% of Congo red was successfully removed after 24 hours by using CTA-PIM with 50 wt.% Aliquat 336. The optimum condition was found to be at pH 2, with temperature and stirring speed of 30 °C and 150 rpm respectively.

1. Introduction

Congo red is an azo dye which is used in textile, paper, plastic and other products. This benzidine based anionic diazo dye can cause allergic reaction to human and becomes carcinogen when it is metabolized into benzidine [1]. The excessive use of dyes will produce considerable amount of coloured wastewater that affect the water quality. Water pollution by dyes will affect downstream beneficial use such as recreation, drinking water, irrigation activity and many others. Besides, the presence of dyes will interfere the penetration of sunlight into water and disrupt the aquatic ecosystem [2]. Different separation techniques such as adsorption and bioremediation have been used in the removal of dyes from the aqueous solution [3, 4]. However, these techniques have their limitations. For example, biological process with microorganisms cannot easily degrade the textile wastewater with refractory pollutants and need further process to refine the water [4]. Meanwhile, the regeneration of activated carbon for adsorption of dyes is chemically and thermally expensive [1].

Over the last five decades, studies on polymer inclusion membrane (PIM) for metals ions removal has gained popularity due to its flexibility, high selectivity and cost effective compared to conventional method such as ion exchange and liquid-liquid extraction [5]. PIM is usually made from cellulose triacetate (CTA) or poly (vinyl chloride) (PVC) as a base polymer, a carrier and/ or plasticizer. The base polymer provides mechanical strength for the membrane whilst, plasticizer and carrier provide elasticity and enables the diffusion of targeted species into the PIM respectively [6].

Until today, many studies have shown promising and successful of PIMs in removing various metal ions [5, 7-9]. However, study of PIM for dye removal is still new and scarcely reported. Therefore, this study aims to investigate the potential of CTA based PIM using Aliquat 336 as a carrier for congo red removal. The composition of carrier and other parameter that affect the removal efficiency of congo rate such as pH, dye concentration, stirring speed and temperature have been optimised. In addition, the surface morphology and functional group of CTA-PIMs were also studied by using FTIR and SEM.

2. Methodology

2.1. Materials

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 a solvent. Congo red purchased from Aldrich was used to prepare stock solution.

2.2. Preparation of CTA-PIM

CTA-PIM was prepared by dissolving CTA and Aliquat 336 at different concentration (0, 20, 30, 40 and 50 wt.%), in 10 mL of DCM and MeOH with a ratio of 8:2. Each mixture contained a combined CTA and Aliquat 336 weight of 500 mg. The mixture was stirred until the solution become homogenous. Then, the solution was poured into petri dish and covered with filter paper for overnight to let the solvent slowly evaporates. The solvent was allowed to evaporate forming a transparent CTA-PIM. Later, the CTA-PIM was peeled and stored in dry condition for further experiment.

2.3. The extraction of dye solution

Extraction study was conducted in bath mode. The CTA-PIMs at different Aliquat 336 concentrations were put into a different conical flask containing 50 mL of 10 ppm congo red each. At first, the pH of dye solution was set neutral and the temperature of the solution was maintained at room temperature (27 °C). The dye solution was stirred continuously at speed rate of 150 rpm. Then, 2 mL of sample was taken at specific time interval for congo red analysis using UV-Vis spectrophotometer. The removal efficiency of congo red was calculated using Eq. 1. From the results, the CTA-PIM with the best Aliquat 336 concentration for congo red removal was determined.

$$Removal\ efficiency\ (\%) = \frac{C_i - C_p}{C_i} x\ 100\% \qquad (1)$$

Where;
C_p and C_i are the permeate and initial absorbance of congo red (abs) respectively.

2.3.1 Optimization of other parameters. The removal efficiency of congo red was investigated by using the same procedure as mention in section 2.3. The procedure was repeated but using different pH (2, 4, 6, 8 and 10), dye concentration (2, 4, 6, 8 and 10 ppm), temperature (30, 40, 50 and 60 °C) and stirring speed (150, 200, 250, 300 and 350 rpm).

