

Synergistic Formulation for Turquoise Blue Dye Extraction Using Mixed Trioctylamine/Cyanex 302 in Liquid-Liquid Extraction System

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ABSTRACT

This study presents the synergistic liquid-liquid extraction (LLE) of turquoise blue dye through the formulation of synergist extractants in the organic liquid phase, their extraction mechanism, as well as the selection of the best stripping agent. The results showed that a single extractant provides 60% extraction performance at a concentration of 0.1 M. The extraction has increased remarkably to 94% using a synergistic system containing 0.08 M trioctylamine (TOA) and 0.01 M dialkyl phosphinic acid (Cyanex 302) with the highest synergistic coefficient of 4.77. Meanwhile, sodium hydroxide (NaOH, 0.1 M) was chosen as the best stripping agent where almost 100% of stripping efficiency was obtained. Thus, the synergistic formulation containing TOA and Cyanex 302 in LLE offers great potential for the high efficiency of dyes removal from the textile industry effluent.

Keywords: Liquid-liquid extraction, synthetic dye, synergistic formulation, textile effluent, extraction mechanism

1. INTRODUCTION

Dyes is a material that is used to transmit color to paper, textiles, leather, plastics, and other materials so that the coloring is not easily altered by washing, heat, light, or other factors to which the material is likely to be exposed. Dyes are used in a large amount in the textile industry to produce various types of patterns on the cloth with a variety of colors. Besides producing attractive cloth, the usage of dyes also contributed to water pollution. This is due to the discharge of dye along with a significant amount of wastewater generated during the washing and rinsing process. The effluent discharge may be harmful as it contains a lot of chemical compositions [1-3]. The polluted wastewater may threaten the algae and aquatic lives and caused the ecosystem to be unstable. Turquoise blue is one of the extensively used dyes due to its fantastic color and water solubility [4]. It is highly mutagenic because of its metal content and has greater resistance to degradation by existing treatment methods [5, 6]. On the other hand, if the used dye is recovered appropriately, it could be reused to reduce the implications of exploiting new sources of supply. To date, various dye wastewater treatment methods have been reported and can be classified into physical, radiation, chemicals, and biological [7-9]. All the treatments have been conducted for years to ensure that living organisms can live with a good quality environment. Physical treatment methods include adsorption on activated carbon [10, 11],

multiwalled carbon nanotubes [12], and metal-organic framework [13]. Gamma radiation has been reported as a favorable treatment for the dye wastewater as the radiation effect is very strong and the dye molecules can be degraded efficiently [14]. Chemical treatment methods have been widely studied such as oxidation, electrochemical oxidation, and precipitation [15-17]. Some of the biological methods that were found in the literature are aerobic [18], anaerobic [19], and enzyme treatment [20]. However, these methods have certain drawbacks such as sludge creation, longer contact time, a large amount of reagent requirement, and uneconomical.

Liquid-liquid extraction (LLE) is one of the simple and practicable alternative methods for the treatment of dye wastewater as it offers high extraction efficiency, high throughput, ease of operation, and low energy requirement [21-23]. The concept of LLE is that a solute can distribute itself between two immiscible solvents in a certain ratio. The extraction performance of this system relies on the solute mass transfer rate. It tends to be advantageous whenever the solvent has a high affinity for the solute that cannot be easily removed by direct separation techniques. In certain cases, an extractant is introduced to the system to facilitate the separation process. For a successful extraction process, sufficiently high loading capacity and high equilibrium selectivity are required, as well as a high extraction rate.

The disadvantages LLE process always related to the solvent/organic liquid and extractant cost. For instance,

high concentrations of extractants are used in conventional technologies. A previous study reported a high concentration of single extractants was required due to the small loading capacity of the solute in the organic phase [24, 25]. One of the solutions to cater to this problem is through the introduction of a synergist extractant system. Synergistic refers to positive interaction when a combination of two or more substances show a higher mechanism than the sum of the single extractant [26]. Several types of extractant mixture can be used to create synergistic extraction, such as two acidic, two neutral, two basics, anionic-cationic, neutral-anionic, etc. For example, Rahman et al. [21] used a mixture of acid-base extractants for synergistic extraction of Orange 3R and achieved 95% of extraction. In another study, vanadium was successfully extracted using a mixture of acidic and neutral extractants [27]. This combination of commercially available extractants is more advantageous compared to the time-consuming development of new reagents.

