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Effect of Different Types of Carrier and Stripping Agent in Liquid Membrane Formulation for Silver Extraction by using Kerosene and Corn Oil

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Abstract: As the world undergoes rapid urbanization, the usage of natural sources growth has increased rapidly to a greater amount causing the rate of waste generation to increase align with it. As the waste production greatly increase, the rate of pollution has also increase especially water pollution. One of the causes of the water pollution is the presence of heavy metals contains in the water such as silver. In order to treat the contaminated water, Liquid Membrane has been introduced as one of the technologies that can extract the heavy metals from the water. Several characteristics were studied, including different types of carriers, and stripping agent. This study aims for the percentage of silver extraction for every liquid membrane formulation in order to decide the best formulation to be used. This research was done with different ratio of Tridodecylamine to Triotylamine (1:2, 2:1) as the carrier for the liquid membrane. This research was also been conducted to determine the effect of stripping agent towards the efficiency of the extraction. The diluent that been used were palm cooking oil and corn cooking oil with the volume of 5 ml for ratio 1:2 and 10 ml for ratio 2:1. Meanwhile, for the determination of silver extraction percentage by using stripping agent, the membrane layer that formed from the previous mixing process of diluent with a carrier were mixed with the stripping agent used which is Hydrochloric acid and Sodium Hydroxide respectively. The result obtained through UV-vis spectrophotometer showed that the percentage of extraction of silver by the liquid membrane formulation without the presence of stripping agent has the highest percentage which are 59% and 61% for corn cooking oil and kerosene respectively with the ratio of 1:2 TDA/TOA solution.

Keywords: Silver Extraction, Liquid Membrane, Water, Carrier, Stripping Agent

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1. Introduction

Water is a necessary thing in life. Every life on earth linked to water. The water has existed since millennium ago and still available until today without disappearing. But the world nowadays has underwent a drastic change, where people need to spend their money to get clean and safe water. As the industrial development increase, the rate of wastewater produced as industrial waste also increase drastically. This means the amount of clean water has reduced compared to the wastewater which its amount increases every day. Therefore, the only way to rebalance this problem is by recycling and reusing the wastewater again for daily humans needs [1].

Wastewater is the water that has been contaminated by human or industrial use. This kind of water contains pollutants that can be categorized into 3 types which is physical, chemical, and biological pollutants. Almost majority of the water utilized in industry is discharged as industrial waste. Anions such as chlorides, fluorides, cyanides, and perchlorates that are present in excess of the allowed amounts in water are harmful to the people and aquatic life [3]. The discharge of this industrial wastewater into the environment leaves a huge environmental footprint and may also pose a number of other hazards [14].

Industrial discharge often has heavy metal in it. One of the heavy metals that presence in the industrial wastewater is silver and when exposed at high concentrations, silver is considered a hazardous substance that can produce a variety of unfavorable health effects in humans, including skin pigmentation disease, liver and kidney deterioration, and respiratory problems [10,15]. Nowadays Emulsion Liquid Membrane is gained a reputation to treat industrial wastewater. Emulsion Liquid Membrane (ELM) is use to separated heavy metal such as silver from waste water and also because it can also cut down on the amount of expensive extractant used, allowing for high fluxes and selectivity.

Dr. Li proposed the emulsion liquid membrane method in 1968 as one type of bionic membrane technology [9]. The organic or oil phase, the internal phase, and the exterior phase are all components of an emulsion liquid membrane and diluent, surfactant, and carrier make up the organic phase. The use of petroleum-based diluent such as kerosene is costly, unsustainable and toxic for the environment was replaced with much more environmentally friendly diluent such as corn oil or palm oil which is non-toxic and can be renew in order to utilize green ELM [2]. This simultaneous extraction and stripping operation are appealing because it allows the solute of concern to be transported from a low concentration solution to a high concentration solution in a single step using a suitable carrier [11].

