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Recovery of Ionized Nanosilver from Wash Water Solution using Emulsion Liquid Membrane Process

Raja Norimie Raja Sulaiman[a,b], Norasikin Othman[a*], Nor Aishah Saidina Amin[b]

[a]*Center of Lipids Engineering and Applied Research (CLEAR), Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia*
[b]*Chemical Reaction Engineering Group (CREG), Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia 81310 UTM Johor Bahru, Johor, Malaysia*

*Corresponding author: norasikin@cheme.utm.my

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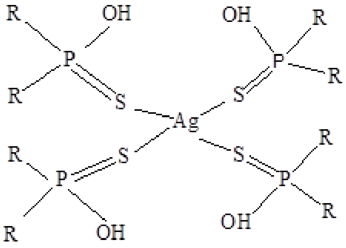
Graphical abstract



Abstract

The increasing numbers of product containing nanosilver have raised a great concern about their possible impact in the environment especially in the ionic form which leads to the toxicity problem when the association occurs with the organism cells. Therefore, the main focus of this study was to investigate several parameters influencing the recovery of ionized nanosilver from wash water using emulsion liquid membrane (ELM) process. This process involves three phases dispersion system including external, membrane and internal phase. The membrane phase was prepared by dissolving bis [2, 4, 4-trimethylpentyl] monothiophosphinic acid (Cyanex 302) as a carrier and Sorbitan Monooleate (Span 80) as a surfactant in kerosene as a diluent. Thiourea in Sulfuric acid (H_2SO_4) was used as a stripping agent in the internal phase. The important parameters such as extraction time, carrier and stripping agent concentrations were investigated. All experiments were conducted in batch system. The concentration of the ionized nanosilver was measured using Atomic Absorption Spectrometry (AAS). The result demonstrated that almost 100% of silver ion was extracted with 91% have been recovered within 5 minute of extraction time using 0.005 M Cyanex 302 and 1.0 M Thiourea in 1.5 M H_2SO_4. Hence, ELM was proven to be a very promising technique for the simultaneous extraction and recovery of ionized nanosilver from wash water.

Keywords: Ionized nanosilver; emulsion liquid membrane; extraction; recovery; wash water

■1.0 INTRODUCTION

Nanotechnology is a newly developed technology which deals with structures of nanoparticles ranging from one to hundred nanometers in one dimension. Nanosilver is one of the nanoparticles which have been widely used in various products such as jewellery, utensils, currency, photography and alloy. Nanosilver introduce their properties as an antimicrobial agent in cotton and take place in medicinal application because they can kill a wide range of bacteria from the wound and dissolve faster once moistered in blood.[1-2] Unfortunately, the release behaviour of this valuable nanoparticle has raised a great concern to the government and public about its impact on the environment. For instance, about 30% of the silver nanoparticles (<15nm) found in paint on building facades are lost within one year of exposure to the ambient weather conditions.[3] In addition, about 1.4 to 270,000 μg Ag is released from consumer product at home.[4] Due to this scenario, there is a high possibility for the terrestrial and aquatic organism to be exposed in the middle of the investigation with long term nanosilver toxicity effect. Silver nanoparticle can be a threat to us as they possess smaller in size which help them easily access to aquatic cell system through many various routes of exposure including inhalation, dermal and oral.[5]The toxicity of silver is significantly proportional to the rate of releasing free silver ions.[1] Some of the nanosilver which has been ionized in water is very harmful to the aquatic organism.[6] Malaysian still do not have the limitation concentration of silver contain in wastewater but the Interim National Water Quality Standard (INWQS) for Malaysian river water concentration is classified 0.05 ppm of silver contain in river water is still under controlled and permissible. The standard limit of silver ion in water is only 0.5 to 2 ppm. Besides, Water Environment Research Foundation (WERF) has found out that at some level, these silver nanoparticles can inhibit the growth of bacterial populations which is crucial for biological treatment process. The effect of silver nanoparticles also inhibits the growth of *Escherichia coli* bacteria.[7] So effective removal of nanosilver ion from the wastewater prior to discharge to the environment is of great importance.