To date, no study has been found regarding the extraction of turquoise blue using a synergistic LLE process. Hence, this study attempted to find synergistic organic liquid formulation using various types of extractant mixtures comprising acidic, neutral, and basic extractants. The concentration effect of base and synergist extractants in the mixture and the extraction mechanism was investigated. Besides, a few potential stripping agent types were studied as well.

2. EXPERIMENTAL

2.1. Materials

The turquoise blue dye was acquired from the Nozi Batik company in Terengganu, Malaysia. Bis-2-Ethylhexyl phosphoric acid, D2EHPA (95% purity), trioctylamine, TOA (98% purity), Tributylamine, TBA (99% purity), sodium carbonate powder, Na_2CO_3 (99% purity), and sulphuric acid, H_2SO_4 (99% purity) were purchased from Merck. Di-2,4,4,-trimethylpentyl mono-thio-phosphinic acid, Cyanex 302 (99% purity), tributyl phosphate TBP (99% purity), and kerosene (78% purity) were obtained from Sigma Aldrich. Sodium hydroxide pellet, NaOH (98% purity) were obtained from J.T. Baker. All reagents were of analytical grades and used without further purification one obtaining from suppliers.

2.2. Synergistic Formulation of Extractants in LLE System

The aim is to select the best combination of the base and synergist extractants to extract turquoise blue from the feed phase solution. The extraction process was initiated by stirring an equal volume (100 mL) of aqueous feed solution (50 ppm turquoise blue) with an organic solution (0.1 M extractant in kerosene). Different types of extractants such

as basic (TOA and TBA), acidic (D2EHPA and Cyanex 302), and neutral (TBP) were tested as a basis in developing the synergistic extraction system. The extraction was carried using a bench type extractor as shown in Figure 1. The solution was agitated at 320 rpm for 1 hour [21]. An amount of 10 mL samples was taken every 15 minutes and allowed to settle in the separation funnel via gravity settling. The concentration of turquoise blue in the aqueous feed phase at the bottom of the funnel was determined using a UV/Vis spectrophotometer (JENWAY 7305, UK) at 635 nm wavelength (λ) [1].



Figure 1 Equipment set-up for LLE process

The extractant with the highest extraction efficiency was selected as a base extractant and mixed with other extractants to formulate the synergistic organic liquid phase. The base and synergist extractants were mixed in equal volume (50 mL) at 0.1 M concentration. Similarly, the extraction, separation, and turquoise blue concentration analysis were conducted using the aforementioned methods. The experiments were repeated with various concentrations of base and synergist extractant (0.01-0.1 M). The one-factor-at-a-time (OFAT) method was employed during the investigations, where the one concentration was fixed at a set of experiments while maintaining the others. All the experiments were conducted at room temperature ($26 \pm 1^\circ\text{C}$).

2.3. Stripping Agent Selection

The stripping of turquoise blue from the organic loaded phase was carried out once obtaining the best combination of base and synergist extractants. The organic phase loaded with turquoise blue were mixed in equal volume (100 mL) with stripping agent including NaOH, Na_2CO_3 , and H_2SO_4 at 0.1 M concentration. The solution was then stirred using an extractor for 1 hour at 320 rpm to conduct the stripping process. Upon completing the stripping process, the solution was carefully poured into a separation funnel and allowed to settle via gravity settling for 30 minutes. The turquoise blue concentration in the aqueous stripping phase was analyzed using UV/Vis spectrophotometer. All the investigations were carried out in three replicates.

