The potential of the composite membranes Ch-AgNP to recover silver from X-ray film processing wastes

N N Rupiasih\textsuperscript{1,2}, W G Suharta\textsuperscript{1}, M Sumadiyasa\textsuperscript{1}, D D Fernanda\textsuperscript{1} and M Y Imas\textsuperscript{1}

\textsuperscript{1} Department of Physics, Faculty of Mathematics and Natural Sciences, Udayana University, Kampus Bukit Jimbaran, Badung, Bali 80362, Indonesia
\textsuperscript{2} Group Research of Material Sciences and Technology-Polymer and Biomaterial Faculty of Mathematics and Natural Sciences, Udayana University, Kampus Bukit Jimbaran, Bali 80362, Indonesia

* rupiasih@unud.ac.id

\textbf{Abstract.} The potential of the composite membranes chitosan-silver nanoparticles (Ch-AgNP) to remove silver (Ag) from X-ray film processing wastes was studied using a filtration method. The study includes the pure water flux (PWF), product flux (PF), and rejection coefficient (R). Several of composite membranes such as Ch-AgNP10, Ch-AgNP100, Ch-AgNP250, Ch-AgNP500, and a pure chitosan membrane (Ch) were used in this study. The filtration was carried out using a dead-end filtration method with a pressure of 260-270 kPa. The concentration of silver waste was determined using Atomic Absorption Spectroscopy (AAS). The results showed that the composite membranes have a better ability to filter silver from X-ray film processing wastes than the pure chitosan membrane. The highest rejection coefficient (R) gave by Ch-AgNP100 of around 95.55% with the pure water flux and product flux of 2051.03 and 1192.28 L/m\textsuperscript{2}.h, respectively. The rejection coefficient of the composite membranes increased with increasing the mass of silver nanoparticles, while the PWF and PF were decreased. These results indicated that chitosan composite membranes are a potential method for recovering silver from X-ray film processing wastes. It's a safe and environmentally friendly method.

\textbf{Key words:} Chitosan composite membrane, silver nanoparticles (AgNP), X-ray film waste, dead-end filtration, rejection coefficient.

1. Introduction
Silver is a metal that is widely used in the electrical, electronics, jewellery, photography and chemical industries [1, 2]. It is used for electronic apparatus, silver ware, dental fillings, mirrors, catalysis and photographic films. Silver is obtained by mining or can be found at the location of hazardous waste mixed with soil or water [1].

Silver is widely used in the photography field because of its light-sensitive properties [3]. The photography division itself allocates about 45% of the silver for radiographic uses, which is thrown away totally after its usage [1]. The photographic wastes contain mostly fixer and bleach solutions which contain high concentrations of silver and other chemicals such as nitrates and sulphates [1, 4]. This produced a serious pollution all over the world, particularly in the aquatic environment. The dissolved form of the metals waste is hazardous since it is easily spread out through the stream and is more easily
available for animals and plants. For people, poisoning by these metals can result in severe kidney dysfunction, liver, reproductive system, central nervous system, and brain [2]. Therefore, the recovery of these metals will solve environmental problems as well as give beneficial potential [2].

The photographic manufacturing has four options in silver recovery i.e., chemical precipitation, electrolytic plating, ion exchange and metallic replacement [4, 5]. Volkan Arslan, et al (2011) reported about 89% silver from radiographic films waste was recovered by chemical leaching using HNO₃ under optimum leaching conditions i.e. radiographic films quantity of 50 g/L, nitric acid concentration of 30 g/L, stirring speed of 180 rpm, and leaching time of 15 min [4]. Ashish Modi, et al (2012) found that a thiourea-modified chitosan resin can be used to recover silver (I) from aqueous medium [2]. The 0.5 M thiourea-2.0 M HCl solution found effectively desorb silver (I) from the resin and this resin could be reused up to 5 times without marked change in the uptake of silver (I). A. Denis Bas, et al (2012), examined the recovery of silver from X-ray film processing effluents by precipitation method using Hydrogen peroxide [3]. It found that the precipitation process is highly exothermic in nature and it is a fast reaction, that almost complete within minutes. High silver recoveries (≥ 95%) from the waste solution (1.1 g/L Ag, 113 g/L S₂O₃²⁻) were obtained only at high levels of H₂O₂ (≥ 37.6 g/L). Van Ryan Kristopher R. Galarpe and Girlie D. Leopoldo (2017) reported a silver recovery from X-ray processing fixer waste using a chemical method of alkaline treatment using sodium hydroxide (NaOH). It found that the NaOH precipitation method works under basic condition with pH of 9 to 12 [6].

