

Preparation and Application of Chitosan Membranes to Filter Silver from X-ray Film Processing Wastes

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Abstract. Chitosan is a natural polysaccharide biopolymer which has been widely used in different processes and applications. Chitosan based membranes have been used in reverse osmosis, gas separation, dialysis and pervaporation. The object of this research was investigating the possibility of chitosan membrane used as a filter for removing silver (Ag) from X-ray film processing wastes. Several of chitosan membranes such as M1, M2, M3 and M4 have been prepared for the purpose and filtration was done using dead-end filtration method. The filtration experiments were performed on a flat sheet membrane using pure water and X-ray film processing wastes as feeds. The analysis of silver concentration has been done by atomic absorption spectrometers (AAS). The results show that chitosan membrane M2 gave the highest filtration coefficient (R_{coeff}) i.e. 99.9%, with the pure water flux (PWF) and product flux (PF) are 2972.56 L/m²h and 1761.18 L/m²h respectively. The rejection coefficient of the membranes decreases with increasing the amount of chitosan, while the pure water flux and product flux are increased. The filtration coefficients show that the chitosan membranes are able to filter silver waste from X-ray film processing wastes with performance dependent on their characteristic such as pores size. This suggests that, chitosan membrane can be used as one method that is safe and friendly environment for recovering silver from X-ray film processing waste to improve the quality of treated to an acceptable quality level.

Keywords: Chitosan membrane, X-ray film processing wastes, silver recovery, dead-end filtration

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1. Introduction

Silver halides known as its' photosensitivity, approximately 8.3% of silver is used in photography [1-2]. In the X-ray film processing involve development and fixing of film, some silver-halide crystals in the film that are not exposed to light are removed by thiosulphate from the film into the processing solution [3]. This cause the film processing wastes (effluents) may contain high levels of silver. That silver is primarily present as soluble silver thiosulfate complex, and some smaller amounts present as silver sulfide. As an illustration, waste fixer and rinse solutions commonly contain silver at concentrations of 5 ppm or more causing them to be toxic hazardous wastes [2]. Therefore, X-ray film processing wastes, spent rinse waters, films and negatives may contain high silver concentrations and require management as hazardous wastes [4].

In Indonesia, there are over 2434 public and private hospitals and healthcare centres and, until July 2015, about 5981 radiodiagnostic X-ray machines spread around the country [5]. From these data, it can be estimated that large amount of scrap films and X-ray film processing wastes discarded. Therefore, treatment of these wastes for recovery of silver provides significant economic and environmental benefits.

There are varieties of recovery methods available for silver from film processing wastes. The most common methods are metal replacement, electrolytic recovery, and chemical precipitation [4]. For low-silver wash waters, ion exchange is used. Reverse osmosis, distillation and evaporation are used to concentrate silver in dilute solutions. Every method has their benefit involve efficiency as well as costs.

Recently, chitosan has great attention in many research fields. Chitosan is a biopolymer that contained linear aminopolysaccharide of glucosamine and *N*-acetylglucosamine units [6]. It is obtained by alkaline deacetylation of chitin which extracted from the exoskeleton of crustaceans such as shrimps and crabs, as well from the cell walls of some fungi [7]. Chitosan is also characterized by being cationic, biocompatible, and antibacterial. It can be processed into several products including flakes, fine powders, beads, membranes, sponges, cottons, fibers and gels [6]. These characteristics make chitosan has considerable application in various industrial areas [8-11], such as pharmaceutical and biomedical engineering, food industry, agriculture and wastewater treatment [12]. Such applications involve as drug carriers, wound-healing agents, hemodialysis membranes and surgical dressing materials, film for food packaging, coating of fertilizers and pesticides for their controlled release to soil. Chitosan membranes have been used for active transport of chloride ions in aqueous solution [12].

With the rapid growth of demand in industries and daily life, water has become an increasingly valuable but scarcer resource for human being. Increasing global demand for clean water and increasing environmental concerns make membrane filtration become the technology of choice for industries seeking to reuse their wastewater and reduce their water footprint as well as for potable water production. Membrane filtration is a separation technique that produces a purified water stream (permeate) and a concentrated stream that contains all the separated pollutants. Membrane processes are increasingly used for removal of bacteria, microorganisms, particulates, and natural organic material, which can impart color, tastes, and odors to water and react with disinfectants to form disinfection byproducts. By physically removing the pathogens, membrane filtration can significantly reduce chemical addition, such as chlorination. Disinfection can be performed without chemicals.