This Emulsion Liquid Membrane is a simple process but comes with a high efficiency of extraction. So, it is a suitable method to be used in the extraction process. Furthermore, the wastewater that are discharge by the industrial or domestic use always contain a small particle of heavy metal which can be reuse again. However, these procedures have a number of drawbacks, including a limited ability to automate, the use of large amounts of toxic organic diluent/solvent, and a lengthier time-consuming process [4,5]. Smelting, hazardous waste sites, cloud seeding with silver iodide, metal mining, sewage outfalls, and especially the photoprocessing industry are all anthropogenic sources of elevated silver concentrations in non-living materials [6].

Emulsion Liquid Membrane is a method of one-step procedure that combines extraction and stripping. This simultaneous extraction and stripping operation is appealing because it allows the solute of interest to be transported from a low concentration solution to a high concentration solution in a single step using a suitable carrier [11].

To formulate the liquid membrane, the usage of combination of carrier technique with a ratio of 1:2 and 2:1 with TOA and TDA as a carrier was used and for the stripping agent, acid hydrochloric (HCL) and natrium hydroxide, (NaOH) been applied in this study. There are two types of diluents that were used, the first one is petroleum-based diluent which is kerosene and organic type diluent which is corn cooking oil. Therefore, the goal of this research is to develop a liquid membrane using various types of carriers and stripping agents, as well as to analyses the liquid membrane's performance in silver extraction.

2. Materials and Methods

2.1 Materials

TOA and TDA are both bought from the same chemical supplier which is BT Science Company, they are specialized in the production and distribution of fine chemicals. Both of the chemicals are stored at a temperature of 2-8°C to avoid the contamination and melt point which is 34°C for TOA and 16°C for TDA. Meanwhile for the diluent which is corn cooking oil was brought from the local supplier at speed mart located at Pagoh, Johor, Malaysia. For the stripping agent HCL and NaOH are both taken from UTHM lab.

2.2 Sample Preparations

Combined carrier was created by mixing 0.5 ml of 0.1 M Trioctylamine, TOA and 0.4 ml of 0.1 M Tridodecylamine, TDA with the ratio of 1:2 and 2:1 respectively. Then, the mixture of combined carrier was mixed with the diluent used in this study which is Kerosene which is 5ml and 10 ml respectively. The mixture then was placed into a shaker for 1 hour at 280 rpm at 37℃. Then, a 10 ml silver solution was mixed with 20ml deionized water for a 30ml volume of mixture. Then, the mixture of silver solution was mixed with the shaken carrier mixture. The final mixture was placed into the shaker for 18 hours at the speed of 280 rpm at 37℃

After 18 hours, the mixture were taken out and were poured into separating funnel. The mixture was left for 15 minutes. After 15 minutes, the emulsion of liquid membrane was completely separated from the aqueous solution. The valve of the funnel was opened to let the aqueous solution flow down into a beaker.

Next, the emulsion liquid membrane was mixed with HCl. A small amount of the mixture was poured into a cuvette and was placed into a DR6000™ UV-Vis spectrophotometer. The UV-vis wavelength was set to 600 and at the point 269, the peak value was recorded. Then, the steps been repeated using different formulation with NaOH as the stripping agent.

2.3 Analytical Method

There are two calculations involved during the study which is the molar calculation and UV-Vis extraction calculation. The first calculation was applied to find the volume of each carriers need to be added into the solution based on their ratio. This calculation used the data such as the molarity, molar weight and specific gravity value of the carrier as well as the volume of the diluent in order to find the accurate volume of each carrier. Then, the second equation was applied in order to determine the exact value of extraction of the silver based on the data gained from the UV-Vis spectrophotometer. These equations formula is as the followings:

$$\frac{molarity \times molar\ weight \times volume\ of\ diluent}{specific\ gravity\ of\ carrier} \qquad Eq.1$$

Where molarity (Mol/L) is the molar concentration of the carrier and molar weight (g/mol) is the molar mass of the carrier. While volume (v) is the volume of the diluent and specific gravity (Sg) is the specific gravity of the carrier. Equation 2 used to find absorbance is as following:

$$\text{Extraction yield (\%)} = \frac{Ai - Af}{Ai} \times 100 \qquad \textit{Eq.2}$$

Where, *[A]i* is the absorbance of 30 ppm $AgNO_3$ solution and, *[A]f* is the absorbance of aqueous phase containing tested component for screening.