3. Results and discussion

3.1 The study of dye extraction

3.1.1 Effect of carrier concentration. The extraction of congo red using CTA-PIMs with different Aliquat 336 concentration was shown in Figure 1. CTA-PIM without Aliquat 336 showed negligible of congo red extraction, suggesting that the transport of congo red was fulfilled by the carrier. In general, the extraction of congo red by Aliquat 336 is based on an ion exchange membrane. Aliquat 336 reacts as an ion exchanger forming an ion pair with a dye anion complex from the aqueous solution. Congo red is an acid dye and usually unites with positively charge ion to form a complex. The negative charge present in the congo red attract to the positively charge of Aliquat 336 (NR_4^+) present in CTA-PIM to form neutral ion pair complex ($CR\text{-}NR_4^+$) as shown in Equation 2. Based on the Figure 1, the removal efficiency of congo red increased as the Aliquat 336 concentration in CTA-PIM increased. From this study, CTA-PIM with 50 wt.% Aliquat 336 has the highest removal efficiency and was used in further experiments.

$$Dye^- aq + [\ NR_4^+] \leftrightarrow [Dye\ (NR)] + H^+ \qquad (2)$$

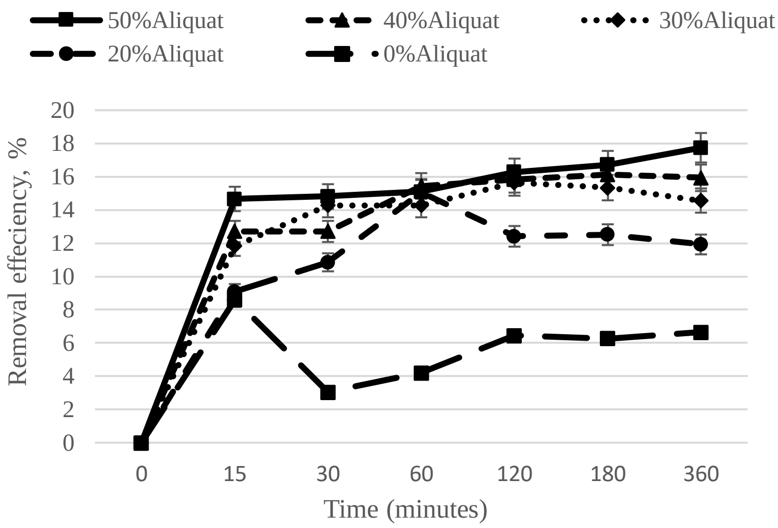

Figure 1. Effect of Aliquat 336 concentration on the removal of Congo red on CTA PIMs.

3.1.2 Effect of pH. pH is one of the important parameters that affects the dye stability as well as surface characteristic of adsorbents thereby facilitating its removal efficiency [10]. Figure 2 shows the effect of pH on the removal of congo red using CTA-PIM with 50 wt.% Aliquat 336 concentration. Based on the figure, the removal of congo red was better in acidic solution than in alkaline. Since congo red is an acid dye with negatively charge, a decrease in pH will increase the concentration of H^+ in the solution. The increment of H^+ in the solution will not compete with the negatively charge of congo red to bind with the Aliquat 336 which has a positive charge functional group [10]. On the other hand, when the pH increased and become alkaline, more OH^- was present and started to compete with the dye anions for the adsorption sites. Thus, the removal efficiency decreased. This finding was similar with study reported by Ozmen and Yilmaz [11], where the extraction of congo red by using cyclodextrin and starch-based polymers was the best in acidic solutions compared to alkaline.

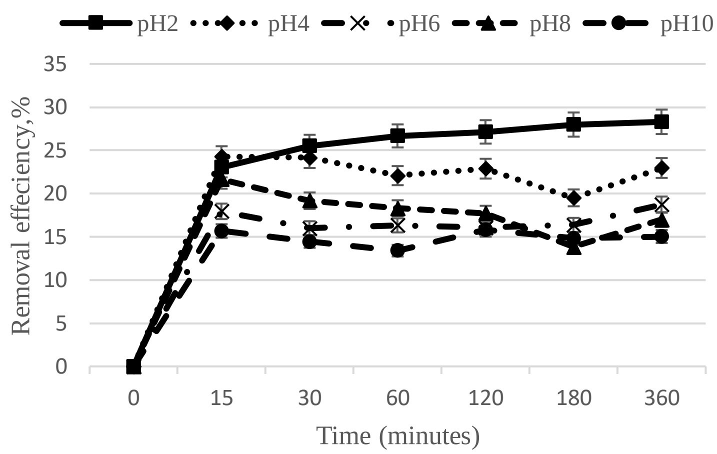

Figure 2. Effect of pH on the removal of 10 ppm congo red on the CTA-PIMs with 50 wt.% Aliquat 336.

3.1.3 Effect of dye concentration. The variation of dye concentrations ranging from 2 to 10 ppm was done and the results are shown in Figure 3. Based on the results, the removal of congo decreases 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 probably due to membrane saturation and lower efficiency of membrane area [12]. This behaviour has also been reported in other studies using PIM with different type of carrier [13,14].

