

Recovery of Ni Metal from Spent Catalyst with Emulsion Liquid Membrane Using Cyanex 272 as Extractant

Yuliusman¹, M Huda¹, I T Ramadhan¹, A R Farry¹, P T Wulandari¹, R Alfia¹

¹Chemical Engineering Department Universitas Indonesia. Universitas Indonesia, Depok 16425. Indonesia

E-mail: usman@che.ui.ac.id

Abstract. In this study was conducted to recover nickel metal from spent nickel catalyst resulting from hydrotreating process in petroleum industry. The nickel extraction study with the emulsion liquid membrane using Cyanex 272 as an extractant to extract and separate nickel from the feed phase solution. Feed phase solution was prepared from spent catalyst using sulphuric acid. Liquid membrane consists of a kerosene as diluent, a Span 80 as surfactant, a Cyanex 272 as carrier and sulphuric acid solutions have been used as the stripping solution. The important parameters governing the permeation of nickel and their effect on the separation process have been studied. These parameters are surfactant concentration, extractant concentration feed phase pH. The optimum conditions of the emulsion membrane making process is using 0.06 M Cyanex 272, 8% w/v SPAN 80, 0.05 M H₂SO₄, internal phase extractant / phase volume ratio: 1/1, and stirring speed 1150 rpm for 60 Minute that can produce emulsion membrane with stability level above 90% after 4 hours. In the extraction process with optimum condition pH 6 for feed phase, ratio of phase emulsion/phase of feed: 1/2, and stirring speed 175 rpm for 15 minutes with result 81.51% nickel was extracted.

1. Introduction

Selective separation of metal ions from industrial waste is frequently required in order to prevent environmental pollution. Currently, the application of solvent extraction process with organic extractant for the recovery of nickel metal from catalyst waste has been described. Most of these studies concerned solvent extraction using organophosphorus acid extractants such as D2EHPA (at (2-ethylhexyl) phosphoric), PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl esters acid) and Cyanex 272 (phosphonic acid) [1].

The emulsion liquid membrane (ELM) technique has been regarded as an advance in relation to solvent extraction for separating and concentrating metal ions from aqueous dilute solutions. Liquid membranes have shown potential results in the extraction process, especially in cases where solute concentrations are relatively low and other techniques cannot be applied efficiently since they combine the process of extraction and stripping in a single unit operation. This membrane technology is also highly selective, efficient, and simple because of the extraction and stripping steps that are carried out safely in one continuous process, resulting in less time consuming and less extractant use as in liquid-liquid extraction [2]. This type of emulsion liquid membrane is the best because it produces the highest degree of separation of metals and can be applied on a large scale [3].



In emulsion liquid membranes the extractant is an organic compound have been applied to separate Ni ions in acidic solution. Several studies related to the use of some extractants such as Cyanex 272, D2EHPA, and PC-88A for extracting nickel in liquid-liquid extraction systems have been reviewed. The efficiency of nickel extraction produced when using 0.1 M Cyanex 272 with kerosene solvent at pH of the feed phase 5,8 was 9%, and when using 0.05 M D2EHPA as solvent and the pH feed phase was 6% [4]. Results indicated by 0.15 kmol/m³ PC-88A with kerosene solvent at pH phase feed at 7.5 also did not show satisfactory results because they were only able to extract 20% of nickel metal [5]. In this study used Cyanex 272 with concentrations varied on the emulsion liquid membrane system because one of the factors that play an important role to produce a good extraction efficiency is extractant concentration.

Surfactants in the emulsion liquid membrane extraction process are used as bridges where the hydrophilic side binds to the water phase and the lipophilic side binds to the oil resulting in a mixture of water and oil [6]. The surfactant also acts as an emulsion stabilizer by forming a protective layer and oriented to the interface and lowering the tension between the dispersed droplets. Emulsion stability is needed to make the extraction process more optimal. Types of surfactants commonly used are derived from the sorbitol ester (Span) or polyoxyethylenated sorbitol ester (Tween) group. Sorbitan mono-oleate (Span-80) is a non-ionic surfactant widely used for water-oil-water emulsion stabilizers [6]. Structure of Span 80 is shown in Figure 1