There are several number of techniques have been approached by a lot of researcher in order to extract and recover metal ions such as electrolysis, electrodialysis, ion flotation, ultrafiltration and chemical precipitation but still provide some limitation such as high cost, higher energy consumption and lead to sludge production.[8-9] In order to overcome the toxicity problem of the ionized nanosilver, liquid membrane technology has been introduced to protect environment in terms of removal and recovery of various metals. This technology provides simple operation, fast, energy saving and less of chemical consumption.[10]The extraction and recovery of the ionized nanosilver via liquid membrane technology is one of the promising techniques in order to reduce the environmental problem. The emulsion liquid membrane has become the selective method to treat nanosilver ion from wash water owing to their unique characteristic over other conventional method especially the extraction and recovery process occur simultaneously. This method has shown the high selectivity of recovering silver ions from photographic waste using the different emulsion liquid membrane (ELM) formulation.[11] However, this technique also provides a drawback which is water in oil emulsion instability. Therefore the operating condition and the selectivity of emulsion liquid membrane formulation such as carrier, surfactant, diluent and stripping agent are great of importance because they influence a lot on the stability of emulsion liquid membrane. Demulsification is one of the critical steps for recovering the solute and membrane phase just after the extraction process. This process is performed in order to separate the phases that make up the emulsion, internal aqueous and membrane phase. At the end of the process, the membrane phase can be reused and the internal phase which is enriched with the concentrated solute can be recovered or recycled.

This paper will present the study of the extraction, stripping and recovery for the ionized nanosilver from wash water with ELM system. This manuscript focuses on the studies to find the favourable conditions for the liquid membrane formulation. Thus the important parameters influencing the extraction and recovery efficiency in the emulsion liquid membrane system such as extraction time, carrier and stripping agent concentrations will be discussed in this paper.

2.0 EXPERIMENTAL

2.1 Materials and Apparatus

Kerosene as a diluent, bis [2, 4, 4-trimethylpentyl] monothiophosphinic acid (Cyanex 302) as a carrier, Sorbitan Monooleate (Span 80) as a surfactant and Thiourea in sulphuric acid as a stripping agent solution were purchased from Sigma Aldrich. Liquid nanosilver in the range <100 nm was procured from one of the company in Malaysia. Wash water was taken from the laundry service. Nitric acid and sodium hydroxide solutions were used to adjust the initial pH of the wash water solutions purchased from Qrec. All these reagents and solutions were directly used as received without further purification. Apparatus used include Homogenizer Heidolph Silent Crusher M Emulsifier, Perkin Elmer Flame Atomic Absorption Spectrometer (AAS) for measurement of silver ion concentrations, Portable Smart pH meter 108 (Milwaukee Model) for pH measurement and High Voltage Demulsifier for the demulsification process.

2.2 Experimental Procedure

An equal volume of 5 ml of organic liquid membrane solution containing Cyanex 302 and Span 80 in kerosene and an aqueous stripping solution (acidic Thiourea) was emulsified continuously at 12000 rpm using motor driven homogenizer for 5 min to attain a stable primary emulsion. The emulsion must be freshly prepared each time before the experiments. Then it was dispersed into the agitated vessel of simulated wash water containing nanosilver with appropriate treat ratio. The mixture was stirred at 150 rpm for 5 minutes of extraction time. Then, the samples were quickly introduced into a separation funnel and left for phase separation for 30 minutes until two layers of aqueous and emulsions were clearly separated. The bottom layer was the aqueous phase and emulsion at the upper layer. The aqueous layer at the bottom was taken for the extraction measurement study. After the extraction process, the emulsion from the upper layer was collected and demulsified using a high voltage demulsifier. The demulsification process stopped when the emulsion showed two layers of complete separation. The membrane phase was recovered and the more concentrated solute ion was obtained. The concentrations of silver ions were measured using Atomic Absorption Spectrometry (AAS). The same procedures were repeated for different conditions and formulations. The extraction, stripping and recovery percentage in the emulsion liquid membrane were measured using the equations as shown below:

$$\%\ Exctraction, E_x = \frac{C_i - C_f}{C_i}\ x\ 100\%$$

$$\%\ Stripping, S_x = \frac{C_{int}}{C_{mem}\ x\ 2TR}\ x\ 100\%$$

$$\%\ Recovery, R_x = \frac{C_{int}}{C_{ext}\ x\ TR}\ x\ 100\%$$

where,

C_i: Initial concentration of silver ion before extraction
C_f: Final concentration of silver ion in aqueous after extraction
C_{int}: Concentration of silver ion in internal phase
C_{mem}: Concentration of silver ion membrane phase
C_{ext}: Concentration of silver ion in external phase
TR: Treat ratio