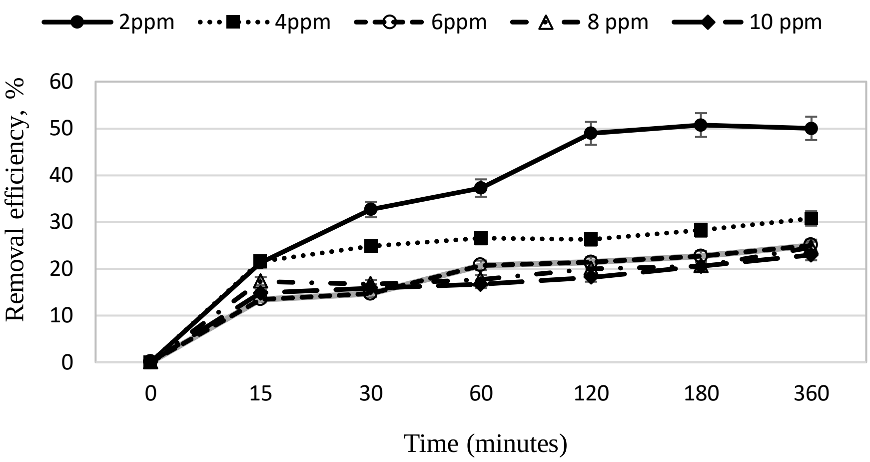

Figure 3. Effect of initial dye concentration on the removal of Congo red on CTA PIMs with 50 wt.% Aliquat 336 at pH 2.

3.2 Membrane characterization

3.2.1 Fourier-transform infrared spectroscopy (FTIR) analysis. FTIR spectra characterization was used to determine the presence of functional group in CTA-PIMs. The spectra of CTA-PIMs without Aliquat 336, CTA-PIMs with 50 wt.% Aliquat 336 and CTA-PIMs with 50 wt.% Aliquat 336 after extraction were shown in Figure 4, 5 and 6 respectively. Based on Figure 4, the Infra-red (IR) spectrum of CTA-PIMs 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 at 1732.89 cm^{-1}. Meanwhile, 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 [12] as shown in Figure 5. These peaks do not exist in CTA-PIM without Aliquat 336 (Figure 4). Figure 6, shows a peak at 3397.64 cm^{-1} which is due to the present of –OH group from the congo red. Since –OH group is polar, therefore it allows the hydrogen bonding between Aliquat 336 and congo red. A short peak at 1457.9 cm^{-1} indicate $–CH_3$ asymmetric deformation vibration. This deformation is related to hydrogen bonding between reaction of Aliquat 336 and congo red.

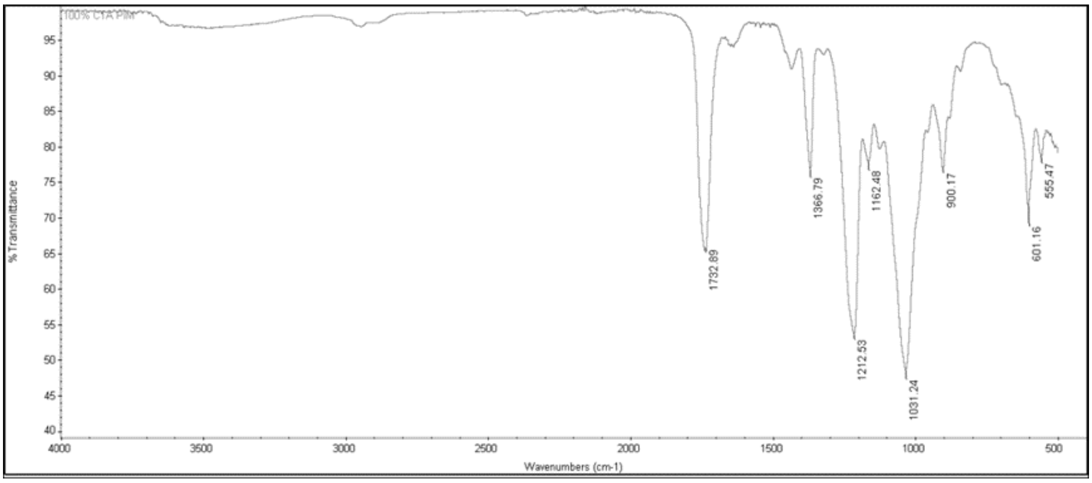

Figure 4. FTIR spectrum of CTA-PIM without Aliquat 336.

