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***Research paper***

# Mercury(II) extraction from solution with W/O type of liquid membrane emulsion using surfactant combination (span-80 + span-20) and 1-phenyl-3-methyl-4-benzoyl-5 -pyrazolone as carrier of cation

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**Abstract**

The study of mercury(II) solution was extracted by using W/O type liquid membrane emulsion combined of Span-80 & Span-20 surfactant and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) as a cation carrier. The emulsion was prepared by mixing a 25 mL internal phase containing a nitric acid solution with a 25 mL membrane phase (surfactant and HPMBP solution in dodecane) then stirring at 2000 rpm emulsification speed for 8 min. Subsequently, the emulsion was mixed into the internal phase which containing mercury(II) solution and stirred at 299 rpm for 12 min. The optimum results show that the surfactant concentration was 2.5% with the emulsion volume and the external phase ratio of 1: 7 in pH condition of 3. In addition, the HPMBP concentration was used of 0.018 M with an internal phase concentration of 2.0 M nitric acid. Based on the results that the 50 mL liquid membrane emulsion could be extracting 30 ppm mercury (II) in 350 mL solution with the optimum extraction was 98.6%. This result is expected to be a reference for dealing with low concentrations of mercury waste in nature.

***Keywords***: *Mercury (II); Membrane; Liquid; Surfactants; Acidity.*

## 1. Introduction

The high quantities of heavy metals are generally toxic to living things but if the low quantities it is very necessary. Accumulate the heavy metal in a human body through various media such as air, food or water. If this condition persists for a long time can reach the amount that endangers human health cause some dangerous diseases such as lung cancer, hepatitis, cirrhosis, diarrhea, Parkinson's, encephalopathy, impaired digestive, and kidney function, dermatitis, etc. Mercury is one of the most dangerous metals and naturally abundant in nature is very small concentration. Meanwhile, this high abundance can become more available in the environment due to the modern industrial world resulting in mercury liquid waste along with technological advances and population growth.

Many industrial wastewater treatment techniques can be applied, but it is also necessary to think about the recovery method of heavy metals so that they can be reused for other industries. Liquid waste processing techniques such as sedimentation and filtration always produce solid waste that requires re-processing, which requires excessive reagents which will eventually become new pollutants. Other processing techniques are solvent extraction, but this method is less efficient and less economical because the extraction and back extraction step done repeatedly. The separation technique is still developing today in the liquid membrane emulsion technique. This technique provides wide and potential application range due to its characteristics such as ease of operation, relatively cheaper operational costs, high and efficient effectiveness (extraction and back-extraction stages occur in one stage). The novelty of this study, we rereview used HPMBP as a cation or extractant carrier which the applicability for the complexometry against mercury ion caused to the industrial wastewater. Recent decade, it is very effective in the extraction of metal ions such as copper, zinc, nickel, manganese, and iron, Pb metal (IV), and Th (IV), La (III), Au (III) and Lu (III). Liquid membrane emulsion techniques have been widely applied to several studies, such as metal extraction of cadmium, copper, lead, chromium, cobalt, Arsenic, extraction and separation of Penicillin G.

The liquid membrane emulsion prepared by forming emulsions in two non-continuous liquid phases and for stabilizing emulsion during the extraction process. The addition of a surfactant serves to lower the surface tension, and dispersed into the external phase. The external phase contains mercury ions to be extracted while the internal phase is the phase of the mercury ion receptor that has been separated after passing through the liquid membrane. Extraction mechanism begins with the reaction in the outer surface of the membrane between the reagent HPMBP as cation carrier (dissolved in the membrane phase) and mercury ions forming complexes Hg $(PMBP)_2$ which dissolves well in the membrane phase.

This complex diffuses in the membrane phase to the internal phase. Hence their liberator's substances in the internal phase ($HNO_3$) the mercury ions to be released from the complex compounds on the surface of the membrane and be dissolved into the internal phase. Furthermore, the HPMBP cation carrier which has released the mercury ion, diffused back to the outer surface of the membrane to form a new complex with other mercury ions.

## 2. Materials and methods

### 2.1. Equipment and materials

Laboratory glassware, digital balance (AND GR-200), pH meter (Lamotte), UV-Vis Spectrophotometer (Perkin Elmer Lambda 25), emulsification/agitation stirrer (0 - 3000 rpm). All chemicals used Merck-Germany quality are mercury chloride, 1-phenyl-3-methyl-5-pyrazolone, benzoyl chloride, nitric acid, hydrochloric acid, sodium hydroxide, calcium hydroxide, 1,4-dioxane, n-hexane, span-20, span-80, dodecane, dithizone, carbon tetrachloride, distilled water.

