

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

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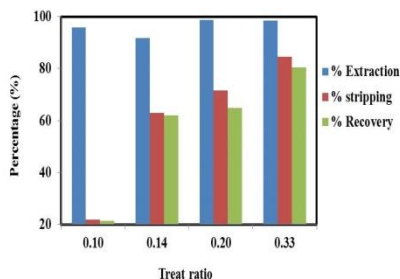
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Graphical abstract



Abstract

Ionized nanosilver is a harmful and highly toxic owing to its association with other organic chemical especially with the aquatic organism cells. Therefore, it is crucial to treat the ionized nanosilver to preserve the environment. In this study, experiments were carried out using emulsion liquid membrane (ELM) process in order to investigate the performance of extraction and recovery of ionized nanosilver from wash water. This process involves three phase dispersion systems including external phase, membrane phase and internal phase. The ELM formulation consists of bis [2,4,4-trimethylpentyl] monothiophosphinic acid (Cyanex 302) as a carrier, Span 80 as a surfactant, kerosene as a diluent and thiourea in sulphuric acid (H₂SO₄) solution as stripping agent. This study has highlighted several effects of parameters including agitation speed, pH of external phase, and treat ratio. The concentration of the ionized nanosilver was measured using Atomic Absorption Spectrometry (AAS). The results have demonstrated that at optimum conditions, the percentages of extraction, stripping and recovery were 96, 84 and 80% respectively at 150 rpm of agitation speed, pH 2 and 0.33 of treat ratio.

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

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1.0 INTRODUCTION

Nowadays, nanoparticles are tremendously utilized in many fields. However, the concerns about their environmental and health impacts remain unresolved. Nanoparticles have become a part of our daily life, in the form of cosmetics, drug delivery system and antibiotics [1-2]. Silver nanoparticles have gained much popularity on the account of their antimicrobial properties. They are extensively used in detergents and wound dressings, which end up in the environment during waste disposal. The commercial applications of the nanoparticles are accompanied by a lack of safety regulations and toxicology data. The presence of silver (Ag (I)) in the natural water environment has been great concern because of its toxicity to aquatic plants and animals, especially when it is in the free ion form (Ag⁺) [2]. USEPA however prescribes maximum concentrations of 3.2 ppb silver in fresh water and 1.9 ppb in salt water based on acute toxicity of silver to macroinvertebrates and fish. Therefore, understanding the fate and transport of silver in wastewater treatment plants is significant in evaluating the impact of silver discharge to the natural water quality. The silver ions are known to complex or precipitate with many organic and inorganic materials such as chloride, sulfide,

thiosulfate, and dissolved organic matter. The release behaviour of nanosilver ion has been investigated by several researchers from commercial socks, nanowashing machine, textiles and facades [3-6]. Benn and Westerhoff [3] have discovered that nanosilver releases to the wash water presences in the ionic silver form where some brands of socks which were being tested have proven about 90% of nanosilver exists as ion in water. This finding assumes that ionic silver formed in solution increased when subjected to prolonged exposure in water as nanosilver is oxidized to dissolve into the ionic form slowly. Farkas *et al.* [4] also have observed the effluents produced from washing machine (Samsung brand) contains nanosilver in the form of nanoparticle of 20 nm in size. The percentage of dissolved ionic silver form give lower than 2% passing through a 1.5 mm filter as it is assumed that most of the ionized silver form have binded to the other organic substances which present in the wastewater. These observation has proven that the silver nanoparticle can easily leak into the wastewater during washing, disrupts other beneficial bacteria which are used in wastewater treatment and also endangers aquatic organisms.

Many methods have been introduced for the removal and recovery of ionized nanosilver but yet there are some limitations or difficulties. For instance, ultrafiltration leads to the membrane

fouling and decomplexation of silver ion whereas electrodialysis involves high operating cost and energy consumption [7-8]. Besides that, electrochemical method leads to large capital investment and expensive electricity supply [9]. Solvent extraction also has been proposed to treat silver ion [10]. This method provides the extraction and stripping process in two separate steps and uses a lot of chemical. Moreover this method also uses a large quantity of carrier compared to liquid membrane technology. Therefore, as an alternative emulsion liquid membrane is one of the configurations liquid membrane technology that has been chosen for this present work due to the several advantages over other methods which are ease of functioning, less energy requirement, large interfacial area, low cost and single stage operation of both extraction and stripping.

This paper presents the influence of several parameters on extraction and recovery of ionized nanosilver from wash water using ELM process such as treat ratio, agitation speed and pH of external phase. Other parameters such as extraction time, carrier concentration and stripping agent concentration have already been discussed in previous studies [11].