2.4. Analytical Procedures

The extraction and stripping percentages were determined using Equations 1 and 2, respectively while the distribution ratio and synergistic coefficient were calculated using Equations 3 and 4, respectively.

$$\begin{aligned} \text{Extraction (\%)} \\ &= \frac{[dye]_{i,aq} - [dye]_{f,aq}}{[dye]_{i,aq}} \times 100 \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Stripping (\%)} &= \frac{[dye]_{f,s,aq}}{[dye]_{i,org}} \times 100 \\ &= \frac{[dye]_{f,s,aq}}{[dye]_{i,aq} - [dye]_{f,aq}} \times 100 \end{aligned} \quad (2)$$

$$\text{Distribution ratio, } D = \frac{[dye]_{i,org}}{[dye]_{f,aq}} \quad (3)$$

$$\begin{aligned} \text{Synergistic coefficient, SC} \\ &= \frac{D_{mixture}}{D_{base} + D_{synergist}} \end{aligned} \quad (4)$$

where, $[dye]_{i,aq}$ and $[dye]_{f,aq}$ are turquoise blue dye concentration (ppm) in the aqueous feed phase before and after the extraction. Meanwhile, $[dye]_{i,org}$, and $[dye]_{f,s,aq}$ represent turquoise blue dye concentration (ppm) in the organic liquid phase after extraction, and final aqueous stripping phase, respectively. In addition, $D_{mixture}$, D_{base} , and $D_{synergist}$ denotes distribution ratio of dyes using mixed, base, and synergist extractants, respectively.

3. RESULTS AND DISCUSSION

3.1. Selection of Base and Synergist Extractants

Three types of extractants such as acidic (Cyanex 302 and D2EHPA), basic (TOA and TBA), and neutral (TBP) were investigated in terms of their capabilities to extract turquoise blue from the aqueous feed solution. The performance of extraction for the different types of extractant on turquoise blue extraction is presented in Figure 2. The results show that the performance of turquoise blue extraction decreased in the following order: TOA (70.6%) > Cyanex 302 (58.4%) > TBP (35.2%) > TBA (16.6%) > D2EHPA (11.0%). From these data, it can be inferred that these extractants have shown to be capable of removing turquoise blue molecules from the feed phase. This is due to the unique structure of turquoise blue that possesses several functional groups (as shown in Figure 3) which enables it to react with different types of extractants.

The extraction of turquoise blue using TOA and TBA was attributed to the complex formation between the amine group in the extractant and sulfonate group of dye. For Cyanex 302, D2EHPA, and TBP the extraction is due to the reaction between the phosphorous group of extractant and amine group of dye.

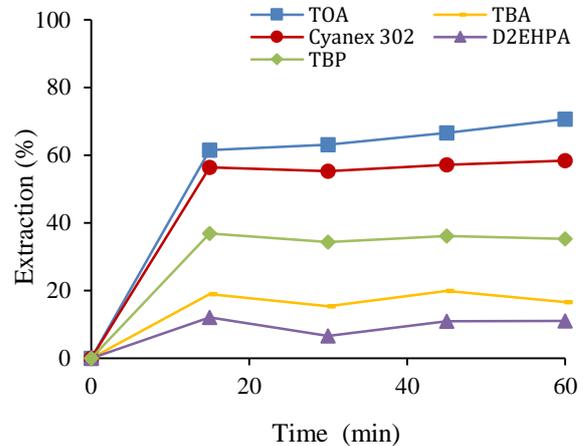


Figure 2 Effect on turquoise blue extraction using different types of extractant (Experimental conditions: [dye]: 50 ppm; [extractant]: 0.1 M; diluent: kerosene; feed volume: 100 mL; organic solution volume: 100 mL; agitation speed: 320 rpm; extraction time: 1 hour)

TOA provides the highest extraction due to the ion exchange mechanism between the anion of the turquoise blue and cation of TOA. Ion-exchange involves an exchange of one or more ionic compounds which takes place between two substances consist of each cation and anion [28]. In this system, turquoise blue exists in the anionic form in the aqueous feed phase and is likely to react with basic extractant in the organic phase. The concept is similar to a study reported by Soniya and Muthuraman [7] during the extraction of methylene blue. The result also illustrates that TOA as a tertiary amine provides a higher percentage of dye extraction compared to TBA which has the same functional group. The differences are due to the fact that the carbon chain in TOA is longer than TBA, thus, the electropositivity difference in TOA is greater than TBA. This is also reported in the extraction of Orange 3R from synthetic wastewater where TDA has higher electropositivity difference compared to TOA [21]. The nitrogen atom in TOA is capable of withdrawing a shared pair of electrons for combination with other molecules. In contrast, other extractants have lower extraction performance due to its structure which lacks positive charges to react with the anionic dye.

