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Formulation of Liquid Membrane for Silver Extraction

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Abstract: Liquid membrane technology has been an uprising method in the removal of heavy metals. Recovery of heavy metals especially from wastewater is vital to ensure the wellness of public health and environment. Silver is one of the heavy metal that is identified to have harmful toxic properties. In this study, an emulsion liquid membrane is formulated by choosing the best formulation to extract silver from wastewater. An emulsion liquid membrane consists of a combination of potential carrier, diluent and stripping agent. Two different types of substances for each component are compared in this study by screening process to determine its extraction yield for silver. 0.2M tridodecylamine (TDA) and tricotylamine (TOA) as carrier, kerosene and palm cooking oil as diluent and 0.1M sodium hydroxide and hydrochloric acid as stripping agent were used as a component in this study. Meanwhile, 30ppm silver nitrate solution is used to act as substitute for silver contaminated wastewater. Results show that TDA and palm oil gives the highest extraction yield which are 67.18% and 94.10% respectively. As for the stripping agent, sodium hydroxide and hydrochloric acid were achieved 82.8% and 81.28% of extraction rate. Thus, an emulsion liquid membrane consists of 0.2M tridodecylamine, cooking palm oil and 0.1M sodium hydroxide exhibits good performance on removal of silver from wastewater

Keywords: Liquid Membrane, Silver, Extraction, Heavy Metal, Wastewater

1. Introduction

Heavy metal effluent is a pollutant that originates from a variety of sources. Some of the frequently traced heavy metals in industrial wastewater are zinc, copper, nickel, silver, arsenic and plumbum [1]. One of the familiar elements that is present in wastewater is silver. Silver had been discovered to be distributed inside all over the body of humans who are exposed to it either by ingestion, inhalation, or absorption [1]. According to [2], human data relating to silver ingestion had documented a number of case reports where people have ingested various amounts of colloidal silver. Thus, it is a requirement to treat the wastewater before it is discharged to the environment. However, normal wastewater

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treatment plants do not have the ability to discard this type of heavy metal. There is a range of methods to address those contaminated metals. Therefore, in the modern manufacturing era, some industrial treatment requirements for the removal of soluble heavy metal ions had been applied by many industries worldwide. The treatments include precipitation, ultrafiltration, coagulation-flocculation, and membrane filtration [2].

Currently, membrane technologies play an essential role in treating wastewater. It is one of the widely used methods in treating wastewater which has confirmed to be effective for the removal of heavy metals [3]. It became popular for its low production cost and high separation yield. There are several types of membranes such as bulk liquid membrane, immobilized liquid membrane, and emulsion liquid membrane. This study aims to formulate an emulsion liquid membrane by utilizing different types of carrier and to elucidate the potential of the liquid membrane in silver extraction. The idea of performing a formulation of liquid membrane for extraction offers a higher chance in removing specific heavy metals in wastewater. It is to prevent further damage caused by toxicity to the environment, ecosystem and public health. In the long run, this study helps to reduce the environmental and economic impact given by silver pollution.

2. Materials and Methods

2.1 Materials

The experiment was carried out by using cooking palm oil (Buruh Cooking Oil) and kerosene as diluents. Tridodecylamine (TDA) was purchased from the brand Acros/Belgium and trioctylamine (TOA) was purchased from the brand Merck/Germany which act as a carrier. For stripping agents, 0.1M of hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used. Meanwhile, silver nitrate powder $AgNO_3$ (AR, Bendosen) also obtained from BT Science Company and has been used as an external aqueous phase solution. 30ppm $AgNO_3$ solution was prepared by dissolving the $AgNO_3$ in 20ml distilled water.

Liquid membrane formulation comprised of three main components, which are carrier, diluents and stripping agent. The membrane phase is a homogenous mixture of carrier and diluent. Liquid-liquid extraction experiment or known as component screening process was started by mixing 20ml of 30ppm $AgNO_3$ solution into membrane phase containing 0.2M TDA and 20ml kerosene. The mixing was carried out using an incubator shaker at 280rpm and temperature of 37 ºC for 24hours to perform the extraction. The mixture was then transferred into a separating funnel and left for 15 to 30 minutes for phase separation. The aqueous phase was separated from the organic phase by gravity settling. Then, the absorbance value of aqueous phase at the bottom was measured using a UV-Vis spectrophotometer at 265nm to measure the extraction yield, while the organic phase was kept aside for FTIR analysis. From the highest absorbance value, extraction rate towards silver was calculated using Equation 1. The experiment was repeated using TOA as carrier and cooking palm as diluent. As for stripping agent screening, an equal volume 5ml of the organic phase from the best diluent was combined with the stripping agents and mixed under the same conditions.

$$\text{Extraction yield (\%)} = \frac{A_i - A_f}{A_i} \times 100 \qquad \textbf{Eq. 1}$$

where A_i is the absorbance of 30ppm $AgNO_3$ solution and, A_f is the absorbance of aqueous phase containing tested component for screening.