3. Results and Discussion

3.1 Effect of Different Ratio of Carrier

The Figure 1 shows the result of silver extraction for different diluent of kerosene and corn cooking oil. The research was carried out to determine the percentage of extraction for 1:2 TDA/TOA and 2:1 TDA/TOA liquid membrane without the presence of stripping agent. All the sample were analyses using UV-Vis Spectrophotometer.

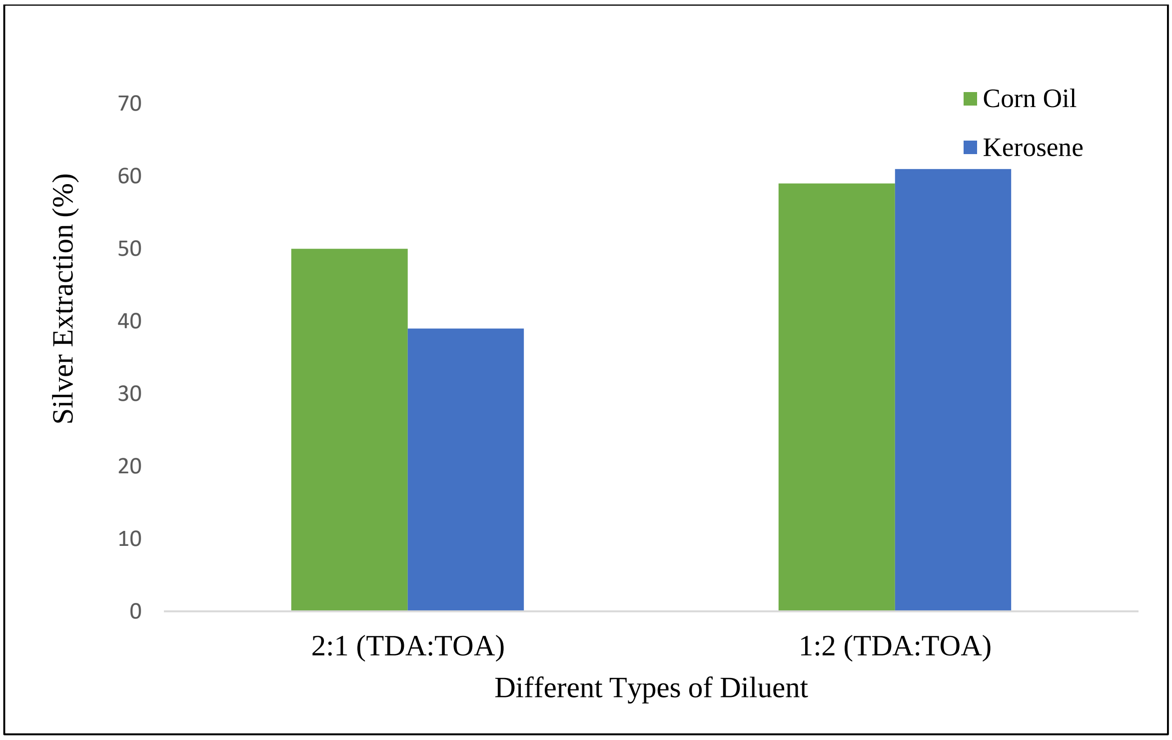

Figure 1: Extraction of the silver from different diluent using UV-vis.

Based on the data in **Fig. 1**, result show that for corn cooking oil, 0.5 or 50% of silver are extracted from the solution when the formulation of 1:2 TDA and TOA was used. Then, for 2:1 TDA and TOA formulation, 0.59 or 59% of silver was successfully extracted from the solution. Meanwhile, for kerosene, the ratio of 1:2 is 0.39 or 39% and for the ratio of 2:1 is 0.61 or 61%.