### 2.2. Synthesis HPMBP, 1-phenyl-3-methyl-4-benzoyl -5-pyrazolone

Dissolve a number of 1-Phenyl-3-methyl-5-pyrazolone in 80 mL of 1, 4-dioxane in a three-neck flask equipped with a reflux cooler, magnetic stirrer, and a funnel, at a temperature of 75˚C. Once dissolved, slowly and gradually added some the calcium hydroxides to homogeneous. While stirred, through the separating funnel is added benzoyl chloride. Then the heating temperature is raised to 100-120˚C and refluxed for 30 minutes. After the reflux is complete, in a hot mixture is feed into a flat bottom flask containing 2M HCl solution while stirring with a magnetic stirrer for 45 minutes. The formed dirty crystals are filtered with a Buchner filter and washed with a little water and 1,4-dioxane and dried. The structure tested using FTIR and H-NMR Spectrophotometer.

### 2.3. Effect of surfactant concentration

The emulsion was prepared by mixing a 25 mL membrane phase (dodecane containing 0.015M HPMBP and a surfactant combination (Span-80 & Span-20) with concentrations varying 2%; 2.5%; 3%; 3.5%; 4%) with a 25 mL internal phase (containing $HNO_3$ 1M). Then stirred with a stirring speed of 2,000 rpm for 8 minutes. In the flask, 56 mL of emulsion was added to 300 mL of 30 ppm mercury solution with pH = 2. The extraction process was carried out at 299 rpm for 12 minutes. After extraction, the external phase was separated from the emulsion and the mercury ion concentration was measured using a UV-Vis spectrophotometer at 490 nm wavelength with dithizone as its complexing agent. This method (experiment 2.3) refer used to the next technique.

### 2.4. Effect of HPMBP concentration

The experiments were conducted similar to experiment 2.3, but by using variations of HPMBP concentrations of 0.015M, 0.018M, 0.020M, 0.022M and 0.025M and using the optimum conditions obtained in experiment 2.3. This method (experiment 2.4) refer used to the next technique.

### 2.5. Effect of $HNO_3$ concentration in the internal phase

The experiments were carried out similar to experiment 2.3, but by using a variation of 0.5M, 1.0M, 1.5M, 2.0M, 2.5M, 3.0M nitric acid concentrations and using the optimum conditions obtained in experiment 2.3 and 2.4. This method (experiment 2.5) refer used to the next technique.

### 2.6. Effect of external phase pH

The experiments were conducted similar to experiment 2.3, but by using external phase pH variation of 2.0; 2.5; 3.0; 3.5 and 4.0 and using the optimum conditions obtained in experiments 2.3; 2.4 and 2.5. This method (experiment 2.6) used to refer the next technique.

### 2.7. Effect of the volume ratio of emulsion and external phase

The experiments were carried out similar to experiment 2.3, but using the variation of the emulsion and the external phase volume ratio of 1: 5, 1: 6, 1: 7, 1: 8 and 1: 9 and using the optimum conditions obtained in experiments 2.3; 2.4; 2.5; and 2.6.

## 3. Result and discussion

### 3.1. Synthesis HPMBP, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone

HPMBP crystal was bright yellow and have a melting point of 88˚C with a synthesis yield of 70.21%. Infra-red spectrum at wave numbers around 3101.54 $cm^{-1}$ indicate the carboxylic -OH stretch while the range of C=C or C=N is shown by their peak at around 1598.99 $cm^{-1.}$ Their range are shown their aromatic group -CH peaks at 3059.1 $cm^{-1}$, whereas the peak at wavenumber 1352.1 $cm^{-1}$ and 1826.59 $cm^{-1}$ indicates uptake bends $-CH_3$ and stretch C=O. The existence of these peaks supports the HPMBP structure.
The H-NMR spectrum showed the singlet peak at 2.0948 ppm chemical shift specific to the methyl group ($-CH_3$) with 3 protons corresponding to the height integral spectrum (3.071). The singlet peak at a chemical shift of 12.7750 ppm identifies the presence of a -OH bond of the carboxyl group with 1 proton with an integral height of 0.607. Whereas the multiplet peak at chemical shift 7.4593 – 7.8957 ppm is specific for the phenyl/aromatic group. All of the chemical shifts obtained to support the HPMBP structure.

### 3.2. Effect of surfactant concentration

Based on the experiment 2 results and the determination of extraction percentage of mercury ions, we have obtained graphs such as Fig. 1.