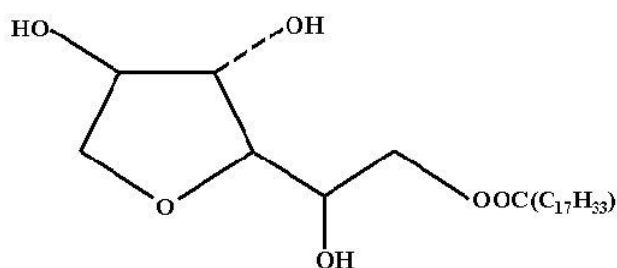


Figure 1. Structure of Span 80

2. Experimental

2.1 Reagents and Apparatus

The liquid membrane phase is composed of surfactant, carrier, and solvent. The non-ionic surfactant used is sorbitane monooleate commercially known as Span-80 which is supplied by Merck Co., Germany. The used carrier is bis (2,4,4-trimethylpentyl) phosphinic acid or commercially known as Cyanex 272 purchased from Cytec Inc. Solvent or organic solvent used is kerosene commercial purchased from Pertamina, Indonesia. Sulfuric acid is used as a stripping phase or internal phase purchased from Merck Co., Germany. Emulsions are prepared using 250 mL Erlenmeyer (Pyrex Inc.) and in homogenization using high-speed homogenizer (IKA, Germany). The pH value was measured using CyberScan 510 pH meters.

2.2.1 Procedure

2.2.2 Emulsion Preparation and Stability Analysis. The emulsion is prepared in a 250 mL Erlenmeyer containing a mixture of non-ionic surfactant Span-80, a carrier that has been dissolved with kerosene and sulfuric acid as an internal phase. The mixture stirred for 60 minutes at 1000 rpm. The internal phase and organic phase (I/O) ratios were kept at 1:1 for all experimental variations. The surfactant concentration was varied from 4% -10% w / v and the carrier concentration (extractant) was varied from 0.06-0.2 M to find the optimum concentration in the emulsion stability. The finished primary emulsion was transferred to a 100 mL measuring glass to observe the emulsion volume change for 240 minutes.

2.2.3 Nickel Extraction. Prepared emulsions with optimum conditions are poured into another 250 mL Erlenmeyer containing Ni 800 mg / L solution as the feed phase. The emulsion and feed phase ratios are maintained at 1: 1. The emulsion and feed phase mixture is stirred with a stirrer at 250 rpm for 15 minutes. The pH of the feed phase was varied from 5 to 8 to determine the effect of pH of the feed phase on the extraction efficiency. Then the emulsion phase mixture and the feed phase (external phase) are separated by a separatory funnel for 30-60 minutes. Phase feed that has separated the nickel metal content then measured using Atomic Absorption Spectrometry (AAS). The schematic of emulsion liquid membrane extraction is shown in Figure 2.

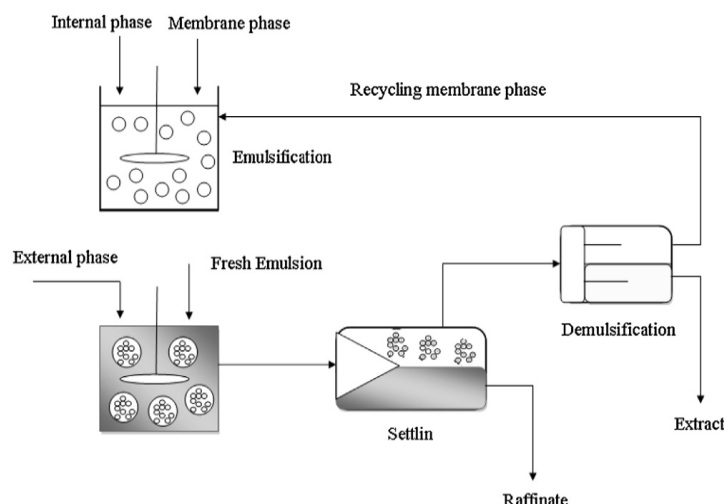


Figure 2. The schematic of emulsion liquid membrane extraction.