Ulisses Condomitti, et al (2014) reported a silver recovery using electrochemically active magnetite coated carbon particles. The basic process is the adsorption properties and the large surface area of carbon, in combination with the super paramagnetic properties of magnetite nanoparticle, so that collect Ag⁺ ions from the solution and to push their rapid confinement at the working electrode surface, using an external magnet [5, 7]. K. V. Radha and C. Arun (2010) reported recycling of exposed photographic X-ray films and recovery of silver using Bromelain enzyme [8]. It found that about 98% of silver can be recovered from X-ray film and the silver can be reused for silver plating of utensils, silver solder, jewels, film manufacture and electrical components. The purity of silver obtained was found to be 99.9%. P. Khunprasert, et al (2008) reported the cleaner technology concept of silver leaching from radiographic film using weak acids such as acetic, malonic acids and oxalic [9]. The results were carried out under low temperature conditions. It found that an oxalic acid solution at 5% (w/v) provided the best leaching condition at 100 °C for 20 min. This achieved 100% silver leaching from the films. The obtained silver was in its metal form and ready for ingot production. Zeferino Gamiño-Arroyo, et al (2015) reported a liquid-liquid extraction method as separation process to recover silver [10]. It found that the best performing extractant is the bis(2-ethylhexyl) dithiophosphoric acid (D2EHDTPA) which efficiently recovers silver from nitric acid solutions. The best extraction conditions are at 0.02 mol/L concentration, ambient temperature (22°C), with an extraction time of 15 minutes and the ratio of aqueous phase (A) to organic phase (A/O) = 0.65.

At the previous study, we investigated removing silver from X-ray film processing wastes using chitosan membranes by a dead-end filtration method. It found that chitosan membrane 2% able to remove silver wastes about 99.9% with product flux (PF) of 1761.18 L/m².h [11]. We have also studied to recover silver from the hospital photography fixer waste by using adsorption method using various amount of chitosan powder and chitosan membrane. It found that the chitosan membrane e.g. chitosan membrane 2% of 5 g gave the highest percentage of silver adsorption of 95.99% compared with chitosan powder [12].

Based on the various methods above and our previous studies, it can be said that the effectiveness of each method in recovering silver waste depended on the method used. So, it is very interesting to study the new method which able to give maximum result. At this study we report removing silver from X-ray film processing wastes by dead-end filtration method using “chitosan-silver nanoparticles composite membranes” (Ch-AgNP). The membrane technology chooses due to friendly and safe to environmental. It is a green technology which does not produce new chemical waste.

Chitosan is a natural polymer that obtained by alkaline deacetylation of chitin; where chitin is a plentiful polymer originate mostly in shellfish such as shrimps, crabs and prawn [13]. Chitosan is also
known as a biomaterial which presents in many useful forms which commercially available such as fiber, film, membrane, multipurpose microcrystalline powders, solutions and gels [11]. Chitosan is characterized to be a cationic, biocompatible, and antibacterial. These characteristics make chitosan has significant application in numerous industrial areas, such as biomedical engineering, pharmaceutical and food industry, wastewater treatment and agriculture [11].

2. Material and experimental

2.1 Materials
The chitosan of molecular weight of 900 kDa of a degree of deacetylation of 87.4% was originated from shrimp shells. The acetic acid and sodium hydroxide (NaOH) were analytical grade (p.a.) and were from Merck. The silver nanoparticles (AgNP) used is a biosynthesized product using Sambiloto extract with particles size distribution of 10-30 nm, surface Plasmon resonance (SPR) wavelength of 423 nm and crystal structure is face center cubic (FCC) of lattice parameter (a) of 4.03 Å. Demineralized water (DW) was used in preparing solutions.

2.2 Membranes preparation
The membranes used are composite membranes: Ch-AgNP10, Ch-AgNP100, Ch-AgNP250, Ch-AgNP500 and a pure chitosan membrane (Ch). The membranes were made by casting method using a chitosan matrix, a solvent of acetic acid 1% and filler of AgNP. The casting protocol has been reported in [14].

