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# SYNERGISTIC EXTRACTANT FOR EXTRACTION OF REMAZOL ORANGE 3R IN LIQUID MEMBRANE FORMULATION

(Pengekstrak Sinergistik untuk Pengekstrakan Remazol Orange 3R dalam Formulasi Membran Cecair)

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**Abstract**

Currently, various synthetic dyes are used in the textile industry and a lot of non-bonded dyes are released into the wastewater; increasing its toxicity and carcinogenicity. Liquid membrane process is one of the potential methods to eliminate these unwanted particles from the wastewater. The most crucial part of the liquid membrane process is its formulation; especially the extractant or carrier. In order to find a suitable extractant, liquid-liquid extraction process was carried out. The effect of synergistic extractant to extract the Remazol Orange 3R reactive dyes in a shorter time and at a lower concentration of extractant was investigated in this study. Several parameters have been studied such as extractant type, extractant concentration, synergist extractant type and synergist extractant concentration. The results show that, Remazol Orange 3R reactive dyes were extracted by tridodecylamine (TDA) as a base and trioctylamine (TOA) as a synergist extractant. Meanwhile, the salicyclic acid (SA) was used to protonate the TDA and TOA, and cooking palm oil was used as a diluent. The performance of extraction of reactive dyes at the 0.1 M concentration of extractant was 70% when synergistic system was applied compared to single extractant which was only 50% of the dyes have been extracted. Therefore, the synergistic extractant has a potential to be further utilised in liquid membrane studies on the extraction of reactive dyes.

**Keywords:** liquid membrane, liquid-liquid extraction, synergistic extractant, synergist, extractant

**Abstrak**

Pada masa ini, pelbagai pewarna sintetik digunakan dalam industri tekstil dan banyak pewarna tanpa terikat dilepaskan ke dalam air sisa sehingga meningkatkan kadar toksik dan karsinogenik. Proses membran cecair adalah salah satu kaedah yang berpotensi untuk menghapuskan zarah-zarah yang tidak diingini dari air sisa. Formulasi membran adalah bahagian paling penting dalam proses membran cecair; terutamanya pengekstrak atau pembawa. Bagi mencari pengekstrak yang sesuai, proses pengekstrakan cecair-cecair telah dijalankan. Kesan sinergis pengekstrak untuk mengekstrak pewarna reaktif Remazol Orange 3R dalam masa yang lebih singkat dan pada kepekatan ekstrak yang lebih rendah telah dikaji. Beberapa parameter telah dikaji seperti jenis pengekstrak, kepekatan pengekstrak, jenis pengekstrak sinergis dan kepekatan pengekstrak sinergis. Keputusan menunjukkan bahawa, pewarna reaktif Remazol Orange 3R diekstrak oleh tridodekilamina (TDA) sebagai asas dan trioktilamina (TOA) sebagai sinergis. Sementara itu, asid salisiklik (SA) digunakan untuk protonate TDA dan TOA, dan minyak kelapa sawit digunakan sebagai pelarut. Prestasi pewarna reaktif yang diekstrak adalah sebanyak 70% apabila sistem sinergistik digunakan berbanding dengan hanya satu pengekstrak digunakan yang hanya 50% daripada pewarna telah diekstrak pada kepekatan 0.1M pengekstrak. Oleh itu, pengekstrak sinergis mempunyai potensi untuk digunakan dalam kajian membran cecair pada pengekstrakan pewarna reaktif dimasa hadapan.

**Kata kunci:** membran cecair, pengekstrakan cecair-cecair, pengekstrak sinergistik, sinergis, pengekstrak

## Introduction

Textile wastewater has massively concerned by the public and the government due to the colour and toxic substances in dye wastewater [1]. It has been approximated that more than 100,000 commercial dyes with over 7 x $10^5$ tons are produced annually [2]. Moreover, around 10-25% of textile dyes are lost during the colouring process and about 2-20% of them are directly discharged as an aqueous effluent [3]. The dyes lost in the textile industry pose a major threat to wastewater sources where these effluents contain high concentrations of both organic and inorganic compounds that can be considered as pollutants, which are mainly from chemical textile finishing processes [4].

