REMOVAL OF IONIZED NANOSILVER FROM WASH WATER USING EMULSION LIQUID MEMBRANE PROCESS

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Dedicated to my beloved parents, siblings and friends
for their endless love, prayer and support

Allah S.W.T tidak akan mengubah nasib sesuatu kaum
melainkan kaum itu sendiri mengubahnya…

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ABSTRACT

The increasing number of products containing nanosilver has raised a great concern over the public due to the release behaviour of ionized nanosilver which create the toxicity problems especially to the aquatic organism. Therefore, there is a necessity for the removal of ionized nanosilver from wastewater. One of the potential techniques is an emulsion liquid membrane process (ELM). This research investigated the extraction and recovery of ionized nanosilver from wash water using ELM process. The membrane phase contained kerosene as diluent, Cyanex 302 as a carrier, Span 80 as a surfactant and acidic thiourea as a stripping agent. The extraction was carried out in batch process using a mixer-settler and the recovery part was performed using a high voltage demulsifier. The ionization of nanosilver was determined using three variables which were effect of triethanolamine concentration, agitation speed and temperature. ELM stability was investigated at different surfactant concentration, ionic liquid concentration, agitation speed, homogenizer speed, emulsification time and extraction time. The parameter of extraction and recovery studied involving pH of external phase treat ratio, carrier concentration and stripping agent concentration. The optimization was done using response surface methodology (RSM) for the recovery process with three significant process variables. Results showed that almost 70% of nanosilver was ionized in the wash water. The most stable emulsion was observed at 3% w/v of Span 80, 150 rpm of agitation speed, 10,000 rpm of homogenizer speed and 5 minutes of emulsification and extraction time. Besides, almost 100% of ionized nanosilver was successfully extracted and the optimum conditions obtained for the recovery process using RSM were 0.256 treat ratio, 0.75 M sulphuric acid concentration and 0.85 M thiourea concentration. At this optimum condition, the maximum recovery of the ionized nanosilver was 84.74%. Thus, emulsion liquid membrane (ELM) method has a great potential in order to treat wash water containing ionized nanosilver.

ABSTRAK

Peningkatan jumlah produk yang mengandungi perak nano telah menimbulkan kebimbangan kepada orang ramai mengenai pembebasan perak nano terion yang memberi kesan toksik terutamanya kepada organisma akuatik. Oleh itu, penyingkiran perak nano terion dari air sisa sangat diperlukan. Salah satu teknik yang berpotensi adalah proses emulsi membran cecair (ELM). Penyelidikan ini mengkaji pengekstrakan dan penghasilan semula perak nano terion dari air basuhan. Pengekstrakan telah dijalankan dengan menggunakan sistem pengaduk-pemisah berkelompok dan penghasilan semula dilakukan dengan menggunakan penyahemulsi voltan tinggi. Fasa membran mengandungi kerosin sebagai bahan pelarut, Cyanex 302 sebagai pembawa, Span 80 sebagai surfaktan dan tiourea berasid sebagai agen pelucutan. Pengionan perak nano ditentukan menggunakan tiga pembolehubah iaitu kesan kepekatan trietanolamina, kelajuan pengadukan dan suhu. Kestabilan emulsi membran cecair dikaji pada kepekatan surfaktan, kepekatan cecair ionik, kelajuan pengadukan, kelajuan penghomogen, masa pengemulsian dan masa pengekstrakan. Pembolehubah yang dikaji dalam proses pengekstrakan dan penghasilan semula termasuklah pH fasa luaran, nisbah rawatan, kepekatan pembawa dan kepekatan agen pelucutan. Pengoptimuman dilakukan dengan menggunakan kaedah gerak balas permukaan (RSM) untuk proses penghasilan semula dengan tiga pembolehubah proses yang memberi kesan. Keputusan menunjukkan hampir 70% perak nano terion dalam air basuhan. Emulsi yang paling stabil didapati pada 3% w/v Span 80, 150 rpm kelajuan pengadukan, 10,000 rpm kelajuan penghomogen dan 5 minit tempoh pengemulsian dan masa pengekstrakan. Di samping itu, hampir 100% perak nano dapat diekstrak dan keadaan optimum yang diperolehi untuk proses penghasilan semula menggunakan kaedah RSM ialah 0.256 nisbah rawatan, 0.75 M kepekatan asid sulfurik dan 0.85 M kepekatan tiourea dengan penghasilan semula sebanyak 84.74%. Oleh itu, emulsi membran cecair dapat merawat air sisa yang mengandungi perak nano terion.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