In the present study, the recovery of silver from X-ray film processing wastes by using chitosan membranes was investigated. To achieve the purpose, we have used dead-end filtration method by using chitosan membranes as a filter. Further, the influence of various ratios of components of matrix/solvent in membranes preparation also examined. The concentration of silver in the feed and permeate solutions were analyzed using AAS. The feed solution is the wastes of X-ray film processing before filtration. Permeate solution is solution that obtained after filtration. The filtration performance of the membranes was evaluated in term of pure water flux (*PWF*), product flux (*PF*) and rejection value or rejection coefficient (R_{coeff}).

2. Materials and methods

2.1 Materials

The materials used are chitosan powder with characteristics i.e. 87.9% of degree of deacetylation, viscosity of 663,000 cps, solubility in acetic acid is 99.4%, and average molecular weight of 900,000. Acetic acid and sodium hydroxide p.a. were analytical grade and were used without further purification. X-ray film processing wastes was obtained from “Sanglah General Hospital Denpasar”, one of the biggest state hospitals in Bali, which was directly used.

2.2 Chitosan membranes preparation

Four sets of chitosan membranes e.g. M1, M2, M3 and M4, have prepared by casting solution method. Those sets obtained by varying the ratios of components of matrix/solvent such as 1%, 2%, 3% and 4% respectively. The preparation involved of dissolving, for example 1% wt chitosan in acetic acid 1% (v/v) solution by stirring at room temperature (30 °C) for 8 h. The casting solution was filtered to remove not-dissolve chitosan and debris, and was kept for 30 minutes for complete degassing of bubbles. Further, it was cast on a glass plate sized of 18.5 cm x 24.0 cm. At this condition, the membrane was allowed to dry at room temperature for 7 d. The dried membrane was immersed in 1 M NaOH for 12 minutes at room temperature. The membrane was then washed thoroughly using distilled water to remove the excess NaOH and dried at room temperature again. Finally, it obtained dry chitosan membrane M1, which are ready to use as filter. Another three sets of chitosan membranes M2, M3 and M4, were prepared by the same procedure. The average pores sizes of those membranes are 19.13 Å, 25.47 Å, 34.00 Å, and 37.09 Å, respectively.

2.3 Experimental set-up

All experiments were conducted in a dead-end filtration set up. The details of the experimental set up are available elsewhere [13]. The experiments were performed at 50-60 kPa pressure using distilled water and X-ray film processing wastes as feed. The X-ray film processing wastes has been directly used without any treatment. The feed and permeate solutions were analyzed using AAS Varian, SpectrAA-30. The filtration performance of the membranes was evaluated in term of pure water flux (PWF), product flux (PF) and rejection coefficient (R_{coeff}). Permeate flux is the filtration rate or flow rate through the membrane $\left(\frac{\Delta V}{\Delta t}\right)$ per unit effective surface area of the membrane (A) as expressed by equation 2.1 [13-14].

$$J = \frac{\Delta V}{A \Delta t} \quad (2.1)$$

Rejection coefficient of the membrane is the membrane's ability to hold back or reject a given molecule, in this regard silver wastes, from passing through [12, 13]. The rejection coefficients (R_{coeff}) were calculated by [13-14],

$$R_{coeff} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2.2)$$

where C_p and C_f is concentration of silver in permeate and feed solutions respectively.

3. Results and discussion

3.1 Pure water flux (PWF) and product flux (PF)

Figure 3.1 show the pure water flow rate (volume of water passing through the membrane per unit time) of membranes M2, M3 and M4, at pressure 50-60 kPa. Figure show that membrane M1 does not show the flow rate that means chitosan membrane M1 cannot pass by the distilled water at operating pressure 50-60 kPa. The gradient or slopes of curves are increased with increasing the amount of

matrix constituent (chitosan) in membrane preparation i.e. M2, M3 and M4. These suggest that the flow rate of the pure water that passes through the membrane at operating pressure of 50-60 kPa is increased with increasing the amount of chitosan from M2 to M4.