2.0 MATERIALS AND METHODS

2.1 Chemicals 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 and were purchased from Qrec. All these reagents and solutions were directly used as received without further purification. The apparatus used including Homogenizer Heidolph Silent Crusher M Emulsifier, Perkin Elmer flame Atomic Absorption Spectrometer (AAS) to measure the concentration of silver ion, Portable Smart pH meter 108 (Milwaukee Model) for pH measurement and High Voltage Demulsifier for the demulsification process.

2.2 Nanosilver Ionization Study

This research focused on ionization of nanosilver during washing machine process. To make simulated wash water containing nanosilver ion, about 0.001 g of nanosilver powder was added in 100 mL wash water and mixed together with 1-4% w/w surfactant of detergent, Triethanolamine. Then the solution was put in the water bath and the temperature was set from 30 - 60°C with speed from 200-350 rpm respectively. The ionization process was carried out for 45 minutes to represent the operation time of real washing machine. The ionized nanosilver in the simulated solution was analyzed using Atomic Absorption Spectrometry (AAS). The amount of nanosilver ionized had been recorded.

2.3 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 250 rpm for 15

minutes. After that, the samples were quickly introduced into a separation funnel and left for phase separation for 30 minutes until the two layers of aqueous and emulsions were clearly separated. The bottom layer is the aqueous phase and emulsion at the upper layer. The aqueous layer was taken for extraction measurement study. After the extraction process, the emulsion from the upper layer is collected and demulsified using a high voltage demulsifier. The demulsification process stops when the emulsion shows two layers of complete separation. The membrane phase is recovered for reuse and the concentrated solute is retrieved from the internal phase. The concentration of silver in the external phase and internal phase after separation and demulsification was measured using Atomic Absorption Spectrometry (AAS). The same procedures were repeated for different condition and formulations. The performance of the ELM was measured using Equations (1-3) as shown below,

$$\text{Percentage of Extraction, } E = \frac{C_o - C_t}{C_o} \times 100 (\%) \quad (1)$$

$$\text{Percentage of Stripping, } S = \frac{C_{int}}{C_{mem} \times 2TR} \times 100 (\%) \quad (2)$$

$$\text{Percentage of Recovery, } R = \frac{C_{int}}{C_{ext} \times TR} \times 100 (\%) \quad (3)$$

where,

C_o : Initial concentration of silver in the external phase

C_t : Concentration of silver ion after extraction

C_{int} : Concentration of silver ion in the internal phase

C_{mem} : Concentration of silver ion in membrane phase

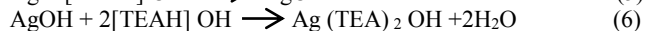
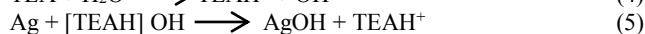
C_{ext} : Concentration of silver ion in the external phase

TR : Ratio of emulsion to the external phase.

3.0 RESULTS AND DISCUSSION

3.1 Nanosilver Ionization Study

Table 1 shows nanosilver ionization study at favourable condition. Almost 70% of nanosilver has been ionized which was confirmed by Atomic absorption spectrometry (AAS) analysis. During the process, triethanolamine as a surfactant was added in order to help the ionization of nanosilver which chemically reacts with silver forming silver-TEA complexes as shown in Equations (4-6),



where TEA = NR_3' , $\text{R}' = \text{CH}_3\text{CH}_2\text{OH}$. This is in line with Benn and Westerhoff [3] who claimed about 90% of nanosilver was ionized in water. Hence, it is proven that nanosilver can potentially ionized into the water especially wash water.

Table 1 Nanosilver ionization study

Variables	Percent ionization (%)
Agitation speed (350 rpm)	
Triethanolamine concentration (4% w/v)	69.13
Temperature (50°C)	

3.2 Effect of Treat Ratio

Treat ratio is defined as the ratio of emulsion to the external phase and is varied by changing the amount of external phase and keeping the volume of the membrane constant. Treat ratio controls the interfacial mass transfer across emulsion liquid membrane process. Figure 1 presents the effect of treat ratio on the extraction, stripping and recovery performance of ionized nanosilver from wash water. When the treat ratio was increased from 0.10 to 0.33, almost 100% of silver ion was extracted. The stripping and recovery percentage also significantly increased. At low treat ratio of 0.10, only 20% of ionized silver was stripped and recovered into the internal phase. It seems possible at this stage, the amount of external phase increased hence the emulsion phase could not disperse very well in order to treat the external phase. This condition has led the contact area between both external and emulsion phases significantly decreases thus resulting in the stripping and recovery inefficiency [12]. Beyond treat ratio of 0.14 up to 0.33, the percentage of stripping and recovery gradually increased. This can be attributed that the high treat ratio provides proper emulsion dispersion, hence increasing the contact area between the two phases. This increases the surface area for mass transfer owing to the formation of a high number of available emulsion globules [13]. Therefore, treat ratio of 0.33 was used for the next experiment owing to the highest percentage of stripping and recovery of ionized nanosilver.