Based on the result, it seems that when concentration of TOA increases, the extraction of silver also increases. The increase of this concentration is because of the increase in the chain length. In addition, the extraction percentage increases linearly with the carrier concentration until it achieves plateau. Thus, it signifies the excess of "free extractant" [12]. Based on Le Châtelier's principle, increasing carrier concentration will increase reaction rate that will contribute to the increase in extraction percentage. Furthermore, the difference of the number of CH2 been attached to the nitrogen atoms in TOA causes this carrier to have greater polarity compared to TDA [13].

3.2 Effect of Different Stripping Agent

The data shown on **Fig. 2** were the extraction of silver by using kerosene and corn cooking oil with the presence of hydrochloric acid as stripping agent. Based on the data above, when 1:2 TDA/TOA solution were mixed with HCl for kerosene, the result shows the extraction rate is 5.8%. For the 2:1 formulation of TDA/TOA, when the HCl is added, the extraction rate is 5.6%. For corn cooking oil, the silver extraction are 35.5% and 40.6% for 1:2 TDA/TOA and 2:1 TDA/TOA respectively.

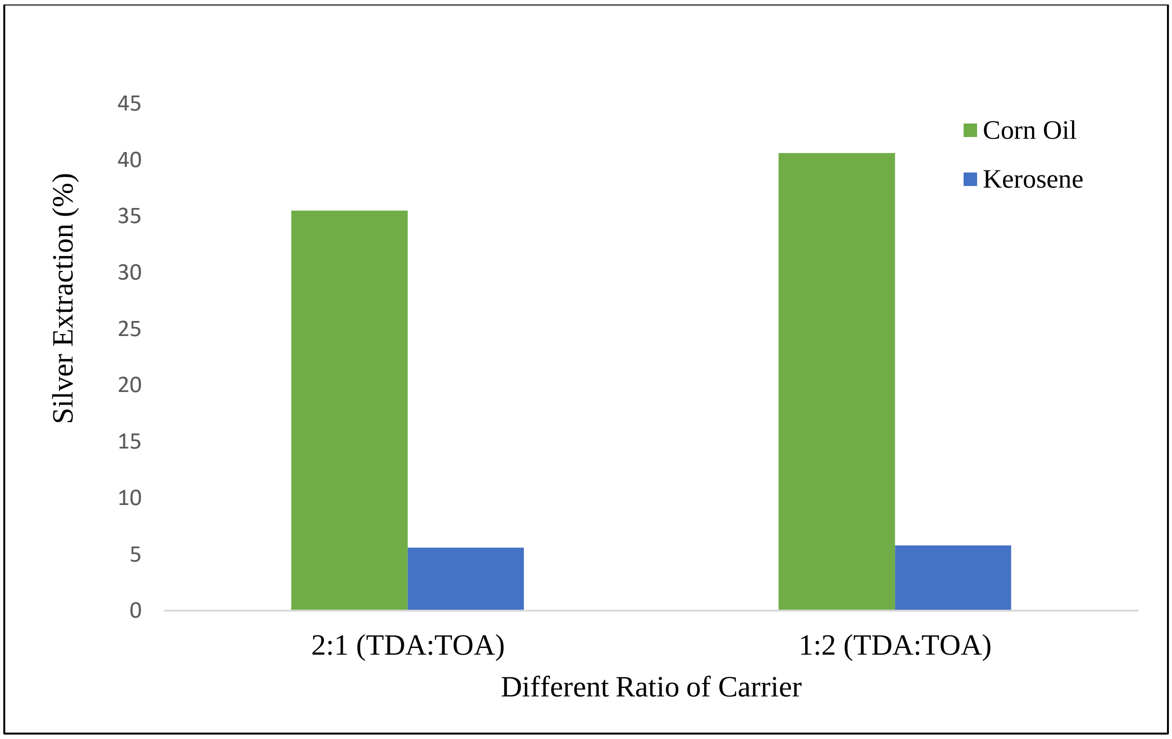

Figure 2: Extraction of Silver with Hydrochloric acid as stripping agent

Based on the result, it shows that the performance of silver extraction is increased when the concentration of TOA is higher compared to TDA. This is because TOA has higher basicity than TDA, so that TOA has a better ability to react with hydrochloric acid, HCI, at higher concentrations [13].