%	-	Percent
nm	-	Nanometer
ppm	-	Part per million
ppb	-	Part per billion
mm	-	Mili meter
^{o}C	-	Degree Celsius
rpm	-	Rotation per minute
w/w	-	Weight per weight
min	-	Minutes
w/v	-	Weight per volume
M	-	Molar
mg/L	-	Milligram per liter
Kgm^{-3}	-	Kilogram per meter cubic
$Kgm^{-1}s^{-1}$	-	Kilogram per meter per second
g/mol	-	Gram per mol
g/cm^{3}	-	Gram per centimeter cubic
g	-	Gram
mL	-	Milliliter
V_f	-	Volume of emulsion after extraction
V_i	-	Volume of emulsion before extraction
C_{int}	-	Concentration of silver ion in the internal phase
C_{ext}	-	Concentration of silver ion in the external phase
TR	-	Volume emulsion to volume external phase ratio

LIST OF ABBREVIATIONS

USEPA	-	United State Environment Protection Agency
WERF	-	Water Environment Research Foundation
Span 80	-	Sorbitan Monooleate
Cyanex 302	-	Diisoocthylthiophosphinic acid
ELM	-	Emulsion liquid membrane
RSM	-	Response surface methodology
TEA	-	Triethanolamine
BMIM]$^{+}$[NTf2]$^{-}$	-	1-butyl-3-methylimidazolium bis (trifluoromethylsulphonyl) imide
Df	-	Degree of freedom
DOE	-	Design of experiment
H_2SO_4	-	Sulphuric acid
ANOVA	-	Analysis of variance
Cdse	-	Quantum dot
ICP-OES	-	Inductively coupled plasma- Optical emission spectroscopy
CARS	-	Coherent anti-Stokes Raman scattering Spectroscopy
EDX	-	Energy dispersive X-ray analysis
TEM	-	Transmision electron microscopy
CNS	-	Central nervous system
NDs	-	Neurodegenerative disorders
UV	-	Ultraviolet
CNTs	-	Carbon nanotubes
TiO_2	-	Titanium dioxide nanoparticles
TGA	-	Thermal Gravimetric Analysis

HIV	-	Human immunodeficiency virus
EPS	-	Extracellular Polymeric Substance
TEM	-	Transmission electron microscopy
NTA	-	Nanoparticle tracking analysis
AgOH	-	Silver hydroxide
Ag2O	-	Silver oxide
Ag-TEA	-	Silver triethanolamine
BLM	-	Bulk Liquid Membrane
SLM	-	Surfactant liquid membrane
PTFE	-	Polytetrafluoroethylene
PP	-	Polypropylene
MIBK	-	Methyl isobutyl ketone
NaOH	-	Sodium hydroxide
CTAB	-	Cetyl trimethylammonium bromide
HLB	-	Hydrophile-lipophile balance
LK-80	-	Biodegradable demulsifier
TOPO	-	Trioctylphosphine oxide
TOA	-	Alamine 300
TIOA	-	Tri-iso-octyl amine
TBP	-	Tri-n-butyl phosphate
$(HR)_2$	-	Dimer of carrier
AAS	-	Atomic Absorption spectrometer
W/O	-	Water in oil
Au(III)	-	Gold
HSAB	-	Hard Soft Acid Base
Na^+	-	Sodium
Mg^{2+}	-	Magnesium
Fe^3	-	Iron
Cu^+	-	Copper
Hg^{2+}	-	Mercury
Pb^{2+}	-	Plumbum
S^{2-},	-	Sulphur
I^-,	-	Iodine

Br^-	-	Bromine
HCI	-	Hydrochloric acid
NH_3	-	Ammonia
PF_6	-	hexafluorophosphate
BBD	-	Box Behnken design

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nanotechnology is a newly developed technology which deal with structures of nanoparticles ranging from one to hundred nanometers in one dimension. Nanosilver is one of the nanoparticle which have been widely used in various products such as jewelery, 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 wound and dissolve faster once moistered in blood (Chen and Schluesener, 2008; Wasif and Laga, 2009). Unfortunately, the fate and transport of nanosilver in the environment have triggered a great concern among the public, especially in the ionic form which have a high propensity to associate with the other dissolved organic matters in waste water which leads to the toxicity effect for aquatic organism. For instance, Kaegi *et al*. (2010) have indicated 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. In addition, about 1.4 to 270,000 ppm of ionized nanosilver is released from consumer products at home (Benn *et al*., 2010). Due to these scenarios, 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 our cell system through various routes of exposure including inhalation, dermal and oral (Wijnhoven *et al*., 2009). The toxicity of silver is significantly proportional to the rate of releasing free silver ions (Chen and Schluesener, 2008). Some of the nanosilver which have been ionized in water is very harmful and highly toxic metal to the aquatic organism (Fabrega *et al*., 2011). United State Environment Protection Agency (USEPA) have prescribed the maximum concentrations of 3.2 ppb silver in fresh water and 1.9 ppb in salt water based on the acute toxicity of silver to macroinvertebrates and fish. These standards are enforced through the issuance of discharge permits at the state level (USEPA, 2008). According to the Environmental Quality Regulations 2009 in Malaysia, the admissible concentration of silver ion in wastewater for discharge must be below 1.0 ppm for industrial and mixed effluent respectively (MKMA, 2009). The observation shows that the exposure of nanosilver ions with concentration of 5 ppm can increase the mortality and heart malformation in zebra fish (Asharani *et al*., 2008). 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 (Dror *et al*., 2009). 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 several researcher in order to extract this nanoparticle such as electrolysis, electrodialysis, ion flotation, ultrafiltration and chemical precipitation but still provide some limitations such as high cost and energy consumption and lead to sludge production (Zodrow *et al*., 2009; Gfiveng and Karabacako, 2005).In order to overcome this problem, liquid membrane technology has been introduced to preserve the environment in term of removal and recovery of various metal ions. This technology provides simple operation, fast, energy saving and less of chemical consumption (Othman *et al*., 2006). 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. In this present research, emulsion liquid membrane has become the selective method to treat the ionized nanosilver from wash water owing to the unique characteristic over other conventional method where the extraction and recovery process occur simultaneously.