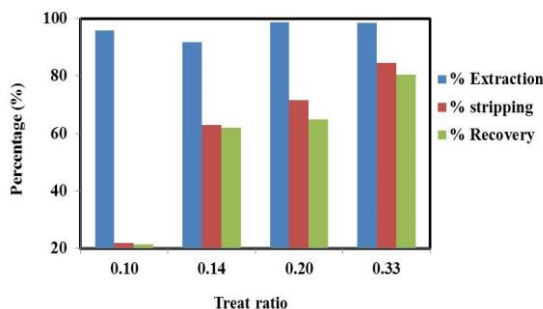


Figure 1 Effect of treat ratio on the extraction, stripping and recovery efficiency of ionized nanosilver (Experimental condition: [Stripping agent] = 1 M Thiourea in 1 M H₂SO₄; [Span 80] = 3% w/v; agitation speed= 250 rpm; emulsifying time= 5 min; homogenizer speed= 12000 rpm; [Cyanex 302] = 0.005 M; extraction time= 15 min; pH of feed phase= 2; diluent= kerosene)

3.3 Effect of Agitation Speed

Figure 2 exhibits the effect of agitation speed on the extraction, stripping and recovery efficiency of ionized nanosilver from wash water. It was observed that the extraction percentage gradually increased when increasing the speed from 150 to 450 rpm. It seems possible that this is due to the production of smaller emulsion globules under high agitation speed. Thus, higher interfacial area has led to the higher mass transfer of Ag-Cyanex complexes through membrane phase into internal phase. However the stripping and recovery efficiency significantly decreased when the agitation speed was increased up to 450 rpm. The higher mixing speeds tend to break the emulsion. This finding is strongly supported by Wan *et al.* [14], who found that entrainment swelling occurs at the beginning of the dispersing operation. It remains unchanged under stable mixing conditions and increases the volume of stripping phase. The higher mixing speed is in favor of improving the dispersion of emulsion in the treated external solutions and then decreases the thickness of membrane phase, which promotes the diffusing process, thus leading to the swelling and the emulsion breakage [15]. Then, 150 rpm of agitation speed

which provides the maximum percentage of stripping and recovery is used for further experiment.

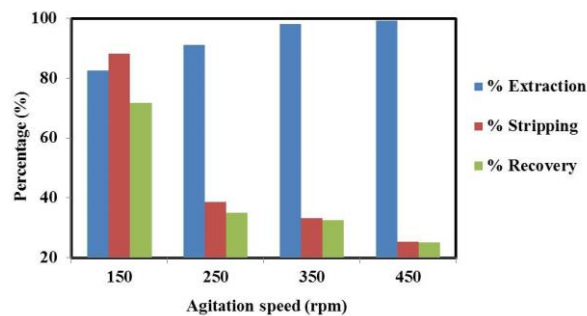


Figure 2 Effect of agitation speed on the extraction, stripping and recovery efficiency of ionized nanosilver (Experimental condition: [Stripping agent] = 1 M Thiourea in 1 M H₂SO₄; [Span 80] = 3% w/v; treat ratio = 0.33; emulsifying time= 5 min; homogenizer speed= 12000 rpm; [Cyanex 302] = 0.005 M; extraction time= 15 min; pH of feed phase= 2; diluent= kerosene)

3.4 Effect pH of External Phase

Figure 3 demonstrates the effect pH of feed phase towards extraction, stripping and recovery of ionized nanosilver. Almost 90% silver ion was extracted when increasing pH from 2 to 5 but gradually decreased thereafter. This can be explained by the fact that in acidic medium, the degree dissociation of the complexes silver-triethanolamine in the external phase increases. This condition facilitates the complexation between silver ion and Cyanex 302 in the external-membrane interface hence increasing the extraction efficiency. In addition, the acidic medium also provides higher concentration of hydrogen ion which induces the transportation of solute into the internal phase. Nevertheless beyond pH 2, the silver extraction, stripping and recovery efficiency slightly decreased. This is due to the less availability of hydrogen ions which helps in inducing silver ions to be transferred into the internal phase. In addition, the hydrolysis of metal ions also decreases the extraction efficiency [5]. Thus, pH 2 is preferable to be used in external phase medium for maximum extraction and recovery percentage of concentrated silver in ELM system.