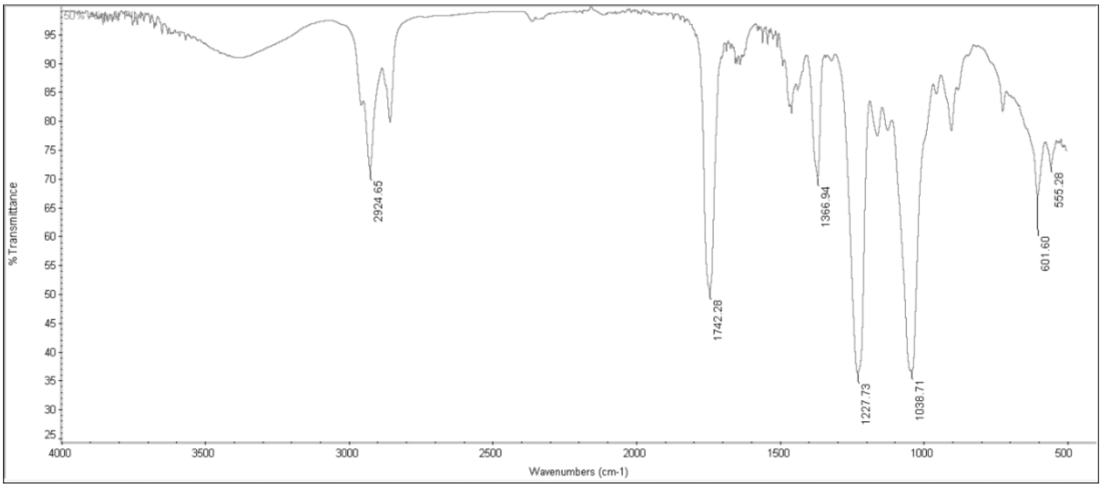

Figure 5. FTIR spectrum of CTA-PIM with 50 wt.% Aliquat 336 before the dye extraction.

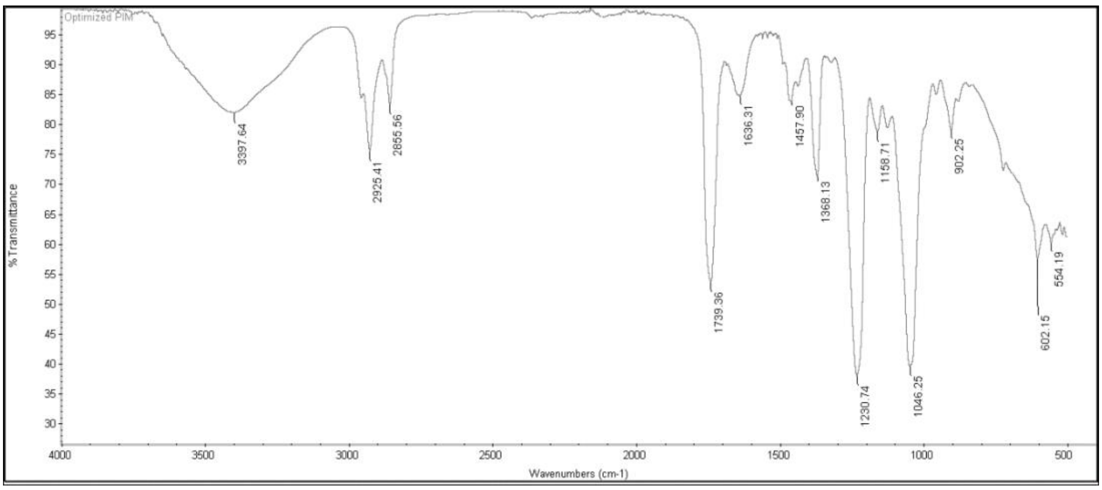

Figure 6. FTIR spectrum of CTA-PIM with 50 wt.% Aliquat 336 after the dye extraction.

3.2.2 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 7. CTA-PIM without Aliquat 336 shows a uniform structure with no apparent pores (Figure 7a). As Aliquat 336 content increase from 20 to 40 wt.%, the surface become rougher compared to CTA-PIM without Aliquat 336. Still, no significant pores were observed (Figure 7b-d). When Aliquat 336 content reach 50 wt.% (Figure 7e), pores structure was observed. The absence of significance pore structure in CTA-PIM containing less than 50 wt.% Aliquat 336 is probably due to extractant molecules 'entangled' with the polymer chain as reported by Xu et al. [15] where the extractant have low activity and mobility through the polymer matrix. However, the structure of CTA-PIM after the dye extraction was cracked (Figure 7f). Besides, there are no visible pores as observed in CTA-PIM before the extraction study (Figure 7e).