Numerous conventional methods have been applied in the textile industry on the removal and recovery of dyes, such as biological [5], liquid-liquid extraction, adsorption, steam distillation and chemical oxidation [6]. Conventional methods possess their own disadvantages including high operating costs, time consuming, and production of secondary pollutants. At the present time, liquid membrane (LM) technology especially emulsion liquid membrane (ELM) technique is anticipated to be the promising method to encounter the drawbacks of conventional methods. This technology has been proven beneficial in various disciplines such as inorganic chemistry, chemical engineering, biomedical engineering, biotechnology, analytical chemistry, and physiology. Generally, a membrane may be defined as a semi permeable barrier which selectively allows a solute to pass through from the external to the internal phase which is dependent on the molecular weight, ionic charge, or type of extractant reacted on it, on top of preventing the mixing of external and internal phase [7]. They can be either an aqueous (W/O/W emulsion) or an organic solution (O/W/O emulsion). Ensuring an effective removal and recovery of dyes through LM process should take into account the suitable carrier, diluent and stripping agent. Previous studies indicated that various petroleum-based substances such as heptane [8], pentanol [9] and kerosene [10, 11] were used as diluent in LM formulation. However, petroleum based LM is non-environmental friendly and can potentially cause other pollutions. Benign based LMs such as coconut oil and palm oil have been proved as suitable diluents in the extraction of chromium performed by Othman et al. [12]. By following their footsteps, benign based ELM has been used in this study to replace the petroleum based ELM and its efficiency and stability on the extraction of reactive dyes have been studied.

Currently, single extractants have been used but they are famous to be time consuming. Thus, a synergistic extractant has been proposed to increase the extraction percentages, which is mixed up by two extractants at low concentration [13]. One molecule would transfer ions from aqueous to membrane phase in order to satisfy both solvation and co-ordination sites of the cation and neutralise charges, while another extractant would serve to replace the water. Synergistic extraction with a specified ration of extractants in the membrane will boost the efficiency of ions transport [14], selectivity [15] and extraction process [16]. The synergistic extractant can be synthesised through the following possible combinations of extractants such as acidic and neutral extractants, two acidic extractants, two neutral extractants, anionic and neutral extractant, cationic and ionic extractant and two anionic extractants [17]. The addition of two extractants into the membrane has had positive results on improving the rate of extraction and the selectivity of solute ions transport.

This paper presents a research to formulate the liquid membrane using synergistic extractant and to determine the optimum extractant concentration of the process. Thus, to fulfil this objective, several parameters such as type of base extractant, concentration of base extractant, type of synergist extractant and concentration of synergist extractant have been investigated.

## Materials and Methods

Emulsion liquid membrane consists of four main components; diluents, extractant, surfactant and stripping phase. The membrane phase used is a homogeneous mixture of cooking palm oil (BURUH) as diluents, Tridodecylamine (TDA) (Merck), Trioctylamine (TOA) (Merck), Aliquat 336 (Merck), Trioctylephosphine oxide (TOPO) (Sigma-Aldrich) and Tributyl phosphate (TBP) (Sigma-Aldrich) as extractants or synergist extractants and salicylic acid (SA) for TDA and TOA protonation. The chemicals for all reagents have been obtained from the manufacturers.

Remazol Brilliant Orange 3R reactive dye has been obtained from NOZI Batik SDN BHD and has been used as an external phase solution. The dye solution is prepared by dissolving the dye in distilled water. All chemicals were of analytical grade and used without further purification.

**Liquid membrane component selection**

Liquid membrane formulation comprised of three main components; diluent, base and synergist extractant. The organic phase is a homogeneous mixture of diluents, base extractant phase, and synergist extractant. In this research, it has been decided that palm oil would be used as a diluent due to its non-toxic and biodegradable properties.

Single extractant extraction was conducted as a basis for the synergistic extractant. Liquid-liquid extraction experiment was started by mixing an equal volume (10 mL) of synthetic reactive dye solution and organic solution that consists of various concentrations of extractant in palm oil as a diluent in a 25 mL conical flask. The mixing process was carried out using a mechanical shaker at 320 rpm for 1 hour to perform the extraction. The mixture was then poured into a separating funnel which was then left for 15-30 minutes for phase separation. The treated aqueous phase was separated from the organic phase through gravity settling. The aqueous phase was analysed using a UV-spectrometer at 494 nm to measure the percentage of extraction.

**Synergistic extractant of liquid membrane formulation**

In order to formulate the synergistic extractant, the mixture of base extractant and synergist extractant was tested. The single extractant was mixed with another extractant as a synergist by the volume percentage (1-10 v/v%). The liquid-liquid extraction (LLE) process was conducted to determine the effect of synergistic extractant on extraction percentages. During the extraction process, a sample of aqueous solution underwent a UV absorbance test every 10 minutes for an hour to check the percentages of dye extraction.

The synergistic effect can be quantified through the synergistic coefficient (S.C) which can be defined using equation 1:

$$S.C = \frac{D_{mix}}{D_{synergist} + D_{extractant}} \quad (1)$$

where $D_{extractant}$ and $D_{synergist}$ are the distribution ratios obtained using each extractant separately, and $D_{mix}$ represents the distribution ratio with the mixture. If the S.C is more than 1, the synergistic effect has occurred but if S.C is less than 1, there is no synergistic effect.