3.0 RESULTS AND DISCUSSION

3.1 Wash Water Characterization

Table 1 shows all the ions found in wash water solutions. Based on Table 1, wash water contains sodium, calcium, and potassium while the anions were chloride, nitrate and sulphate. Even though there were many ions in the external phase, silver ion was targeted to be extracted and recovered in this process. This could be attributed to the carrier properties chosen in this process where previously Cyanex 302 had been developed as a carrier for some transition metals extraction like cadmium, copper, gold, and lead.[12-15] The silver extraction using some commercial sulfur containing extractant like SFI-6R, MSP-8, Cyanex 302 and Cyanex 301 indicated that the carrier containing P=S and P(S)SH functional groups were strongly extracted the silver in the whole range of hydrochloric acid except for the very high concentration.[16] In addition, sulphur substitution could increase the acidity of the carriers, making them particularly suitable for the extraction of soft lewis acid metal ions such as Ag(I), Ni (II), Zn (II) in accordance to the Hard Soft Acid Base (HSAB) principle. Cyanex 302 also had provided a good extractability on silver compared to the other two extractants , Cyanex 272 and D2EHPA.[19] The proposed structure of Ag-Cyanex 302 complexes was shown in Figure 1.

According to the proposed structures, hard base oxygen donor ligands did not take part owing to the low stability of the forming complexes. Since the metal ion was coordinated by four sulphur atoms, each contributing an electron pair, the total number of electrons around the metal centre added up to eighteen (18 electron rule) which was the most favoured closed shell configuration for transition metal ion of silver.[16]

Table 1 Anion and cation content in wash water

Cations	Concentrations (ppm)
Na	9.918
K	1.540
Ca	1.583
Ag	4.829
Anions	Concentrations (ppm)
Cl	56.828
NO_3^-	3893.47
$S0_4^{2-}$	103.643

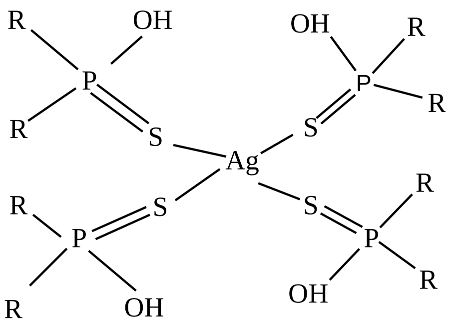


Figure 1 The proposed structure of silver-Cyanex 302 complexes

3.2 Recovery Mechanism of Ionized Nanosilver

The mechanism for the extraction and recovery of ionized nanosilver is exhibited in Figure 2. Cyanex 302 act as a carrier in this process. Silver ion chemically reacts with the carrier to form the silver-carrier complexes, $AgR_2(HR)_2$ on the external interface as illustrated by Equation 4. Then, these complexes diffuse through the liquid membrane to the internal interface.

$$Ag(TEA)_2OH + 2(RH)_2 \rightarrow AgR_2(HR)_2 \text{ (org)} + TEAH^+ \text{ (aq)} + H_2O \text{ (aq)} \quad (4)$$

At this interface, silver ion from the silver-carrier complexes are stripped by the acidic Thiourea into stripping phase to form stable complexes of Ag-Thiourea which cannot penetrate reversibly into the membrane phase and the carrier diffuse back to the external interface. The reaction at stripping phase can be expressed by Equation 5:

$$AgR_2(HR)_2 + CS(NH_2)_2H^+ \leftrightarrow (RH)_2 + Ag\ (CS(NH)_2)_2^+ \quad (5)$$