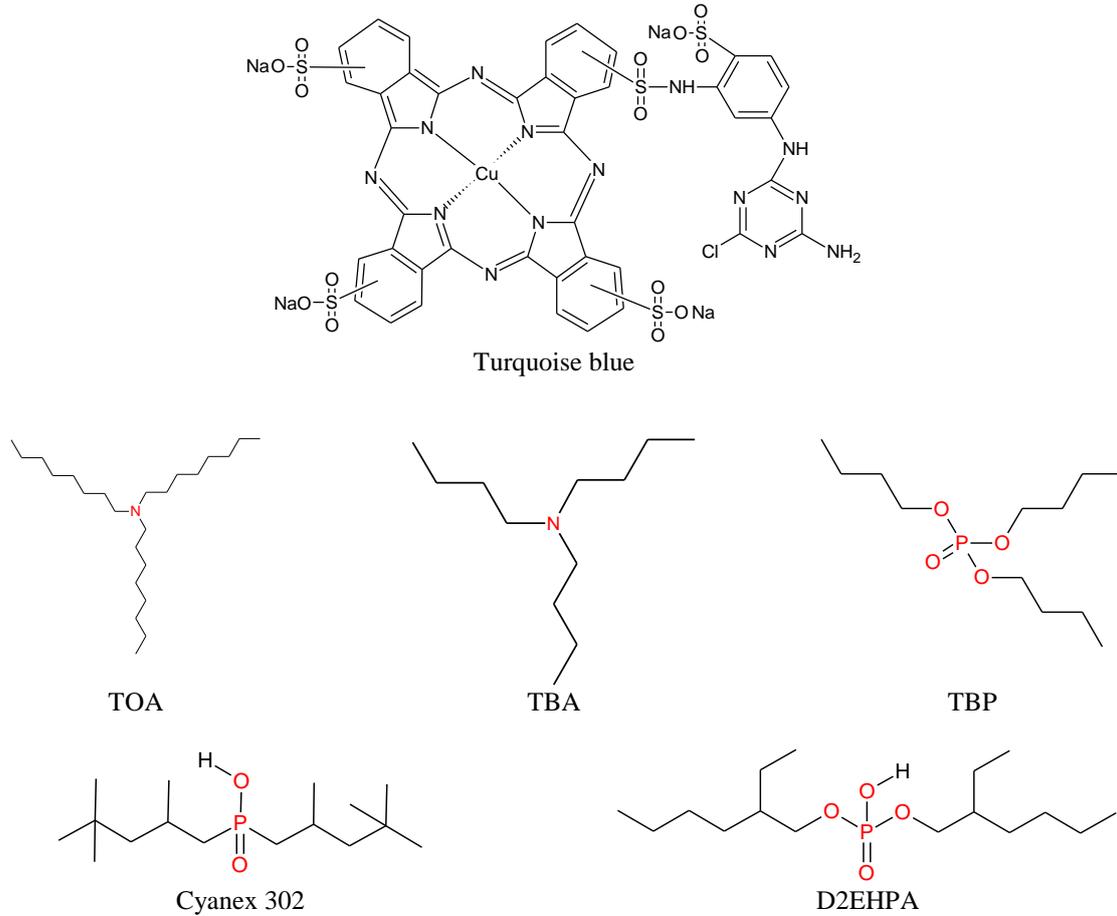


Figure 3 Chemical structure of turquoise blue and different types of extractants

The use of a single extractant normally led to a tiny loading capacity of solute in the organic liquid phase [29]. Synergistic extraction system of turquoise blue was developed by combining the selected base extractant (TOA) with different types of synergist extractants including TBA, TBP, D2EHPA, and Cyanex 302. Figure 4 illustrates the effect of the synergistic extraction system on turquoise blue extraction performance. The results show that the combination of TOA/Cyanex 302 improved the extraction performance to 94%. This is due combined effect of ion exchange mechanism between turquoise blue and TOA with reaction between the phosphorous group of Cyanex 302 and amine group of turquoise blue. Conversely, no significant effect of other combination towards the synergistic system, where the combination of TOA/TBA, TOA/D2EHPA, and TOA/TBP resulted in 13%, 18%, and 29% of extraction, respectively. This indicates that only the mixture of TOA/Cyanex 302 gives a synergism effect, while the rest undergo antagonism effect.