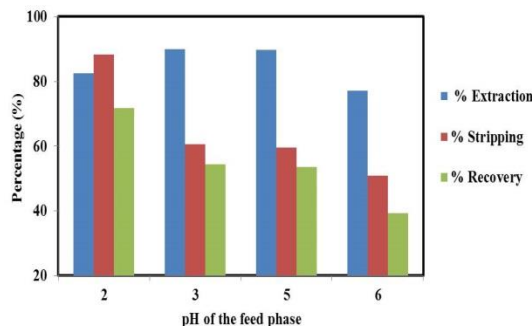


Figure 3 Effect of pH external phase on the extraction, stripping and recovery efficiency of ionized nanosilver (Experimental condition: [Stripping agent] = 1M Thiourea in 1M H₂SO₄; [Span 80] = 3% w/v; agitation speed= 150 rpm; emulsifying time= 5 min; homogenizer speed= 10000 rpm; [Cyanex 302] = 0.005 M; extraction time= 15 min; treat ratio= 0.33; diluent= kerosene)

■4.0 CONCLUSION

The extraction of ionized nanosilver as well as its stripping and recovery efficiency were analysed with different parameters studied. The results show that the emulsion liquid membrane is a very promising process as it can be used to recover ionized nanosilver from wash water. All three parameters such as treat ratio, pH and agitation speed that have been investigated worked positively. At the optimum condition of 150 rpm agitation speed, treat ratio 0.33 and pH 2 almost 96% of silver was extracted, 84% got stripped, and 80% was recovered.

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References

- [1] Elechiguerra, J. L., J. L. Burt, A. Morones, H. H. Gao, M. J. Lara and M. J. Yacaman. 2005. Interaction of Silver Nanoparticles with HIV-1. *Nanobiotechnology*. 3: 1–10.
- [2] Chen, X. and H. J. Schluesener. 2008. Nanosilver: A Nanoproduct in Medical Application. *Toxicology Letters*. 176: 1–12.
- [3] Benn, T. M. and P. Westerhoff. 2008. Nanoparticle Silver Released Into Water from Commercially Available Sock Fabrics. *Environment Science Technology*. 42: 4133–4139.
- [4] Farkas, J., H. Peter, P. Christian, J. A. G. Urrea, M. Hasselov, J. Tuoriniemi, S. Gustafsson, E. Olsson, K. Hylland and K.V. Thomas. 2011. Characterization of the Effluent from a Nanosilver Producing Washing Machine. *Environment International*. 37: 1057–1062.
- [5] Lorenz, C., L. Windler, N. V. Goetz, R. P. Lehmann, M. Heuberger and B. Nowack. 2012. Characterization of Silver Release from Commercially Available Functional (Nano) Textiles. *Chemosphere*. 80: 817–824.
- [6] Kaegi, R., B. Sinnet, S. Zuleeg, H. Hagendorfer, E. Mueller, R. Vonbank, M. Bollner and M. Burkhardt. 2010. Release of Silver Nanoparticles from Outdoor Facades. *Environmental Pollution*. 158: 2900–2905.
- [7] Desai, K. R. and Z. V. P. Murthya. 2012. Removal of Silver from Aqueous Solutions by Complexation–Ultrafiltration Using Anionic Polyacrylamide. *Chemical Engineering Journal*. 185–186: 187–192.
- [8] Gfiveng, A. and B. Karabacako. 2005. Use of Electrodialysis to Remove Silver Ions from Model Solutions and Wastewater. *Desalination*. 172: 7–17.
- [9] Chen, J. P. and L. L. Lim. 2005. Recovery of Precious Metals by an Electrochemical Deposition Method. *Chemosphere*. 60: 1384–1392.
- [10] Sole, K. C., T. L. Ferguson and J. B. Hiskey. 1994. Solvent extraction of silver by Cyanex 272, Cyanex 302 and Cyanex 301. *Solvent Extraction and Ion Exchange*. 12(5): 1033–1050.
- [11] Sulaiman, R. N. R., N. Othman and N. A. S. Amin. 2013. Recovery of Ionized Nanosilver from Wash Water Using Emulsion Liquid Membrane Process. *Jurnal Teknologi (Sciences & Engineering)*. 65: 4:33–36.
- [12] Mortaheb, H. R., H. Kosuge, B. Mokhtarani, M. H. Amini and H. R. Banihashemi. 2009. Study on Removal of Cadmium from Wastewater By Emulsion Liquid Membrane. *Journal of Hazardous Materials*. 165: 630–636.
- [13] Kumbasar, R. A. and O. Tutkun. 2008. Separation of Cobalt and Nickel from Acidic Leach Solutions by Emulsion Liquid Membranes using Alamine 300 (TOA) as a Mobile Carrier. *Desalination*. 224: 201–208.
- [14] Wan, Y. and X. Zhang. 2002. Swelling Determination of W/O/W Emulsion Liquid Membranes. *Journal of Membrane Science*. 196: 185–201.
- [15] Tang, B., G. Yua, J. Fang and T. Shi. 2010. Recovery of High-purity Silver Directly from Dilute Effluents by an Emulsion Liquid Membrane-Crystallization Process. *Journal of Hazardous Materials*. 177: 377–383.