Using equation (2.1), where $\frac{\Delta V}{\Delta t}$ is the pure water flow rate that is equal to the gradient of curve in Fig. 3.1, the effective membrane area (A) used in the filtration experiments is 0.000984 m^2 , the pure water flux (PWF) can be calculated. The results showed in Table 3.1. It shows that the pure water flux increased with increasing the amount of chitosan from M2 to M4. These results are consistent with the pores size of the chitosan membranes which are increased with increasing the amount of chitosan in membrane preparation.

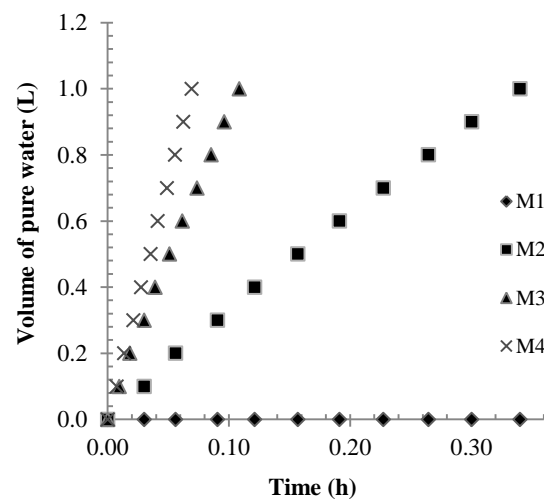


Figure 3.1 The pure water flow rate (volume of pure water passing through the membrane per unit time) of membranes M1, M2, M3 and M4 at pressure 50-60 kPa

Table 3.1 Pure water flux (PWF) of chitosan membranes M1, M2, M3 and M4 at operating pressure of 50-60 kPa

Membranes	Gradient (L/h)	$A \text{ (m}^2\text{)}$	$PWF \text{ (L/m}^2\text{.h)}$
M1	0	0.000984	0
M2	2.92		2972.56
M3	9.15		9297.76
M4	14.45		14684.96

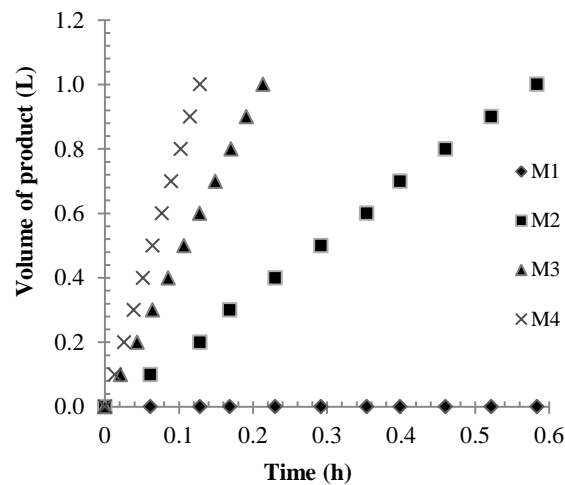


Figure 3.2 The flow rate of product (volume of wastes passing through the membrane per unit time) of membranes M2, M3 and M4 at pressure 50-60 kPa.

Figure 3.2 shows the flow rate of product (volume of X-ray film processing wastes passing through the membrane per unit time) of membranes M1, M2, M3 and M4 at pressure 50-60 kPa. It shows similar pattern with the pure water flux in Fig. 3.1. Figure show that membrane M1 does not show the flow rate of product that means chitosan membrane M1 cannot pass by X-ray film processing wastes at operating pressure 50-60 kPa. The gradient is increased with increasing the amount of matrix (chitosan) from M2 to M4. These suggest that the flow rate of X-ray film processing wastes that passes through the membrane at operating pressure of 50-60 kPa is increased with increasing the amount of chitosan in membranes preparation from M2 to M4.