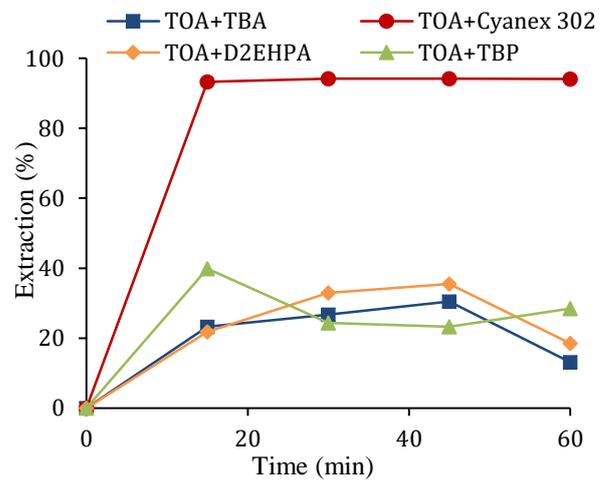
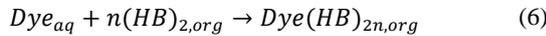
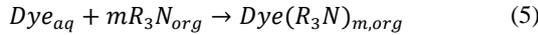


Figure 4 Effect of types of synergist extractant on turquoise blue extraction (Experimental conditions: [dye]: 50 ppm; [extractant]: 0.1M; diluent: kerosene; feed volume: 100 mL; organic solution volume: 100 mL (extractant 50mL + synergist extractant 50 mL); agitation speed: 320 rpm, extraction time: 1 hour)

3.2. Extraction Mechanism

In order to analyse the stoichiometry of extraction, the reaction of turquoise blue with TOA (denoted as R_3N) and Cyanex 302 (HB) can be presented as follows.



The equilibrium constant, K can be determined from Equation 7 and 8.

$$K = \frac{[Dye(R_3N)_m]_{org}}{[Dye]_{aq}[R_3N]_{org}^m} \quad (7)$$

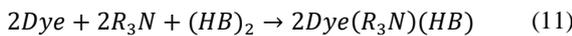
$$K = \frac{[Dye(HB)_{2n}]_{org}}{[Dye]_{aq}[(HB)_2]_{org}^n} \quad (8)$$

By substituting the distribution ratio (Equation 3) in Equation 7 and 8 and writing in a logarithmic form, the following Equations will be obtained.

$$\log D = \log K + n \log [R_3N]_{org} \quad (9)$$

$$\log D = \log K + n \log [(HB)_2]_{org} \quad (10)$$

The stoichiometric reaction of the mixed extractants with turquoise blue was studied by plotting the graph of $\log D_{mix}$ versus $\log [TOA]$ and $\log D_{mix}$ versus $\log [Cyanex\ 302]$ [21, 30]. The number of extractants and dye involved in the reaction could be determined from the slope of the graph. The stoichiometric relation between turquoise blue and TOA is presented in Figure 5. Based on the graph, the slope (m) provides a value of around 1, which specifies that 1 mol of TOA form complex with 1 mol of dye. Meanwhile, Figure 6 shows the stoichiometric relation between turquoise blue and Cyanex 302. It can be seen from the graph that the value of the slope (n) is 0.5, which shows that 1 mol of Cyanex 302 participated during complexation with 2 mol of dyes. The negative slope of $\log D_{mix}$ versus $\log [Cyanex\ 302]$ indicates the decrease of extraction with Cyanex 302 concentration, while y intercept indicates the equilibrium constant value. Substituting the value of m and n in Equation 5 and 6, the chemical equilibrium which responsible for turquoise blue extraction involving TOA and Cyanex 302 is shown in Equation 11.