2.3 Experimental
The filtration process is conducted using a dead-end filtration method at a pressure of 260-270 kPa. The filtration performance was evaluated in term of pure water flux (PWF), product flux (PF) and rejection coefficient (R). The PWF and PF were obtained using demineralized water and X-ray film processing wastes. The concentration of silver in the feed and permeate were analyzed using AAS (atomic absorption spectroscopy) AA-700 Shimadzu. The fluxes were obtained using equation 1 [11],

\[ J = \frac{\Delta V}{A \Delta t} \]  

where, \( J \) is the flux, \( A \) is an effective surface area of the membrane of 0.000972 m\(^2\) and \( \Delta V \) is the volume of filtrate collected in a time interval (\( \Delta t \)). The rejection coefficients were calculated using equation 2 [11],

\[ R = \left( 1 - \frac{C_p}{C_f} \right) \times 100\% \]

where, \( C_p \) and \( C_f \) is the concentration of silver in the permeate and feed, respectively.

3. Results and discussion

3.1 Filtration
Figure 1 and 2 shows graphs of flowrate of the pure water across membranes Ch, Ch-AgNP10, Ch-AgNP100, Ch-AgNP250 and Ch-AgNP500, at pressure of 260-270 kPa. The membranes Ch-AgNP250 and Ch-AgNP500 did not give a flowrate because that distilled water could not pass through the both membranes at that pressure. By doing linear regression, it obtained the gradient of each graph which is equal to the flowrate (dV/dt). Using equation 1, the pure water flux (PWF) and product flux (PF) can be calculated. The results showed in Table 1.
Figure 1. The pure water flowrate of the Ch, Ch-AgNP10, Ch-AgNP100, Ch-AgNP250, and Ch-AgNP500 membranes, at pressure of 260-270 kPa.

Figure 2. The product flowrate of the Ch, Ch-AgNP10, Ch-AgNP100, Ch-AgNP250, and Ch-AgNP500 membranes, at pressure of 260-270 kPa.

Table 1. The pure water flux (PWF) and product flux (PF) of the Ch, Ch-AgNP10, Ch-AgNP100, Ch-AgNP250, and Ch-AgNP500 membranes, at pressure of 260-270 kPa.

| No. | Membranes     | PWF (L/m².h) | PF  (L/m².h) |
|-----|---------------|--------------|--------------|
| 1.  | Ch            | 3430.86      | 1453.50      |
| 2.  | Ch-AgNP10     | 2421.30      | 1243.52      |
| 3.  | Ch-AgNP100    | 2051.03      | 1192.28      |
| 4.  | Ch-AgNP250    | 0            | 0            |
| 5.  | Ch-AgNP500    | 0            | 0            |

The data in Table 1 can be displayed in graphical form as shown in Figure 3.

Figure 3. The pure water flux (PWF) and product flux (PF) of the Ch, Ch-AgNP10, Ch-AgNP100, Ch-AgNP250, and Ch-AgNP500 membranes, at pressure of 260-270 kPa.
Figure 3 shows that the pure water flux as well as product flux decreased with increasing the amount of AgNP from 10 to 100 µg, even Ch-AgNP250 and Ch-AgNP500 membranes do not produce flux. This might be caused by the increasing number of silver nanoparticles spread in the membrane so that it covers more membrane pores.

3.2 Rejection coefficients
The concentration of silver in the feed and permeate solutions were analyzed using AAS as shown in Table 2. By using this data and equation 2, the rejection coefficient (R) of the Ch, Ch-AgNP10, Ch-AgNP100, Ch-AgNP250, and Ch-AgNP500 membranes can be calculated, as shown in Table 2.

Table 2. The concentration of silver in the feed and permeate solutions; The rejection coefficient (R) of the Ch, Ch-AgNP10, Ch-AgNP100, Ch-AgNP250, and Ch-AgNP500 membranes.

| No. | Membrane     | Concentration of silver (mg/L) | Rejection Coefficient (%) |
|-----|--------------|--------------------------------|---------------------------|
| Feed| 715.00       |                                |                           |
| 1.   | Ch           | 97.36                          | 86.38                     |
| 2.   | Ch-AgNP10    | 73.21                          | 89.76                     |
| 3.   | Ch-AgNP100   | Permeate                       | 31.80 95.55               |
| 4.   | Ch-AgNP250   | -                              | -                         |
| 5.   | Ch-AgNP500   | -                              | -                         |

Table 2 shows that composite membranes have the ability to filter silver better than the pure chitosan membrane. The filtration ability of the composite membranes increased with the increased in the amount of AgNP from 10 to 100 µg, but the addition of AgNP of 250 and 500 µg did not produce flow, in the filtration with a pressure of 260-270 kPa. This might be caused by the increasing number of silver nanoparticles spread in the membrane so that it covers more membrane pores as explained above.