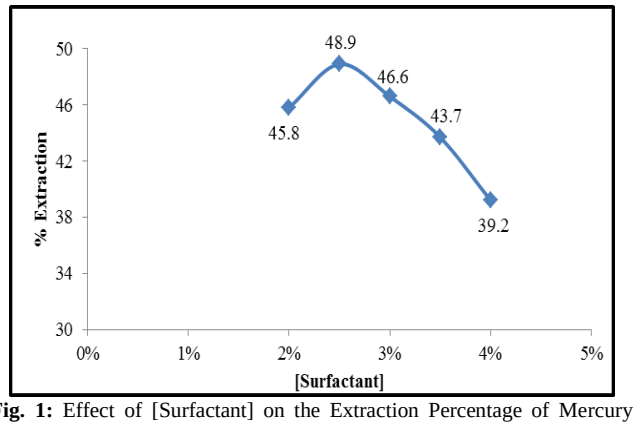


**Fig. 1:** Effect of [Surfactant] on the Extraction Percentage of Mercury Ions.

Fig. 1 shows that the concentration of surfactant giving the largest percentage of extraction is at a concentration of 2.5%. The surfactant is not sufficient to reduce the surface tension between water (internal phase) and dodecane (membrane phase) in 2.0% concentration so that the emulsion formed is less stable and ultimately affects the diffusion process. However, at a concentration of 2.5% seen percent extraction increases with increasing surfactant concentration while at concentrations above 2.5% extraction percentage tends to decrease. This is due to the increasing surfac-

tant concentrations in the membrane phase will also increase the viscosity of the emulsion thus slowing the transport process or complex diffusion in the emulsion.

### 3.3. Effect of HPMBP concentration

Fig. 2 shows a graph of the effect of HPMBP concentration on the extraction percentage of mercury ions. This graph shows that greater concentration of HPMBP up to 0.018 M will give a higher extraction percentage as well. But at concentrations above 0.018 M percentage extraction tends to decrease. This is due to the increase in HPMBP concentration, although all mercury ions have been extracted but the overuse of HPMBP allows for the interaction of HPMBP polar groups with water in the external phase thus inducing the osmosis process. In addition, very high HPMBP concentrations can lead to increased membrane viscosity, thus slowing down the transport process, thus lowering the percentage of extraction.

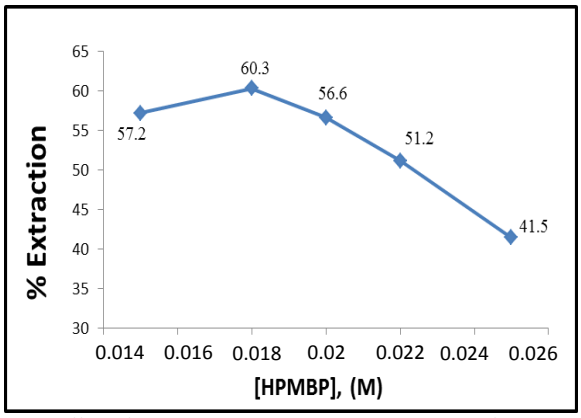


**Fig. 2:** Effect of [HPMBP] on the Extraction Percentage of Mercury Ions.

### 3.4. Effect of nitric acid concentration

Based on the results of experiment 4 and the calculation of extraction percentage of mercury ions obtained graphs such as Fig. 3.

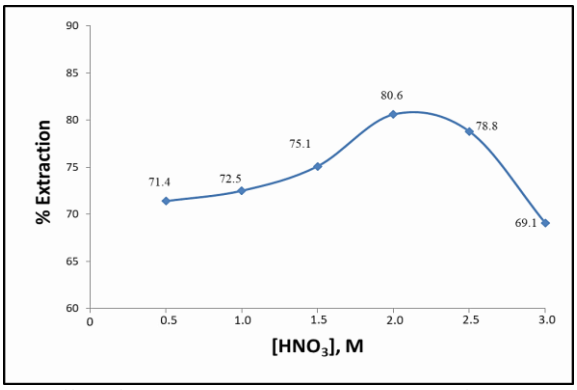


**Fig. 3:** Effect of [$HNO_3$] on the Extraction Percentage of Mercury Ions.

Nitric acid in the internal phase serves as a stripping agent. The high concentration of hydrogen ions in the internal phase will force the equilibrium to shift toward the release of mercury (II) ions. This can be seen in Fig. 3, the higher concentration of nitric acid up to 2.0M, the percentage of extraction is also higher. But at higher concentrations than 2.0M, the percentage of extraction seems to decrease. This decrease is due to the reaction between the nitric acid (high concentration) and the surfactant involving the reduction of surfactant properties resulting in the destabilization of the emulsion.