3. Result and Discussion

3.1 Effect of Surfactant Concentration

The emulsion was prepared by mixing kerosene as diluent, Cyanex 272 as carrier, H₂SO₄ 0.2 M as stripping agent and Span 80 as surfactant. The internal phase/organic phase ratio was kept 1:1 for all experiment and the concentration of Cyanex 272 was kept 0.06 M for this experiment. After the emulsion was formed, it was removed from erlenmeyer to 100 ml measuring cylinder for immediate stability for 4 hours. The 4 hour time is ideal time to see the stability of the emulsion [7]. Emulsion stability study was observed by visual with the eye of how the emulsion volume decreased. The decrease in the volume of the emulsion may be characterized by a separate organic phase or an internal phase separated from the emulsion. To facilitate readability, the emulsion stability can also be represented by the volume of the emulsion. The Equation 1 shows the percentage formula of emulsion stability dependent on the emulsion volume. The comparison of surfactant variation to emulsion stability is shown in Figure 3.

$$\text{Emulsion Stability (\%)} = \frac{\text{Final Emulsion Volume (ml)}}{\text{First Emulsion Volume (ml)}} \times 100 \% \quad (1)$$

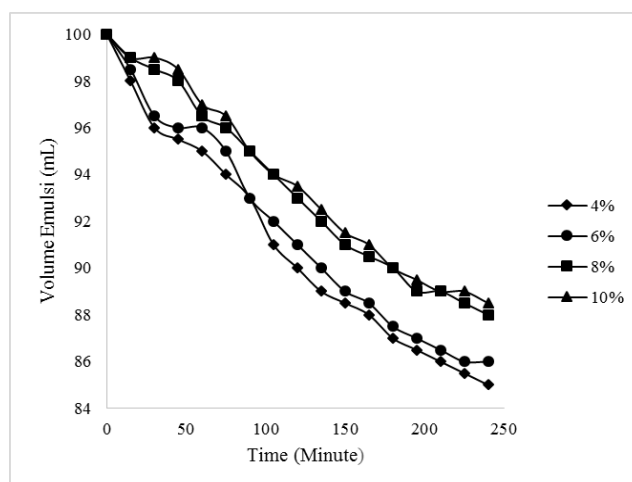


Figure 3. The effect of surfactant Span 80 concentration on the stability of emulsion liquid membrane. Cyanex 272 0.06 M, H_2SO_4 2 M, I/O ratio 1/1

The results of the emulsion stability observation were shown in Figure 3 shows that the Span-80 surfactant concentration increases from 4% w/v to 10% w/v the longer separation between the organic and aqueous phase of the emulsion. This is characterized by a decrease in the emulsion volume that indicates that the effect of surfactant concentration on the emulsion liquid membrane stability is significant.

In Figure 3 was known that with increasing surfactant concentration will increase the emulsion stability. However, in this experiment the use of Span-80 surfactant has not obtained a perfect emulsion stability or in other words there is no emulsion phase which is completely constant or stable in maintaining its volume after 4 hours of observation. This is characterized by the separation of the organic phase and the internal aqueous phase from the emulsion continuously. Although the organic phase separation and the internal aqueous phase of the emulsion take place more slowly at Span-80 concentrations above 8% w/v which is characterized by increasingly sloping curves formed. However, there has not been a constant or stable volume of emulsions for a long period of time.

If surfactant concentration was increased the more surfactants occupy the position in the emulsion interface layer. So the emulsion stability is increased because the surfactant can reduce the surface tension between oil (nonpolar phase) with water (polar phase) by means of the adsorption event in the interface layer of liquids. This is supported by research that has been done by [8], that too low a surfactant concentration can not be a strong enough protector to prevent emulsion droplets from breaking out. While the addition of surfactant levels of more than 8% produce better emulsion stability but not significant. This indicates that the placement of the surfactant in the interface layer through the adsorption event is close to saturation. The event is also due to the higher level surfactant having a limit for the formation of good droplets to produce a good emulsion [9]. Therefore, a further increase in surfactant concentration will only lead to surfactant residues that can not be adsorbed again and accumulate in the membrane/extractant phase. The accumulation of this surfactant residue will increase the viscosity of the whole emulsion phase, giving rise to excess resistance when the extractant wants to transport metal ions from the feed phase to the internal phase.