2.2 Fourier Transform Infrared Spectroscopy (FTIR)

The characterization for functional groups of the liquid membrane organic phase after extraction were performed by Fourier transform infrared spectrophotometer (FTIR; Agilent Tech cary 600 series) under wavelength range 1250–4000 cm^{-1}.

3. Results and Discussion

3.1 Effect of Different Carriers

The highest absorbance value was taken at wavelength in the range of 265nm which is the wavelength range for silver. **Figure 1** shows the extraction performance of different types of carriers on silver extraction. The result shows that higher percentages of silver extraction were obtained from TDA and low percentages were obtained from TOA. Chemically, TOA and TDA are categorized as basic type of extractant. Metal extraction by a basic carrier has progressed into one of the most promising tools in aqueous separation chemistry and is still increasing [1]. This group of carrier is comprise of primary amines (RNH_2), secondary amines (R_2NH), tertiary amines (R_3N) and quaternary ammonium salts (R_4N)+. The efficiency of extraction of a complex metal species by amines follows an order: quaternary > tertiary > secondary > primary [1]. Typically, aliphatic amines are the best carriers at most when bonded to a nitrogen atom. Although both TDA and TOA are tertiary and aliphatic amines, TDA provide a higher extraction rate due to higher number of carbon atoms in its chain, thus providing a higher number of anions for ion exchange. Previous study done by [4] proves that the extractability of tertiary amine increases with its chain length. It increases the availability and formation of amine-metal complex [4]. Palm oil was chosen to be a constant diluent in carrier screening because it can reach up to 99% of efficiency value of extraction rate [5]. Furthermore, [6] found that extraction of lignosulfate using trioctylamine (TOA) as carrier can achieve around 98% efficiency in extraction process [6]. Thus, the potential of TOA in kerosene can be elucidated in the next future studies.

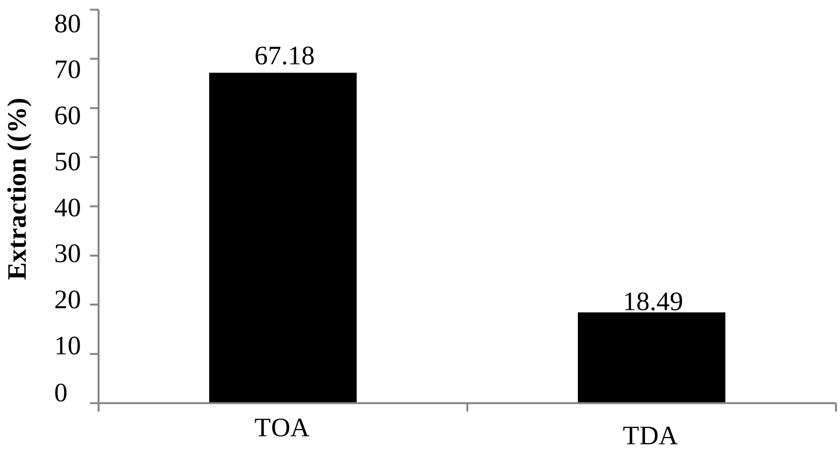


Figure 1: Effect of silver extraction using different types of carrier (Experimental conditions: Diluent type = kerosene, Agitation speed = 280rpm, Temperature = 37ºC)

3.2 Effect of Different Diluents

Two types of diluents, consisting of green vegetable-based diluents and petroleum-based diluent, which are cooking palm oil and kerosene, were screened in this study. The yield for both diluents has a very small difference in their efficiency in silver extraction as shown in **Figure 2**. In most cases, petroleum-based diluents such as kerosene is used in the extraction of silver, where almost 100% extraction was reported [5]. However, **Figure 2** shows that cooking palm oil provide slightly higher extraction yield than kerosene which is 94.10% over 93.84%. This is because TDA can solubilise well in palm oil rather than kerosene, which indicates that TDA is a compatible carrier for palm oil. Without the presence of TDA and only palm oil in the organic phase, the silver ion will not be soluble [6]. Both are potential diluents, but palm oil is more preferable as an alternate organic diluent that it is non-toxic, easy to acquire and low cost.