1.2 Problem Statement

Release behaviour of ionized nanosilver has been reported by several researchers such as from textiles (Lorenz *et al*., 2012; Benn and Westerhoff, 2008), nanowashing machine (Farkas *et al*., 2011), and facades (Kaegi *et al*., 2010). Benn and Westerhoff (2008) have discovered some nanosilver was released into wash water in term of ionic silver form. This finding also claims that the ionic silver form in solution will increase when subjected to prolonged exposure in water as nanosilver is oxidized slowly to dissolve into ionic form. Even though the release of ionized nanosilver is in low concentration, the huge toxicity effect can be seen when one study has observed that the exposure of nanosilver with concentration of 5 ppm can increase the mortality and heart malformation in zebra fish (Asharani *et al*., 2008). The discharge of ionized nanosilver from domestic waste has proven that ionized nanosilver can easily leak into the wash water during washing process, hence disrupts the other beneficial bacteria and endangers the aquatic organisms (Benn *et al*., 2010).

Previously, several methods have been introduced for the removal and recovery of silver ion but still provide some limitation or difficulties. For instance, ultrafiltration leads to the membrane fouling and decomplexation of silver ion whereas electrodialysis involves high operating cost and energy consumption (Desai and Murthya, 2012; Gfiveng and Karabacako, 2005). Besides, electrochemical method leads to the large capital investment and expensive electricity supply (Chen and Lim, 2005). Solvent extraction also has been proposed by Sole *et al*. (1994) to treat silver ion. This method provides excellent extraction and stripping process but used large amount of chemicals and not in single stage process. Thus, an alternative method has been introduced which is emulsion liquid membrane (ELM) process. Liquid membrane technology contribute several advantages over other methods including ease of functioning, less energy requirement, large interfacial area, low cost and single stage operation of both extraction and stripping process. Based on the literature review, there were no research reported for the treatment of the ionized nanosilver using ELM process.

The main problem of this method is the emulsion instability. Thus, room temperature ionic liquids which are constituted by salts comprising organic anions and cations have been expected to provide a great potential application as an alternatives stabilizer candidate in liquid membrane technology. They have been reported by several researchers as a stabilizer in liquid membrane for metal removal (Ng *et al*., 2011; Goyal *et al*., 2011a). In this study, the performance of ionic liquid was observed in the emulsion liquid membrane stability study.

1.3 Research Objectives

This research contribute three objectives including:

a. To determine the ionization of nanosilver in wash water

b. To investigate the parameters affecting emulsion liquid membrane stability and extraction performance for ionized nanosilver from wash water

c. To optimize the parameters influencing the performance of ionized nanosilver recovery using response surface methodology.

1.4 Research Scopes

The main focus of this present study is to observe the applicability of emulsion liquid membrane system (ELM) in order to extract and recover ionized nanosilver from wash water. First of all, an excellent understanding of emulsion liquid membrane system is very important in order to successfully apply the design or process in this research. The studies include the ionization of nanosilver, the stability study of primary emulsion and ELM extraction for ionized nanosilver and optimization of the parameters afecting the efficiency of recovery using response surface methodology (RSM). The first objective addresses the study on the ionization of nanosilver in wash water. Four variables which possibly influence the ionization of nanosilver in wash water was studied including triethanolamine (TEA) concentration, agitation speed (200 to 350 rpm) and temperature (30 to 60^{o}C). Triethanolamine is one of the emulsifier which is commonly used in liquid detergent that can interact or react chemically with nanosilver ion and promote releasing this nanoparticle into wash water. The amount of triethanolamine used are ranging from 1- 4% w/w as reported above 5% w/w of triethanolamine (TEA) concentration will lead to the toxicity problem (Beyer *et al.*, 1983). The maximum speed and temperature are following the standard properties of real washing machine operation. The running time taken is 45 min represent the real world washing machine cycle.