The wash water containing silver-triethanolamine complexes, Ag $(TEA)_2OH$, are derived from Equations 6 to 8. Actually Triethanolamine is a common surfactant used in liquid detergent and has been found to be chemically react with silver ions.[17]

$$TEA + H_2O \longrightarrow TEAH^+\ OH \quad (6)$$
$$Ag + [TEAH]\ OH \longrightarrow AgOH + TEAH^+ \quad (7)$$
$$AgOH + 2[TEAH]\ OH \longrightarrow Ag\ (TEA)_2\ OH + 2H_2O \quad (8)$$

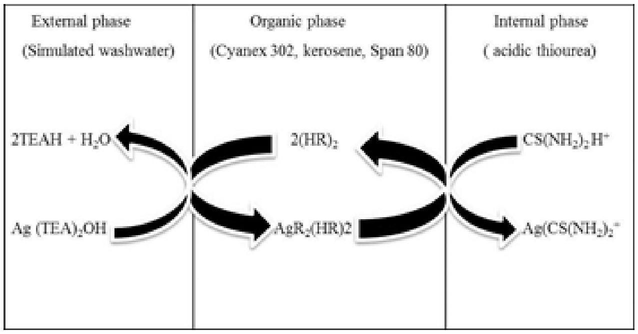


Figure 2 Mechanism for the extraction and recovery of ionized nanosilver by ELM

3.3 Effect of Carrier Concentration

Figure 3 exhibits the effect of carrier concentrations on the extraction, stripping and recovery performance of ionized nanosilver from wash water. In this study, the carrier concentration was varied from 0.00005 to 0.05 M. The result showed that further increase the carrier concentration up to 0.5 M, almost 100% of silver ion was extracted. Basically, more Ag-Cyanex 302 complexes were formed and get stripped into the internal phase upon increasing the carrier concentration. It could be observed that beyond 0.005 M onwards, the stripping and recovery capacity increased with increasing carrier concentration until it achieved plateau due to an excess of free carrier in the membrane phase. This means that 0.005 M of carrier concentration is adequate for the ionized nanosilver extraction and recovery. It also could be seen that the more concentrated of carrier concentration have resulted the membrane phase to be more viscous. This effect reduces the mass transfer of solute-carrier complexes hence leading to the inefficiency of stripping and recovery. In addition, the extraction percentage kept on increasing when increasing carrier concentration but the stripping rates remain constant during the whole process. Then, the complexes accumulate and remain unstripped in the membrane phase.[19] Hence, 0.005M was adequate for the formation of carrier-silver complexes in this experiment.

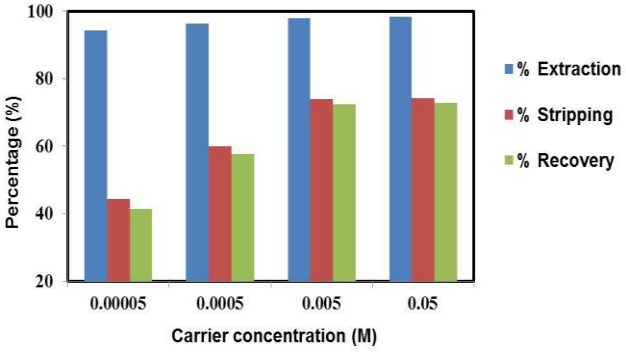


Figure 3 Effect of carrier concentration on the extraction, stripping and recovery performance of ionized nanosilver (Experimental condition: stripping agent = 1 M Thiourea in 1 M H_2SO_4; emulsifying time= 5 min; treat ratio = 1:3; Agitation speed= 150 rpm; extraction time= 5 min; homogenizer speed=10000 rpm; pH of feed phase= 2; diluent= kerosene)

3.4 Effect of Stripping Agent concentration

The effect of stripping agent concentrations on the extraction, stripping and recovery efficiency of ionized nanosilver is presented in Figure 4. Concentrations of H_2SO_4 was varied from 0.5 to 2.0 M. The result demonstrated that an increment in the H_2SO_4 concentration until 1.5 M increased the silver stripping and recovery up to 91 percent. It seems possible that this result is due to the fact that this solution is acidic enough to strip Ag from the complexes into the internal phase. Beyond 1.5 M H_2SO_4 concentration, the stripping and recovery percentage significantly decreased. A possible explanation is the difference in the hydrogen ion concentration gradient between external and internal phase which induce the transportation of the solute into the internal phase. Therefore, it is very crucial to keep the pH of the external and internal aqueous phase in optimum condition in order to avoid the instability of the membrane and to enhance the recovery process.[20] However, this condition had induced higher ionic strength in the internal phase hence leading to the transportation of water molecules inside internal phase. The emulsion also tends to destabilize due to the reduction in the properties of the surfactant by acidity in the internal phase.[21] Therefore 1 M Thiourea in 1.5 M H_2SO_4 was suitable to act as a stripping agent in this process.