For the same, using equation (2.1), where $\frac{\Delta V}{\Delta t}$ is product or wastes flow rate, which is equal to the gradient of the curve in Fig. 3.2, the effective membrane area (A) used in the filtration experiments is 0.000984 m^2 , the product flux of X-ray film processing wastes (PF) can be calculated. The results showed in Table 3.2. It shows that the product flux increased with increasing the amount of chitosan from M2 to M4. These results are consistent with the pores size of the chitosan membranes which are increased with increasing the amount of chitosan in membrane preparation.

Table 3.2 Product fluxes of X-ray film processing wastes (PF) of chitosan membranes M1, M2, M3 and M4 at operating pressure of 50-60 kPa

Membranes	Gradient (L/h)	$A \text{ (m}^2\text{)}$	$PF \text{ (L/m}^2\text{.h)}$
M1	0	0.000984	0
M2	1.73		1761.89
M3	4.70		4778.86
M4	7.82		7950.00

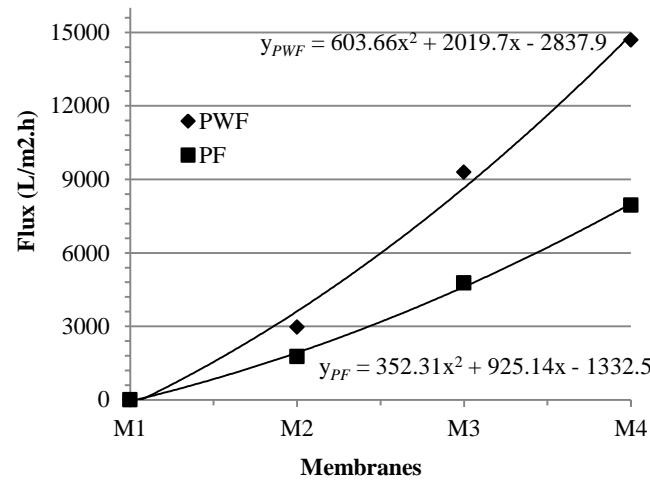


Figure 3.3 Pure water flux (*PWF*) and X-ray film processing wastes flux (*PF*) as a function of chitosan membranes at pressure 50-60 kPa.

Figure 3.3 shows that the flux increases with increasing the amount of matrix (chitosan) making up the membranes. This can be attributed to the pores of the membrane where the pores membrane is getting bigger with increasing the amount of chitosan [14]. The greater the pores size, the easier water pass through the membrane [15]. In laminar flow system, if the membrane consists of straight capillaries, the flux J revealed as Hagen-Poiseuille relationship as

$$J = \frac{\varepsilon r^2}{8\eta\tau} \frac{\Delta P}{\Delta x} \quad (3.1)$$

where r is the pore radius, Δx is membrane thickness, η is viscosity, ε is porosity, and τ is tortuosity factor (the magnitude is one if the form of the pores are cylindrical). Equation 3.1 shows that flux is proportional to the pressure gradient $\left(\frac{\Delta P}{\Delta x}\right)$ and to the square of the pores radius of the membrane (r^2), which is in accordance with the curve fitting in Fig. 3.3 i.e. the second-order of polynomial (quadratic) with y is the fluxes and x is chitosan membranes M1, M2, M3 and M4. It also observes that the product flux lower than the pure water flux. As revealed by Lojkin 1992, in laminar flow system, the permeate flux (J) is formulated by Darcy's law, equation (3.2) [16].

$$J = \frac{\Delta P}{\eta_p R_t} \quad (3.2)$$

Where J is the permeate flux, ΔP is Trans membrane pressure (*TMP*), η_p is permeate dynamic viscosity, and R_t is total filtration resistance. R_t is the sum of the resistance of membrane in a clean state (R_m) and in precipitation (fouling) condition (R_f), that mathematically is written as

$$R_t = R_m + R_f \quad (3.3)$$

The physical properties of the feed solution are presented by its' viscosity (η_p) and fouling condition (R_f). From both equations (3.2) and (3.3), it shows that the flux also influenced by the viscosity and total filtration resistance due to the precipitation, which is inversely. Thus, the greater the viscosity and precipitation will give smaller flux. X-ray film processing wastes is comprised of a number of molecules that caused a greater viscosity than the pure water, that allow for the precipitation. As result the flux of X-ray film processing wastes becomes smaller.