Next, the data that shown in **Fig. 3** is for the extraction of silver by using NaOH as the stripping agent. Based on the data, when the 1:2 TDA/TOA solution were mixed with Sodium Hydroxide, NaOH, the extraction percentage was 15.7 or 0.157. Then, the steps been repeated using 2:1 TDA/TOA solution with NaOH as stripping agent and the extraction percentage gained was 16.2% or 0.162. Meanwhile, for corn cooking oil, the silver extraction are 37.5% and 43.3% for 1:2 TDA/TOA and 2:1 TDA/TOA respectively.

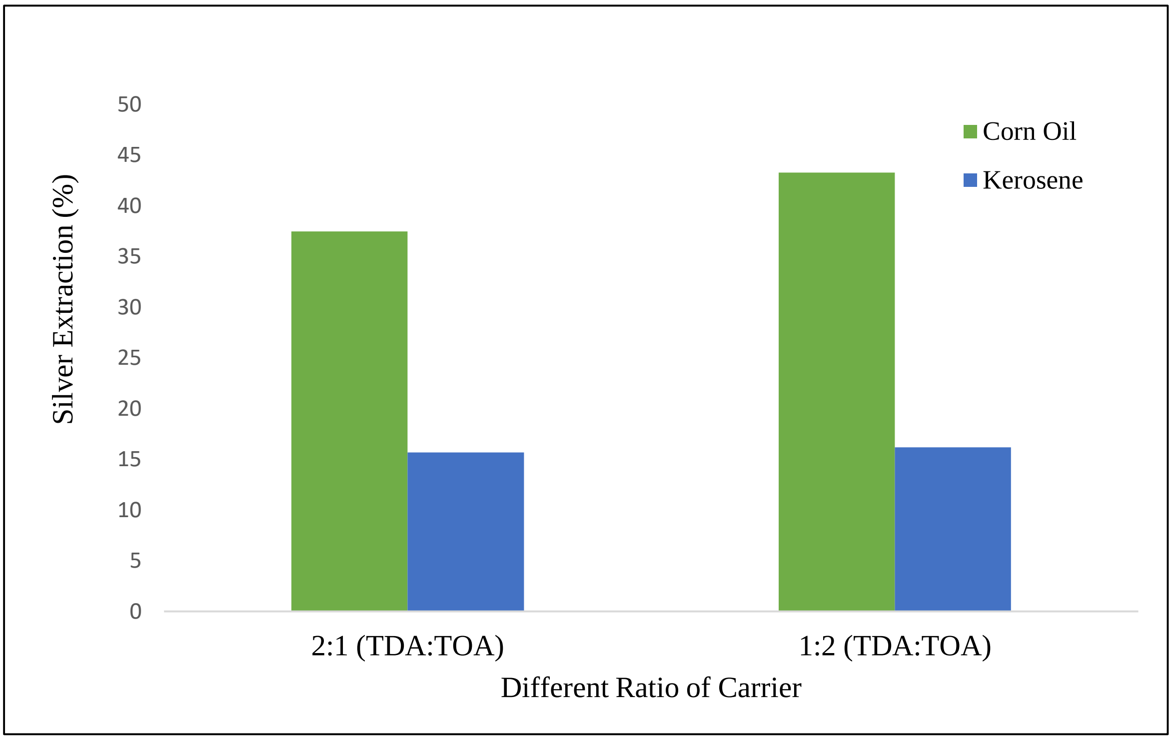

Figure 3: Extraction of the silver using Sodium Hydroxide (NaOH) as stripping agent.

For result in **Fig. 4**, it shows the comparison of silver extraction between stripping agent of HCI and NaOH. From the result, it can be seen that the percentage of silver extraction for both kerosene and corn cooking oil is higher in NaOH compared to HCI.