3.3. Effect of Extractant Composition

The mixture of TOA/Cyanex 302 exhibits excellent ability to extract turquoise blue, however, an appropriate concentration should be determined to ensure the minimal use of extractants. Besides, every extractant plays a unique role during the extraction process. The extraction will be affected by the inadequate use of one of the extraction

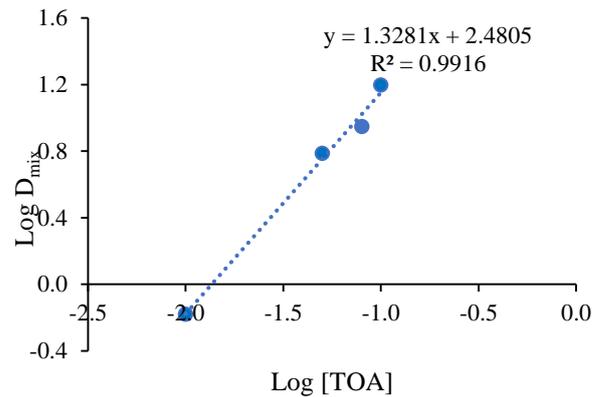


Figure 5 Influence of TOA concentration at a fixed concentration of Cyanex 302 on turquoise blue extraction (Experimental conditions: [dye]: 50 ppm; [Cyanex 302]: 0.01 M; diluent: kerosene; feed volume: 100 mL; organic solution volume: 100 mL (50 mL extractant + 50 mL synergist extractant); agitation speed: 320 rpm; extraction time: 1 hour)

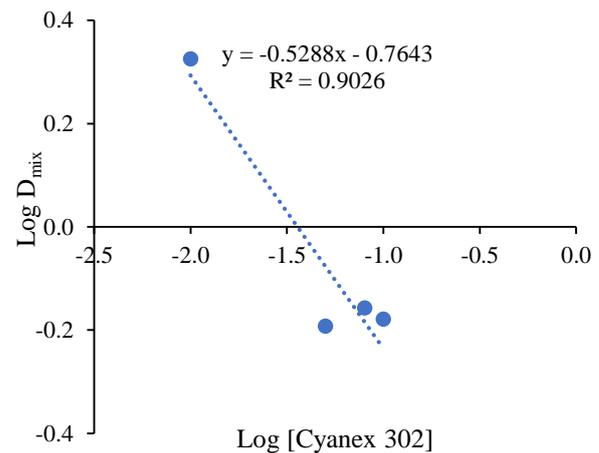


Figure 6 Influence of Cyanex 302 concentration at a fixed concentration of TOA on turquoise blue extraction (Experimental conditions: [dye]: 50 ppm; [TOA]: 0.05 M; diluent: kerosene; feed volume: 100 mL; organic solution volume: 100 mL (50 mL extractant + 50 mL synergist extractant); agitation speed: 320 rpm; extraction time: 1 hour)

concentrations. The effect of mixed TOA/Cyanex 302 concentration on the dye extraction performance was investigated and the data are presented in Table 1. At one time, the concentration of TOA as the base was fixed while synergist Cyanex 302 concentration was altered ranging from 0.01 to 0.1 M. It can be seen from the data that at fixed TOA concentration, there is no significant trend of dye extraction was found with Cyanex 302 concentration and vice versa.

Table 1 Influence of base and synergist extractant concentration on percentage of dye extraction (Experimental conditions: [dye]: 50 ppm; diluent: kerosene; feed volume: 100 mL; organic solution volume: 100 mL (50 mL base extractant + 50 mL synergist extractant); agitation speed: 320 rpm; extraction time: 1 hour)

[Cyanex 302] (M)	[TOA] (M)			
	0.01	0.05	0.08	0.10
	Extraction (%)			
0.01	68	91	95	91
0.05	39	92	93	88
0.08	41	94	94	88
0.10	40	86	90	94

Meanwhile, the extraction performance was increased from 68% to 94% with an extractant concentration mixture from 0.01 to 0.08 M at an equimolar ratio. Increasing the mixed extractant concentration facilitates the formation of the transport structure and creates a favorable condition for the extraction of dyes into the organic liquid phase. The results of this study further support the idea of Rajewski and Religa [31] who examined chromium extraction using a mixed carrier system. Similarly, Rahman et al. [21] reported that synergist extractant acts as a phase transfer catalyst for the transport of Orange 3R into the organic phase.