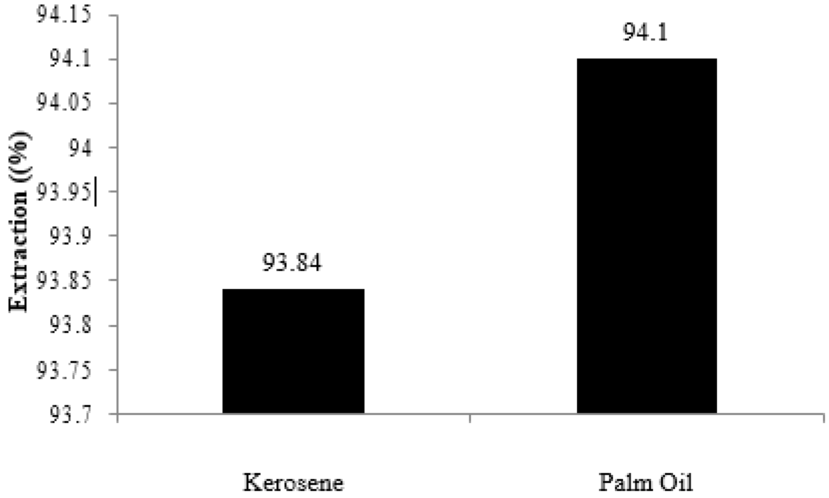


Figure 2: Effect of silver extraction using different types of diluents (Experimental conditions: Carrier type = TDA, Agitation speed = 280rpm, Temperature = 37ºC)

3.3 Effect of Different Stripping Agents

A suitable stripping agent should be properly chosen so that it can strip out the solute (silver) from the solute-carrier complex selectively. **Figure 3** shows the effect of different stripping agent on silver extraction efficiency. The results show NaOH performs better in stripping silver compared to HCl which were 82.8% and 81.28% respectively. NaOH is more preferable in extraction due to its larger reaction capacity [7]. Since TDA is a basic carrier type, an alkaline stripping agent is efficient in creating the chemical potential between the membrane and stripping phases [8]. It contains ionizing (OH-) anionic group which will react on the positive charge of Ag+ ions in ion-exchange extraction [9]. Hence, NaOH was preferred as the best stripping agent.

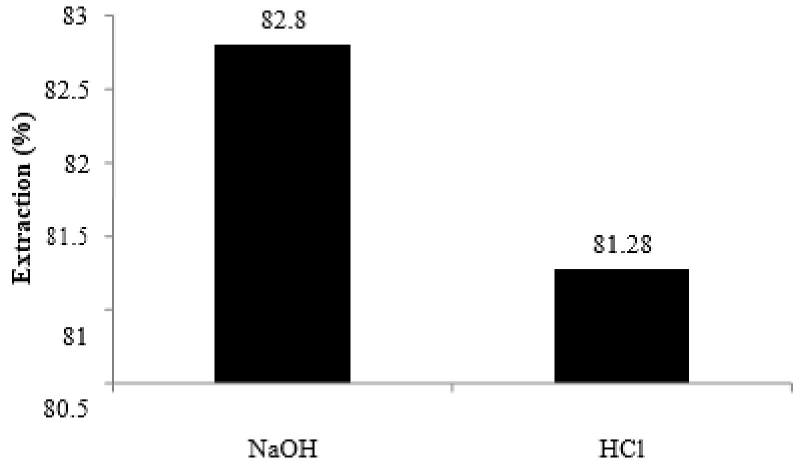
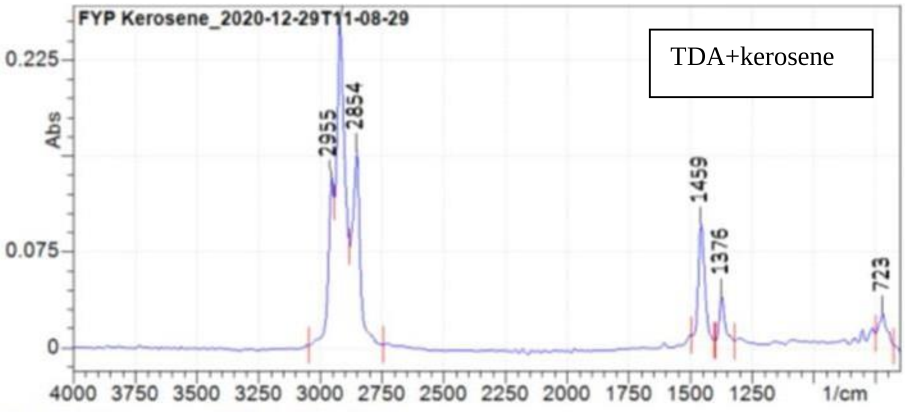


Figure 3: Effect of silver extraction using different types of stripping agents (Experimental conditions: Carrier type = TDA, Diluent = Palm oil, Agitation speed = 280rpm, Temperature = 37ºC)