4. Conclusion
The study has demonstrated the utilization of composite membranes as a filter to remove silver from X-ray film processing wastes. It found that the composite membranes able to remove silver better than the pure chitosan membranes. It recommended that the composite chitosan membranes can be used as a filter to recover silver from X-ray film processing wastes before being discharged into the environment.

5. References
[1] Satyanarayana D N V, & Chandra K R 2018 Recovery of Silver from X Ray Waste from Electro Deposition International Journal of Latest Technology in Engineering, Management & Applied Science (IJILTEMAS) 7 7 80-87
[2] Modi A, Shukla K, Pandya J, & Parmar K 2012 Extraction of Silver from Photographic Waste International Journal of Emerging Technology and Advanced Engineering 2 11 599-606
[3] Bas A D, Yazici E Y, & Deveci H 2012 Recovery of silver from X-ray film processing effluents by hydrogen peroxide treatment Hydrometallurgy 121-124 22-27
[4] Arslan V, Ucurum M, Vapur H, & Bayat O 2011 Recovery of Silver from Waste Radiographic Films by Chemical Leaching Asian Journal of Chemistry 23 1 67-70
[5] Jariwala Sunny Y & Padhya H J 2015 An Overview of Physibility of Silver Particle in Photographic Waste IJSRD - International Journal for Scientific Research & Development 3 01 251-255
[6] Galarpe V R K R & Leopoldo G D 2017 Potential Recovery of Silver (Ag) from X-ray Fixer Waste by Alkaline Treatment Engineering, Technology & Applied Science Research 7 5 2094-2097

[7] Condomitti U, Silveira A T, Condomitti G W, Araki S H, T K, Toma H E 2014 Silver recovery using electrochemically active magnetite coated carbon particles Hydrometallurgy 147-148 241-245

[8] Radha K V & Arun C 2010 Recycling of exposed photographic X-ray films and recovery of silver using Bromelain WIT Transactions on Ecology and the Environment 142 421-430

[9] Khunprasert P, Grisdanurak N, Thaveesri J, Danutra V, & Puititavorn W 2008 Radiographic film waste management in Thailand and cleaner technology for silver leaching Journal of Cleaner Production 16 1 28-36

[10] Zeferino Gamiño-Arroyo, Antonio Tapia-Cisneros, Osvaldo M. Zamacona-Saucedo, Irene Cano-Rodríguez, Alberto F. Aguiler-Alvarado, Lorena E. Sánchez-Cadena and Fernando I. Gómez-Castro 2015 Silver Recovery from Spent Silver Oxide Button Cell by Liquid-Liquid Extraction Journal of Materials Science and Chemical Engineering 3 148-153

[11] Rupiasih N N, Purnomo R R, & Sumadiyasa M 2016 Preparation and Application of Chitosan Membranes to Filter Silver from X-ray Film Processing Wastes Journal of Physics: Conference Series 710 012009

[12] Fernanda D D, Rupiasih N N, Wendri N & Sandriani N W E 2019 Chitosan as A Silver (Ag) Adsorbent on Hospital Photography Fixer Waste Bulletin Fisika 20 1 6 – 10

[13] Rupiasih N N, Sumadiyasa M, Putra I K, & Rasmini N M 2018 Study on Transport Properties of Chitosan Membrane in Different Types of Electrolytes J. Math. Fund. Sci. 50 2 182-191

[14] Rupiasih N N, Suharta W G, Sumadiyasa M, & Islami M N 2019 The Current-Voltage Properties of Ch/AgNP Composite Membranes: A Study on the Effect of AgNP Content IOP Conf. Series: Materials Science and Engineering 515 012064.

Acknowledgments
The author thanks the Ministry of Research, Technology and Higher Education of the Republic of Indonesia for the Fundamental Research Grant of Udayana University for the budget year of 2018/2019.