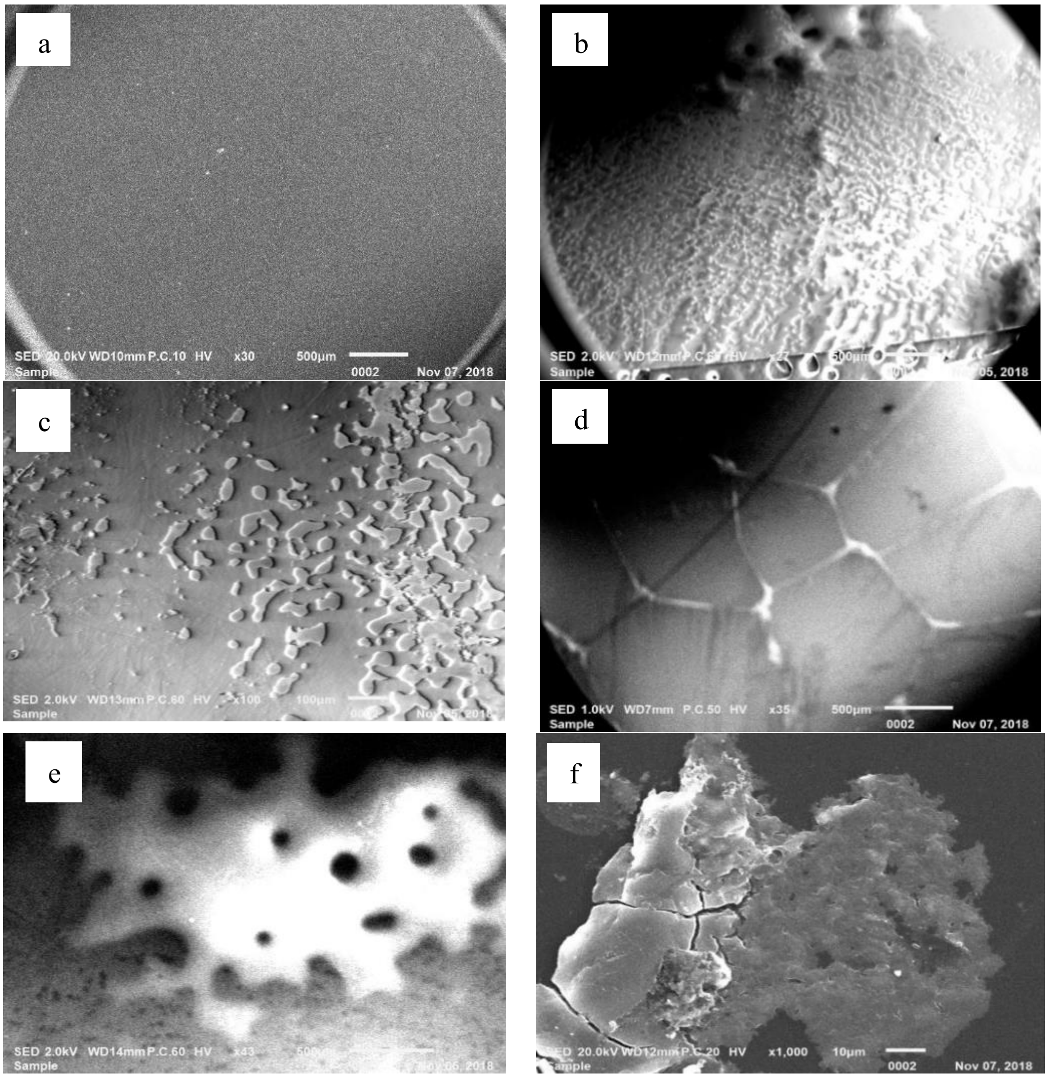

Figure 7. The surface morphology of CTA-PIMs: (a) without Aliquat 336, (b) with 20 wt.% Aliquat 336 before congo red extraction, (c) with 30 wt.% Aliquat 336 before congo red extraction, (d) with 40 wt.% Aliquat 336 before congo red extraction, (e) with 50 wt.% Aliquat 336 before congo red extraction and (f) with 50 wt.% Aliquat 336 after congo red extraction.

4. Conclusion

In this preliminary study, the potential of CTA-PIM in removing congo red was investigated. The removal efficiency depends on many parameters such as carrier concentration, pH and dye concentration. Under optimum conditions, 50% of congo red (2ppm) can be removed within 2 hours using CTA-PIM incorporated with 50 wt.% Aliquat 336. Although the removal efficiency is not satisfying yet, this can be further improved by using larger surface membrane area and longer contact time (ie 24 hours). Besides, future studies on different type of dyes and its suitability with carrier can be conducted. In addition, actual dye wastewater can be used to determine the real potential of CTA-PIM in treating dyes.

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