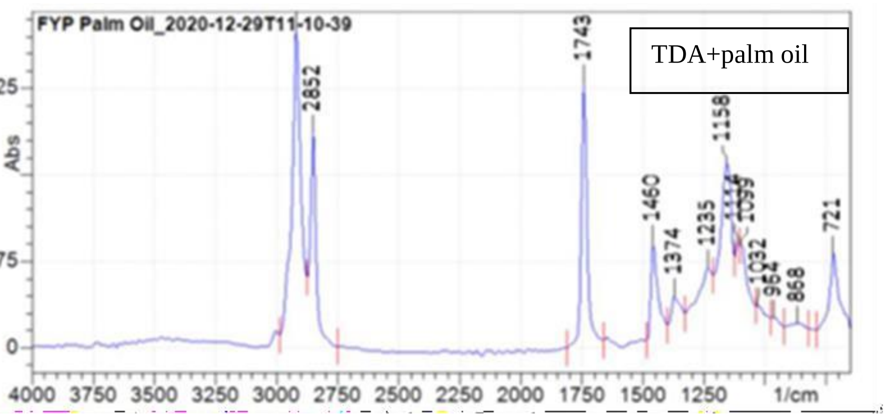
3.4 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR analysis was conducted to confirm the existence of functional groups in the organic phase after extraction process which was taken from gravity settling during screening test. **Figure 4 (a)**, **(b)**, and **(c)** shows the configuration of peaks for the carrier (TDA+kerosene), diluent (TDA+palm oil) and stripping agent (organic phase from diluent+NaOH) respectively. From the spectrums, the obvious peaks at 2900, 2852, 2955, and 2854cm^{-1} are due to C-H bond, while the wags at 721cm^{-1} and 723cm^{-1} were results from N-H bond by tertiary amine that is present in TDA. This shows that both **Figure 4 (a)** and **(b)** contain TDA in the solutions after extraction. Meanwhile, and C=O stretching at 1743cm-1 O-H stretch at 3301cm^{-1} indicates the triglycerides contained in cooking palm oil in **Figure 4 (b)** and **(c)**. From **Figure 4 (a)**, it shows that the peaks at 2854 cm^{-1} and 2955 cm^{-1} contain an alkane bond which is C-H3 bond that is present in kerosene. The adsorption peaks at 1376cm^{-1}, 1374cm^{-1} and 1370cm^{-1} proves that there are traces of silver ions (Ag+) in the all **Figure 4 (a), (b)** and **(c)** since the extraction was not 100% yield. As for **Figure 4 (c)**, a very broad peak 3277cm^{-1} was attributed by the stretching mode of O-H acid bond which proves the presence of NaOH.

(a)



(b)



(c)

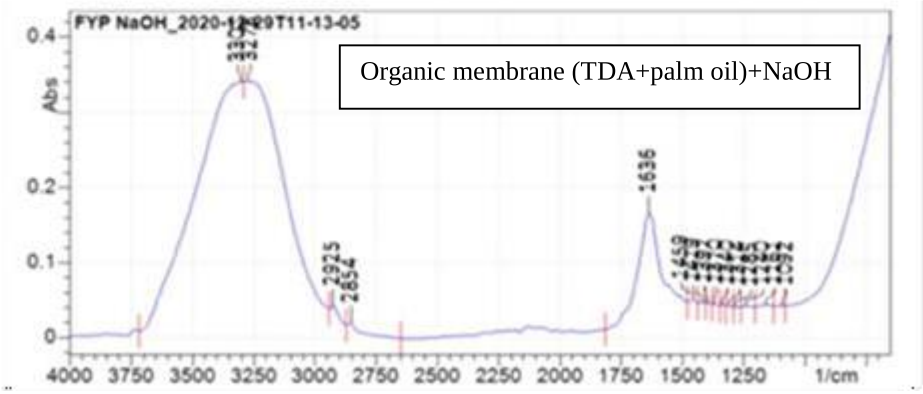


Figure 4: FTIR analysis of organic membrane solutions for (a) carrier, (b) diluent and (c) stripping agent after extraction

4. Conclusion

The selection of emulsion liquid membrane components for the extraction of silver was investigated by screening process and the extraction yield was determined. The most suitable components are tridodecylamine (TDA) as carrier, cooking palm oil as diluent and natrium hydroxide, NaOH as stripping agent. Based on this formulation, the percentage of silver extraction and stripping are 94.1% and 82.8% respectively. In the future, further studies on the difference of pH, temperature, agitation speed and components concentration can be conducted to explicate its effects in formulating a highly effective liquid membrane. Overall, it can be concluded the emulsion liquid membrane formulated have provide has a good potential in extracting silver and can be used in the recovery of silver from wastewater.

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