3.2 Rejection study

The concentration of silver in the feed and permeate solutions were analyzed using AAS. The results show in Table 3.3. The rejection coefficient (R_{coeff}) of chitosan membranes have been calculated using equation (2.2). The values obtained also were shown in Table 3.3. It shows that membrane M2 gave the highest rejection coefficient compare with M3 and M4. The rejection coefficients decreased as increasing the amount of matrix (chitosan) in making the membranes from M2 to M4. With these results described that the membrane M2 shows the highest ability to hold back or reject silver wastes from passing through compared with M3 and M4. The rejection coefficient is equal to 100% means all the wastes got filtered by the membrane. In sub 2.3 above, it was mentioned that X-ray film processing wastes has been directly used without any treatment. This is a highlight that, membrane filtration using chitosan membrane is one method which is safe and friendly environment for recovering silver from X-ray film processing waste.

Table 3.3 Concentration of silver (Ag) in the feed and permeate solutions, and the rejection coefficients (R_{coeff}) of chitosan membranes

Membranes	Concentration of silver (mg/L)		R_{coeff} (%)
	feed	569	
M2	permeate	0.55	99.90
M3		107	81.20
M4		121	78.73

4. Conclusion

From the experimental data, the study has demonstrated that chitosan membranes prepared by casting method are able to filter silver (Ag) from X-ray film processing wastes. The filtration performance of the membranes was dependent on their characteristics such as the pores size. It suggests that, chitosan membranes can be used as one of method that is safe and friendly environment to recover of silver waste from X-ray film processing wastes to improve the quality of treated to an acceptable quality level.

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References:

- [1] Bas A D, Yazici E Y and Deveci H 2012 *Hydrometallurgy* **121–124** pp 22–27
- [2] MPCA 2011 *Waste/Hazardous waste #4.46* (w-hw4-46)
- [3] Bober T W, Vacco D, Dagon T J and Fowler H E 2006 *Treatment of photographic wastes* In: Wang L K, Hung Y T, Lo H H, Yapijakis C (Eds.) *Hazardous Industrial Waste Treatment* (CRC Press) pp 361–408
- [4] U S EPA 1999 RCRA in Focus: Photo Processing
<http://www.epa.gov/osw/inforesources/pubs/infocus/photofin.pdf>
- [5] Nuclear Energy Regulatory Agency of Indonesia (BAPETEN) 2015
- [6] Mohamed E I Badawy and Entsar I Rabea 2011 *International Journal of Carbohydrate Chemistry* 460381 p 29
- [7] No H K and Meyers S P 1997 *Preparation of chitin and chitosan* in *Chitin Handbook*

- Muzzarelli R A A and Peter M G (Eds.) (European Chitin Society, Grottammare, Italy) pp 475–489
- [8] Rabea E I, Badawy M E T, Stevens C V, Smaghe G and Steurbaut W 2003 *Biomacromolecules* **4** (6) pp 1457–1465
- [9] Hirano S 1996 *Biotechnology Annual Review* **2** pp 237–258
- [10] Shigemasa Y and Minami S 1996 *Biotechnology and Genetic Engineering Reviews* **13** pp 413–420
- [11] Shahidi F, Arachchi J K V and Jeon Y J 1999 *Trends in Food Science and Technology* **10** (2) pp 37–51
- [12] Rupiasih N Nyoman, Yayuk Eka Puspita and Sumadiyasa Made 2015 *J. Phys.: Conf. Series* **622** 012004
- [13] Rupiasih Ni Nyoman, Sumadiyasa Made, Ratnawati A A and Hery Suyanto 2011 *Indonesian Journal of Materials Science* **13** (1) pp 54-58
- [14] Swapna Rekha Panda, Munmun Mukherjee and Sirshendu De 2015 *Journal of Water Process Engineering* **6** pp 93–104
- [15] Mulder M 1996 *Basic Principles of Membrane Technology* (Netherlands: Kluwer Academic)
- [16] Evenblij, Herman 2006 *Filtration Characteristics in Membran Bioreactor* (Printed by: Pasmans Offsetdrukkerij Gravenhage)