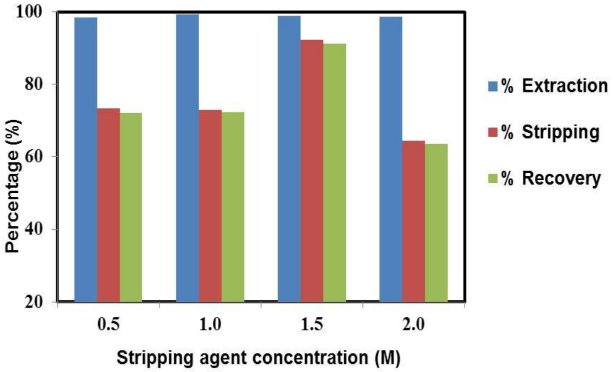


Figure 4 Effect of stripping agent concentration on the extraction and recovery performance of ionized nanosilver (Experimental condition: [Thiourea] = 1 M; emulsifying time= 5 min; treat ratio = 1:3; agitation speed= 150 rpm; extraction time= 5 min; [Cyanex 302] = 0.005 M; homogenizer speed=10000 rpm; pH of feed phase= 2; diluent= kerosene)

3.5 Effect of Extraction Time

Figure 5 shows the effect of extraction time on the extraction, stripping and recovery performance of ionized nanosilver. It could be seen that almost 100% of silver ion was extracted with varying extraction time from 5 to 20 minutes. It seems possible that these results are due to the reaction kinetic in emulsion liquid membrane system which occurs in a short time. Moreover, the main advantage of emulsion liquid membranes is fast extraction rates due to availability of high specific surface area.[18] Nevertheless, the stripping and recovery efficiency gradually decreased. This could be attributed that longer extraction times promotes more transfer of water molecules inside the internal phase, hence causing membrane to swell. This is due to the surfactants which continuously carry water molecules entering the internal phase. An increase in the volume of internal phase decreases the stripping and recovery efficiency owing to the dilution of the concentrated silver ion in the internal phase. Thus 5 minute of extraction time was adequate for the satisfactory of extraction, stripping and recovery efficiency.

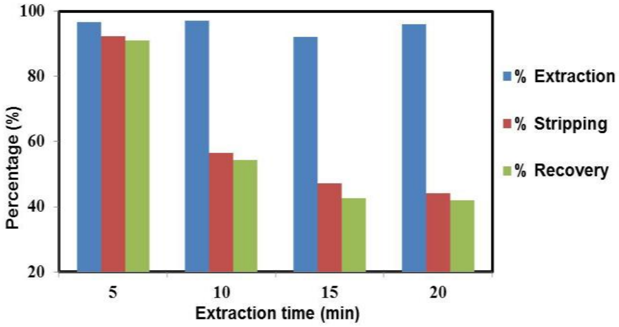


Figure 5 Effect of extraction time on the extraction, stripping and recovery efficiency of ionized nanosilver (Experimental condition: Stripping agent = 1 M Thiourea in 1.5 M H_2SO_4; [Cyanex 302] = 0.005 M; emulsifying time= 5 min; Treat ratio = 1:3; Agitation speed= 150 rpm; homogenizer speed=10000 rpm; pH of feed phase= 2; diluent= kerosene)

4.0 CONCLUSION

As a conclusion, all the parameters studied had shown a significant influence on the extraction, stripping and recovery performance where almost 100% of ionized nanosilver was extracted, 92% get stripped while 90% was recovered on the favourable condition of 5 minute extraction time, 0.005 M Cyanex 302 and 1.0 M Thiourea in 1.5 M H_2SO_4 solution.

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