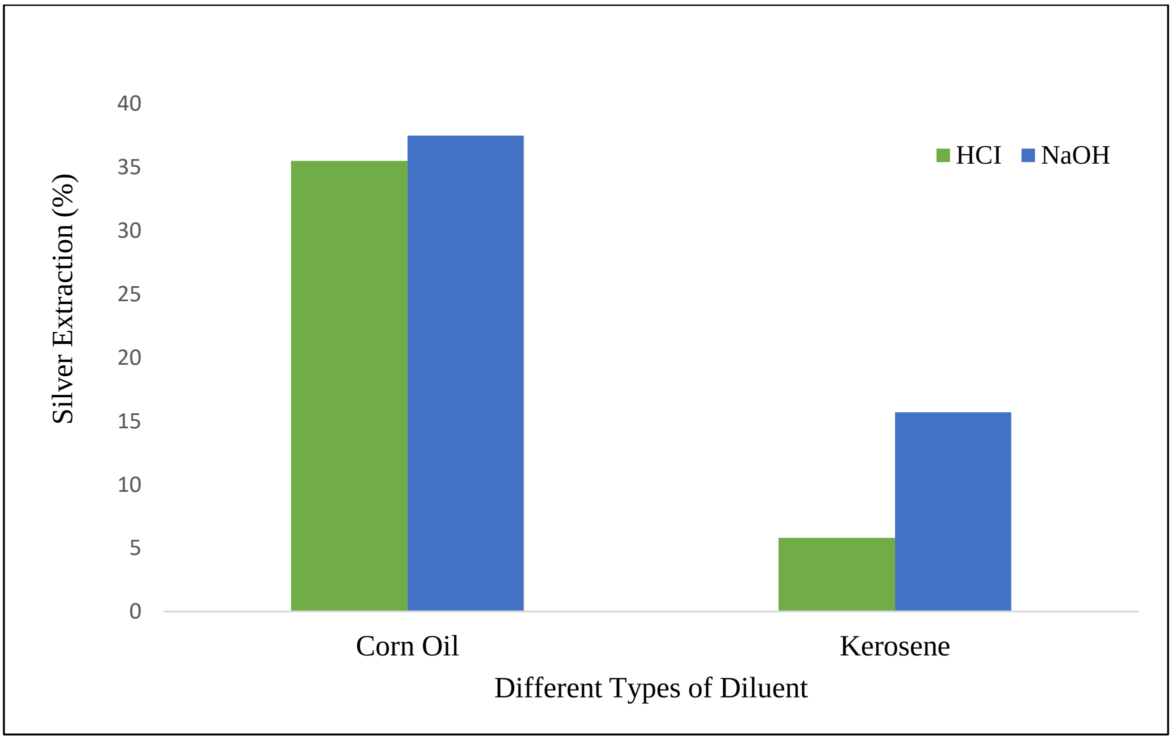

Figure 4: Comparison between different stripping agents

This happen because NaOH is a strongly caustic base and alkali decomposes proteins at normal ambient temperatures. Therefore, it means that it can be easily decomposed the protein in the mixture of diluents and silver, with leaving only the silver in it. Because of its better reaction capability with TOA and TDA, sodium hydroxide is the most preferred stripping agent for extracting silver because it maintains a higher hydrogen ion gradient between the feed and stripping phases [12].

4. Conclusion

This study concludes that different liquid membrane formulations affect the extraction percentage and the efficiency for the silver extraction. Based on the data, the extraction percentage are the highest when the formulation of liquid membrane without the presence of stripping agent which are 59% and 61% for corn cooking oil and kerosene respectively with the ratio of 1:2 TDA/TOA solution. However, due to the limited supplies for the carrier, the usage of carrier needs to be reduced and stripping agent need to be used in order to replace the amount of carrier that has been reduced. Based on the results, it has been proven that mixing the TDA/TOA solution with Sodium Hydroxide as stripping agent shows the better performance of extraction than using hydrochloric acid as stripping agent. The selection of liquid membrane component for silver extraction was determined by using liquid-liquid method. Based on the study, TOA and TDA as carriers with the ratio of 2:1, corn cooking oil as diluents, and NaOH as a stripping agent are the most suitable combinations for the formulation as it gives off the highest extraction rate of silver in this study which is 43.3%.

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