3.2 Effect of Cyanex 272 Concentration

The emulsion is prepared by mixing Span 80 as a surfactant, H_2SO_4 0.2 M as the internal phase, kerosene as solvent and Cyanex 272 whose concentration is varied as a carrier. The internal phase/organic phase ratio is 1:1 and the concentration of Span 80 is kept constant at 8% w/v. Figure 4 shows the effect of Cyanex 272 concentration on emulsion stability. Effect of Cyanex 272 concentration on emulsion stability The higher concentration of cyanex 272 used stability is decreasing, this is because cyanex 272 also has hydrophilic group and hydrophobic group. Therefore,

if extractant quantity is too much it will replace the position of the surfactant at the interface position. Since the concentration and its complex ion are present at the interface it will provoke the loss of the extracted membrane phase and provoke the loss of the internal phase due to swelling [10].

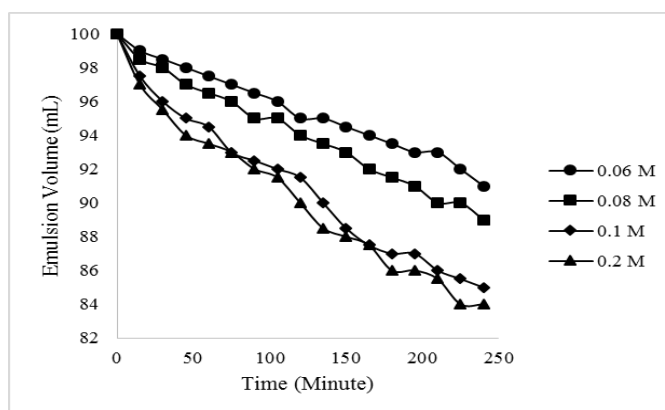


Figure 4. The effect of surfactant Cyanex 272 concentration on the stability of emulsion liquid membrane. Span 80 8% w/v, H_2SO_4 2 M, I/O ratio 1/1.

At low concentrations, the effects of Cyanex 272 concentrations are less visible because at concentrations of 0.06 M this extractant has not been able to compete with surfactants. When the concentration of the extractant was increased to 0.08 M to 0.2 M the effect on the emulsion stability becomes more apparent, as in the graph above, this occurs because the extractant already has a strong enough influence to replace the surfactant position in the interface layer so that it may interfere the stability of the emulsion. When the surfactant position in the interface layer is replaced by the extractant, the surface tension between the polar and polar phases will increase so that the emulsion becomes more susceptible to breakage, since the extractant replacing the surfactant cannot reduce the surface tension as a surfactant function.

The use of high concentration of extractant will also negatively affect the extraction process, because high concentration of extractant will disrupt the emulsion droplets dispersion process, causing the contact surface area between the feed phase (external phase), the membrane phase and the internal phase (Stripping agent) to be reduced which can slow the rate of metal extraction. Meanwhile, from the economic side, the use of extractants at high concentrations is also avoided, because in the manufacture of liquid membrane emulsion extractant price is the most expensive component.

3.3 Effect of Feed Phase pH on Extraction Efficiency

The pH of the feed phase is varied from 5 to 8 as shown in Figure 5. From the figure is known that as the pH of the feed phase increases from 5 to 6, the amount of nickel extraction efficiency produced also increases with the highest value of 81.51% at pH 6. However, when the pH of the feed phase was further increased to 7, the nickel extraction efficiency decreased significantly to only 77.61%. Based on the conditions in the previous study, the pH of feed phase 6 was the optimum condition in the nickel extraction process using Cyanex 272 extractant with an emulsion liquid membrane system [11].