### 3.5. Effect of the external phase pH

The process of complex formation Hg $(PMBP)_2$ on the outer surface of the membrane, involving the exchange of two hydrogen ions from an ion HPMBP with mercury(II). The complex must be sufficient to allow the concentration gradient between the outer surface and the inner surface of the membrane so that the complex diffusion is effective. Therefore, the hydrogen ion concentration in the external phase must be relatively small so it is necessary to determine the optimum pH of the external phase. From the experimental results and calculations, the effect of external phase pH on the extraction percentage of mercury ions are described as graphs as in Fig. 4.

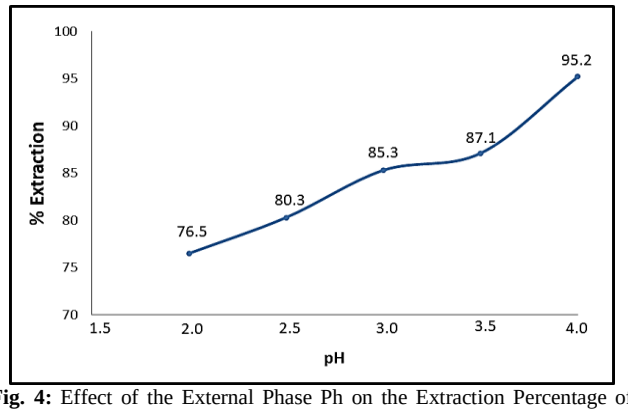


**Fig. 4:** Effect of the External Phase Ph on the Extraction Percentage of Mercury Ions.

Fig. 4 shows that the percentage extraction will increase as the pH increases from 2.0 to 4.0. However at pH 3.5 the solution is slightly turbid as it starts to form mercury (II) hydroxide. The high percent of extraction at pH above 3 is not due to extraction perfection but because before the extraction is done, there are already many mercury ions precipitating as its hydroxide so that the remaining mercury (II) ions in solution will be perfectly extracted.

### 3.6. Effect of the volume ratio of emulsion and external phase

Fig. 5 shows that the volume ratio of emulsion and the external phase giving the largest percentage of extraction is at a 1: 7 volume ratio. In a 1: 5 volume ratio, a small percentage of extraction is due to the higher emulsion amounts can lead to increased emulsion breakdown. This is because with the increased volume of emulsion, the phenomenon of bloat becomes faster accompanied by the incorporation of internal phase drops that can lead to emulsion breakdown. Whereas in a smaller volume ratios seen the extraction percentage tends to decrease as the volume of external phase increases. This is due to the increasing volume of external phase resulting in the number of mercury ions increasingly so that the internal phase is not able to accommodate all mercury ions that are in the external phase. As a result the percentage of extraction will decrease.

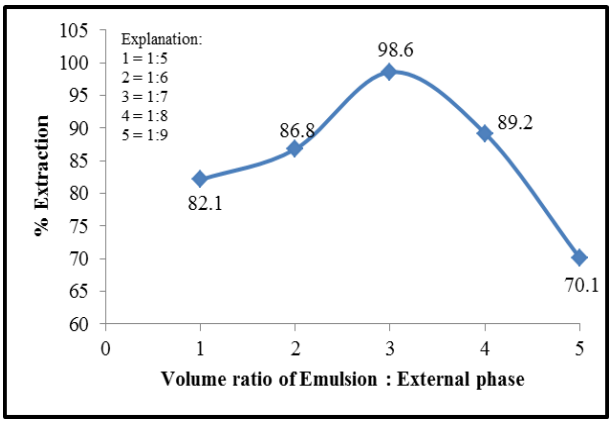


**Fig. 5:** Effect of Volume Ratio of Emulsion and External Phase on the Extraction Percentage of Mercury Ions.

## 4. Conclusions

The optimum conditions of mercury ion extraction that the concentration of surfactant combination (span-20+span-80) was 2.5%, HPMBP concentration was 0.018 M, the concentration of $HNO_3$ in the internal phase was 2 M, pH of external phase was 3, the volume ratio of emulsion and the external phase was 1: 7. By using the optimum conditions, 50 mL of a liquid membrane emulsion can extract 30 ppm mercury ions present in 350 mL nitric acid solution with extraction percentage of 98.6%.

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