On the other hand, the data on the synergistic effect of TOA/Cyanex 302 at various concentrations are presented in Table 2. Based on Sarkar et al. [32], the synergistic effect takes place when the mixture distribution ratio is higher compared to the total distribution ratio of a single extractant. This is represented in terms of synergistic coefficient (SC) as given in Equation 4. If the SC is greater than 1, the synergistic effect occurs, while the SC below than 1 indicates the antagonistic effect. It can be seen from the data that the synergistic effect increases when both extractants are used in equimolar ratio. The highest value of SC obtained using 0.08M TOA and 0.01M Cyanex 302, which is 4.77. Therefore, the mixture of TOA/ Cyanex 302 at the concentrations of 0.08M and 0.01M, was selected for the following investigations.

3.4. Selection of Stripping Agent

Several stripping agents' types including NaOH, Na₂CO₃, and H₂SO₄ were studied to strip turquoise blue from the loaded organic solution and the results are shown in Figure 7. It is apparent from the results that almost 100% of dye concentration was stripped using NaOH and Na₂CO₃ as the stripping agents. Meanwhile, only 1% of turquoise blue was stripped by H₂SO₄. These results suggest that basic stripping agents are more suitable to strip anionic turquoise blue. The order of the stripping agent is NaOH > Na₂CO₃ > H₂SO₄. Note that the basicity of the stripping agents is likely to be related to the concentration of the hydroxide ion in the aqueous solution. The presence of hydroxide ion in NaOH and Na₂CO₃ made the stripping process to occur while the presence of sulfate ion in H₂SO₄ prevents the stripping process to take place. This study produced results which corroborate the findings of a great deal of the previous work in the stripping of succinic acid anion using basic stripping agents [33]. The finding of study is similar to Rosly et al. [1] who found basic stripping agent is preferable for anionic and reactive dyes extraction. Therefore, NaOH was selected as the best stripping agent in this study.

Table 2 Influence of base and synergist extractant concentration on synergistic coefficient (Experimental conditions: [dye]: 50 ppm; diluent: kerosene; feed volume: 100 mL; organic solution volume: 100 mL (50 mL base extractant + 50 mL synergist extractant); agitation speed: 320 rpm; extraction time: 1 hour)

[Cyanex 302] (M)	[TOA] (M)			
	0.01	0.05	0.08	0.10
	Synergistic Coefficient (SC)			
0.01	0.56	2.67	4.77	2.53
0.05	0.17	3.00	3.57	1.86
0.08	0.18	4.03	4.03	1.86
0.10	0.17	1.61	2.33	4.14

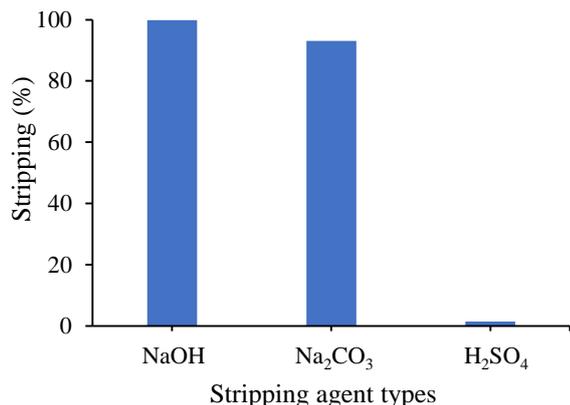


Figure 7 Effect of stripping agent type on turquoise blue stripping (Experimental conditions: [TOA]: 0.08 M; [Cyanex 302]: 0.01 M; diluent: kerosene; [stripping agent]: 0.1 M; stripping agent volume: 100 mL; organic loaded volume: 100 mL, agitation speed: 320 rpm; stripping time: 1 hour)

4. CONCLUSION

The synergistic LLE system for turquoise blue was successfully studied. The suitable synergistic formulation consists of a mixture of TOA and Cyanex 302 as the base and synergist extractants, respectively. A maximum extraction percentage of 94% was obtained at 0.08M TOA and 0.01M Cyanex 302. Additionally, 0.1 M NaOH appears as the best stripping agent with the highest stripping efficiency of almost 100%. Thus, the developed synergistic LLE has improved the extraction performance and highly potential for dyes removal from industrial textile effluent.

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