## Results and Discussion

**Effect of extractant type**

The extraction performance of different types of extractant on Remazol Orange 3R extraction was studied and the results are presented in Figure 1. The results show that high percentages of extraction were obtained from basic extractants (TDA, TOA, Aliquat 336), and very low to negligible percentages were obtained from neutral extractants (TOPO and TBP) and acidic extractant (D2EHPA). This is because neutral extractants have no charges to extract dyes, and an acidic extractant has the same charge as the dye which makes them repel each other. Therefore, Remazol Orange 3R which is an acidic dye with a positive charge can be extracted using extractants of the opposite charge, which is the basic extractants.

The efficiency of basic extractant can be arranged in the following order: TOA>TDA>Aliquat 336. TOA has greater polarity [18, 19] compared to TDA solely due to the difference in the number of $CH_2$ attached to their respective nitrogen atoms. TDA has a higher number of $CH_2$ attached on its nitrogen atom $(CH_2)_{11}$ compared to that of TOA $(CH_2)_7$. This is due to the basicity of TOA that is stronger than that of TDA. Therefore, dyes can easily substitute the $CH_2$ group of TOA. As for Aliquat 336, $Cl^-$ ions reacted with $Dyes^+$ to form a precipitate. The solid phase in the LLE process cannot be considered because it will affect the extraction phase. Hence, TOA was chosen as the most effective extractant for Orange 3R dye extraction. Figure 2 shows the chemical structure for TDA and TOA.

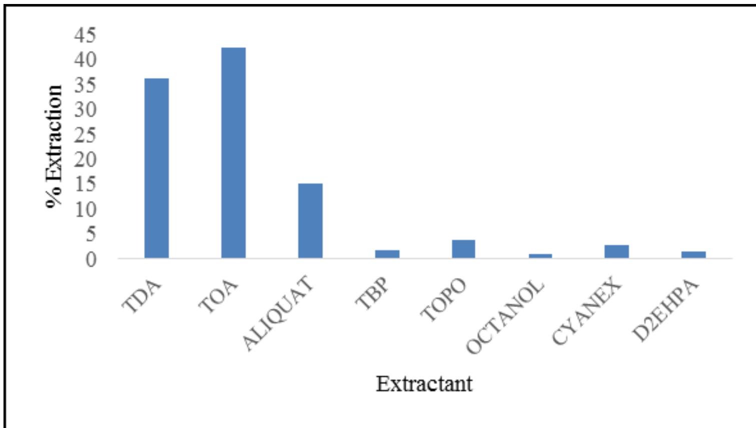
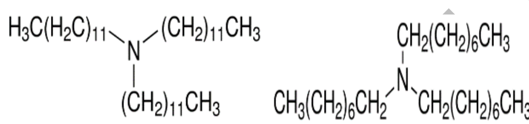



Figure 1. Effect of extractant type (experimental condition: concentration of each extractant = 0.1 M, shaker speed = 320 rpm, time = 1 hour, volume or organic = 10 mL, volume of dye = 10 mL)




(2a) TDA (2b) TOA

Figure 2. Chemical structure for TDA and TOA

**Effect of extractant concentration**

The extraction performance of different extractant concentrations was studied in the range of 0.04 to 0.2 M. Figure 3 (a and b) shows the effect of different concentrations of TDA and TOA on the extraction of Remazol Orange 3R in one hour. The results show that the percentage of extraction increased significantly as concentration increases. The maximum extraction percentages for both extractant were 51% at 0.16 M for TDA and 78% at 0.2 M for TOA.