The second objective focus on the parameters study for emulsion liquid membrane stability and ionized nanosilver extraction. Parameters involve include emulsification and extraction time (5 to 25 min), homogenizer speed (7,000 to 14,500 rpm), agitation speeds (150 to 450 rpm) , Span 80 concentration (1 to 7% w/v) and ionic liquid (1-butyl-3-methylimidazolium bis (trifluoromethylsulphonyl) imide ($[BMIM]^{+}[NTf2]^{-}$) concentration (1 to 5 % w/v). ELM formulation consists of carrier, surfactant, diluent and stripping agent. In this study, Cyanex 302 is used as carrier, Span 80 as a surfactant, kerosene as diluent and acidic thiourea as a stripping agent solution. The selectivity of these components in ELM formulation are capable to extract and recover the silver from waste water (Othman *et al*., 2006).

In order to optimize the parameters influencing the performance of ionized nanosilver recovery, response surface methodology (RSM) design was used. This research consider three variables which possibly or significantly affect the performance of ELM recovery efficiency of ionized nanosilver including thiourea and sulphuric acid concentration (0.5 to 1.5 M), and treat ratio (0.14 to 0.33). A total of 15 number of experiment was required based on the design of experiment (DOE) created using Statistica software. ANOVA analysis is used in order to determine the validity of the model and the significant parameter involved. For recovery process, high voltage demulsifier was used to break the emulsion for silver recovery collection. All the experiment are carried out in batch process.

1.5 Significance of Study

Liquid membrane technology is one of the promising and another alternative method used for the wastewater treatment. The main advantage of this process is the removal and recovery of solute ion in one single stage operation. Moreover, it involve less of chemical consumption as well as reducing the cost. In this research, emulsion liquid membrane is employed to treat ionized nanosilver from wash water that normally cause severe to human and toxic to the aquatic organism. Although ELM was used to treat the silver ion from the previous work however no work was reported on the treatment of ionized nanosilver using ELM process from wash water. Besides the formulation used in this study can be used as a reference particularly for larger scale process.

1.6 Thesis Outline

This thesis consists of five chapters, which present the research in sequential order. Chapter One introduces the research background, problem statement, research objective and research scope. Chapter Two describes the detailed reviews which related to the nanosilver and their exposure and toxicity problem, liquid membrane technology, ELM components and future development of ELM process. Chapter Three describes the materials used and methodology involved in this study. Experimental procedures including ionization study, emulsion stability study and recovery process were discussed in detail in this chapter. The results and discussions are presented well in Chapter Four. In this chapter, experimental data collections have been discussed and analysed in detailed. The conclusion and recommendation are presented in Chapter Five for further improvement in future research.

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APPENDIX A

PUBLICATIONS

1) **Raja Norimie Raja Sulaiman,** Norasikin Othman, Nor Aishah Saidina Amin (2013). Emulsion liquid membrane stability in the extraction of ionized nanosilver from wash water solution. *Journal of Industrial and Engineering Chemistry*, 20(5), 3243-3250.

2) **Raja Norimie Raja Sulaiman,** Norasikin Othman, Nor Aishah Saidina Amin (2014). Parameter study and optimization of ionized nanosilver recovery by emulsion liquid membrane process. Submitted to *Desalination and water treatment* (Under review).

3) **Raja Norimie Raja Sulaiman,** Norasikin Othman, Nor Aishah Saidina Amin (2013). Recovery of ionized nanosilver from wash water solution using emulsion liquid membrane process. *Jurnal Teknologi (Science and Engineering)*, 65:4, 33-36.

4) **Raja Norimie Raja Sulaiman**, Norasikin Othman, Nor Aishah Saidina Amin (2013). Stability study of water in oil emulsion in emulsion liquid membrane process. *Special Issue in Journal of Science and Technology*, 51(5B), 97-101.

5) **Raja Norimie Raja Sulaiman**, Norasikin Othman, Nor Aishah Saidina Amin, Norul Fatiha Mohamed Noah (2013). Parameter study of ionized nanosilver recovery from wash water using emulsion liquid membrane process. *Accepted published in Jurnal Teknologi (Science and Engineering).*

6) **Raja Norimie Raja Sulaiman**, Norasikin Othman, Nor Aishah Saidina Amin, Noor Haziqah Kamaludin, Nur Na Illah Sallih Uddin (2012). Extraction of Ionized Nanosilver by Emulsion Liquid Membrane Using Cyanex 302 as a Mobile Carrier. *Topics of Science*, *Technology and Social Sciences.* Accepted published by Springer.