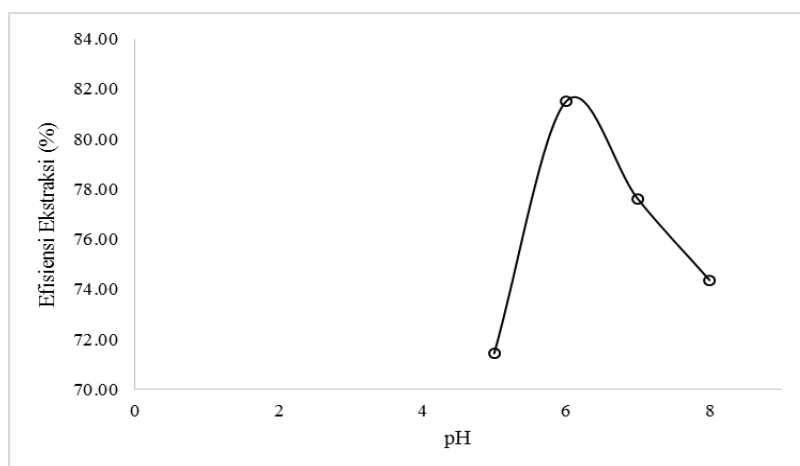


Figure 5. The effect of feed phase pH on nickel extraction

The feed phase pH is too high not can be used in the emulsion liquid membrane system due to the use of SPAN 80 surfactant. Surfactant SPAN 80 is a type of surfactant having a low molecular mass compared to other types of surfactants and has a large hydrophilic group dominantly composed of oxygen atoms with high electronegativity. Therefore, in the alkaline condition SPAN 80 is easily hydrolyzed and causes the emulsion leakage

At pH above 6 (high pH) it is estimated that metal hydroxide precipitation may occur. Metal hydroxide precipitation may occur as the increase in pH means the number of H^+ decreases and the amount of OH^- increases to allow the formation of insoluble metal hydroxide species in the distribution process [12].

The effect of pH on the efficiency of extraction is caused by the competition between H_3O^+ and Ni^{2+} in fighting anions. It is therefore desirable to increase the pH of the extraction capacity by increasing the amount of H^+ so that the competition of H^+ and Ni^{2+} for the extractant anion is reduced and Ni^{2+} can more easily react with the anion than the extractant.

4. Conclusion

As conclusion 81.51% of nickel were extracted under favorable conditions which are feed phase pH 6, Cyanex 272 concentration 0.06 M, Span 80 concentration 8% w/v, 2 M sulphuric acid as stripping agent and 15 min of extraction time.

Acknowledgement

The authors would like to acknowledge the laboratory head and laboratory assistant of Intensification Process Technology Laboratory at Chemical Engineering departement, Universitas Indonesia and Universitas Indonesia for making this research possible

References

- [1] Pospiech, B. 2015 *Physicochem. Probl. Miner. Process.* **52** 353-364
- [2] Harimu L, Sabirin M., Dwi S and Sri J 2010 *Indonesian journal of chemistry* **10**
- [3] Kislik V S 2010 *Liquid membranes principles & applications in chemical separation & wastewater treatment*. Amsterdam: Elsevier.
- [4] Pospiech B 2015 *Physicochem. Probl. Miner. Process.* **52** 353-364.
- [5] Nguyen V T, Lee J C, Jeong J, Kim B S and Pandey B D 2014. *Korean Chemical. Eng. Res* **53** 137-144.

- [6] Abou-Nemeh I and Van Peteghem A P 1992 *Journal of membrane science*, **70**.
- [7] Zainuddin S 2003 Hg (II) *Ions Extraction using Emulsion Liquid Membrane with Oleat Acid as Carrier, Span 80 and Tween 20 as Mixed Surfactants, and Kerosene as Organik Diluent*. Depok: Universitas Indonesia.
- [8] Elsayed F and Farooq A 2014 *International Journal of Chemical and Environmental Engineering* **05** 281-289.
- [9] Ahmad A L 2011 *Emulsion Liquid Membrane for Heavy Metal Removal: An Overview on Emulsion Stabilization and Destabilization*. Universitas Negeri Semarang: Semarang.
- [10] Valenzuela F, Salinas C, Basualto C, Hagar J S and Tapia C 2003 *Journal of the Chilean Chemical Society*, **48**
- [11] Chauduri J B and Pyle D L 1992 *Chemical engineering science*, **47**
- [12] Sulaiman R N, Norasikin R, Amin O and Saidina N 2013 *Emulsion Liquid Membrane Stability in The Extraction of Ionized Nanosilver from Wash Water*. Malaysia: Universiti Teknologi Malaysia