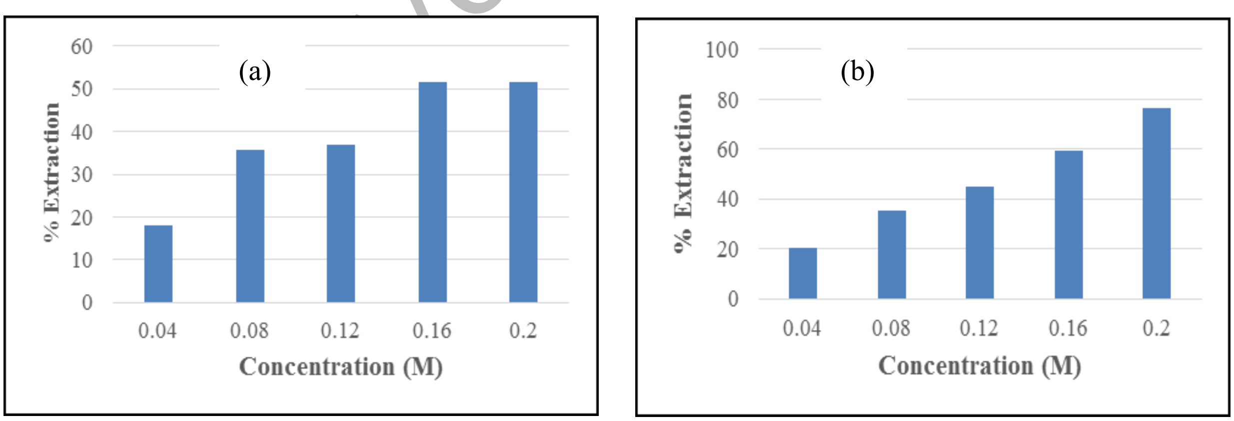



Figure 3. Effect of extractant concentration (experimental condition: extractant = (a) TDA and (b) TOA, shaker speed = 320 rpm, time = 1 hour, volume or organic = 10 mL, volume of dye= 10 mL)

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According to Le Châtelier's principle, increasing the extractant concentration will increase the reaction rate by increasing the rate of collisions [20]. Based on the results obtained, the extraction percentage increased due to increasing extractant concentration. This condition created the potential gradient for both feed and organic phases which stimulated the complexation of dye-extractant [21]. TOA shows higher potential for the extraction of Remazol Orange 3R compared to TDA.

**Selection of synergist extractant type**

Synergistic extraction of Remazol Orange 3R was conducted in the binary extractant system by varying the synergist extractant (TDA and Aliquat 336 (basic), TBP and TOPO (neutral), and D2EHPA (acidic)) with TOA as the base extractant. The total volume of extractant and the concentration of base and synergist extractant were set at 10 mL and 0.1 M, respectively. As shown in Table 1, at 0.1 M mixture concentration, around 20% increment was obtained for TOA-TDA. Other combinations also showed the increasing of extraction performance.

Table 1. Effect of synergist extractant type

| Extractant | % Extraction | Synergistic Coefficient |
|---|---|---|
| TDA | 51 | 0.8 |
| ALIQUAT | 28 | 0.4 |
| TBP | 29 | 0.5 |
| TOPO | 9 | 0.1 |
| D2EHPA | 0 | 0 |

Experimental condition: base extractant = TOA, concentration of base and synergist extractant = 0.1 M, agitation speed = 320 rpm, time = 1 hour, volume of organic = 10 mL, volume ratio base: synergist = 1:1, volume of dye = 10 mL

In addition, the results also show that when 0.1 M TDA was used as a single extractant, 36% of dyes was extracted and when it was synergised with TOA, the extraction increased around 15%. As expected, there was a significant enhancement in dyes transport across the organic phase in the presence of a synergist extractant in the organic phase as compared to that without the synergist extractant. This shows that the combination of these two extractants have potential to be a synergistic system at the optimum ratio of its concentration.

**Effect of synergist extractant concentration**

Table 2 shows the extraction efficiency of TOA and synergist TDA with varied molar ratio on the extraction of Remazol Orange 3R. The experimental condition was set up at a total organic concentration of 0.2M, volume ratio of 1:1 and with TDA: TOA molar ratio of 0.04:0.16, 0.08:0.12, 0.12:0.08 and 0.16:0.04.

Table 2. Effect of synergist extractant concentration

| Mole Percentage of TDA (%) | % Extraction | Synergistic Coefficient |
|---|---|---|
| 20 | 51 | 0.63 |
| 40 | 50 | 0.73 |
| 60 | 49 | 0.85 |
| 80 | 69 | 1.7 |

Experimental condition, shaker speed = 320 rpm, time = 1 hour, volume of organic = 10 mL, volume of dye = 10 mL)

The results display that the percentage of dye extraction increased from 51 to 69% as the mole percentage of TDA increased from 20 to 80%. Ultimately, the synergist coefficient also increased, from 0.63 to 1.7. According to Guezzen and Didi [23], the synergistic coefficient should be greater than 1, then synergic effect will occur. If the synergistic coefficient is lower than 1, antagonistic effect will take place instead. In this experiment, only TDA at 80% mole percentage had a synergistic effect, while the rest experienced antagonistic effect. Compared to TDA as a single extractant, the percentage of extraction increased almost 20% with the presence of TOA. Therefore, it can be concluded that the TOA and TDA function as a synergist and base extractant, respectively.

## Conclusion

Synergistic extractant for the extraction removal of Remazol Orange 3R was formulated using liquid-liquid extraction process. Base extractant, TDA and synergist extractant, TOA were chosen as a suitable combination of synergistic extractants. The extraction efficiency was improved from 51% to 69%. The results show that the synergistic extractant of TOA and TDA has potential to extract dyes under lower extraction time and concentration and would be usable in LM formulation for textile dye extraction.

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