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Study the Effect of Tannic Acid (phenolic compounds) and Iron oxide (inorganic particle) on Fouling of Hollow-Fiber Microfiltration Membrane

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ABSTRACT

Characteristics of membrane fouling by organic and inorganic foulants were investigated in this study. Two feed waters with organic matter (100 mg/L of tannic acid (TA)) and mixture of organic and inorganic matter (100 mg/L of tannic acid and 10 mg/L of Fe_2O_3 (TA-Fe_2O_3)) were tested. A bench-scale filtration experiment was tested on a PVDF hollow-fiber microfiltration (MF) with a nominal pore size of 0.02 μm. Filtration protocol included several steps i.e. filtration, physical cleaning, air scrubbing and drainage of retentate. The system was operated in a constant-flux dead-end mode of filtration. The operational parameter that represents membrane fouling was stopped when transmembrane pressure (TMP) reached 75 kPa for physical cleaning. Fouling on membrane was measured using digital pressure gauges. The quality of feed and permeate water were measured by checking total organic carbon (TOC), chemical oxygen demand (COD), total suspended solid (TSS), and turbidity. Filtration experiment was operated for 22 cycles within 10 days. Results of TOC and COD indicate that MF membrane could not reject organic compounds. Although after each cycle the membrane was soaked in NaOCl solution, irremovable fouling gradually increased, up to 36% of the maximum TMP after 22 filtration cycles. TSS and turbidity indicate that MF membrane can completely reject suspended solid in wastewater. TA-Fe_2O_3 water made MF membrane fouled faster than TA water alone. TMP at filtering TA-Fe_2O_3 increased faster than TA because the membrane surface was covered by accumulation of suspended solids. These results demonstrate that both feed water characteristics should be thoroughly investigated for appropriate operation of membrane processes.

Keywords : microfiltration; irremovable fouling; transmembrane pressure; physical cleaning

INTRODUCTION

Currently, polymeric hollow-fiber membrane is increasingly used for water treatment, water reuse, and wastewater treatment, especially in food and beverage industries [1, 2]. Food and beverage industries normally generate exhausted water from various operations such as fruit processing, cleaning of the tanks and pipes, and bottle washing. Moreover, food waste contains a variety of compounds such as phenolic, proteins, and lactose. Wastewater contains tannic acid as a surrogate of organics which is dissolved components and colloids that would attach to the membrane by adsorption, tannic acid with iron oxide as a surrogate of inorganic colloids which can physically bind to the membrane surface and block pores or hinder transport to the membrane surface that tend to precipitate on membrane surface, then develop a cake layer. Consequently, membrane suffered from fouling because of organic and inorganic compounds present in the feed water. Subsequently, effluents from food and beverage industries pose a hazard to the environment and require appropriate management approaches. Meanwhile, technology innovation has been introduced into industry to treat wastewater that are able to recycle spent process waters onsite and to reduce the amount of wastewater discharged into municipal sewage treatment plants. Therefore, membrane filtration processes offer promising perspectives and key advantage over conventional technologies in the treatment of wastewaters from industries. Microfiltration (MF) membrane frequently experience a major problem with fouling that deteriorates the membrane properties and performance like hydrophobicity, pore size distribution, permeate flux decline [3]. MF membrane has a small footprint and pore size of 0.1 to 10 μm that be able to remove suspended solid, bacteria, particle, and reduced chemical use. Furthermore, polyvinylidene fluoride (PVDF) is largely used as a polymeric membrane material due to its outstanding properties i.e. high mechanical strength, flexibility, thermal stability, and chemical resistance [4]. However, it is typically fouled by inorganic particle and the main limitation of the use of membrane technology in wastewater treatment is membrane fouling, which cause a significant reduction of permeate flux during long term filtration.

In this study, MF was used to filtrate synthetic wastewater simulating process water from cashew nut processing (food industry), which mainly contains of tannic acid (phenolic compound). Thus, the objective of this study aims to investigate the effects of phenolic compounds and inorganic colloid on fouling of polymeric hollow-fiber MF membrane, which was evaluated in terms of permeate quality, trans membrane pressure development and irremovable fouling.

METHODOLOGY

MF process

PVDF hollow-fiber MF membrane (LE-1-US02-125 model, outside-in pressurized membrane, Kuraray AQUA Co., Ltd. Japan) was used in a bench-scale filtration system. The nominal pore size of MF membrane was 0.02 μm with an effective length of 27 cm. This type of membrane is typically employed in water and wastewater treatment. Mini-modules are composed of 102 membrane fibers, of which each fiber has diameter of 1.0 mm, were prepared for the test. The filtration protocol included several steps, i.e. filtration, physical cleaning, air scrubbing and drainage of retentate as shown in Figure 1. The system was operated in a constant-flux dead-end mode of filtration and performed the outside-in pressurized membrane [5]. The pressure at the raw water side was set to 100 kPa to check how flux was changed. Filtration operation was stopped at transmembrane pressure (TMP) of 75 kPa for the physical cleaning. TMP was measured by using digital pressure gauges (Nagano Keiki Co., Ltd. Japan) installed at inlet and outlet of filtration module. Pressure data was recorded in every 1min by using a data logger (GL-100, GRAPHTEC Co., Ltd. Japan). The data on GL100 was monitored using the software and controlled by computer. Flux was measured every 30 sec during operation time using electronic balance (A&D company., Ltd. Japan).

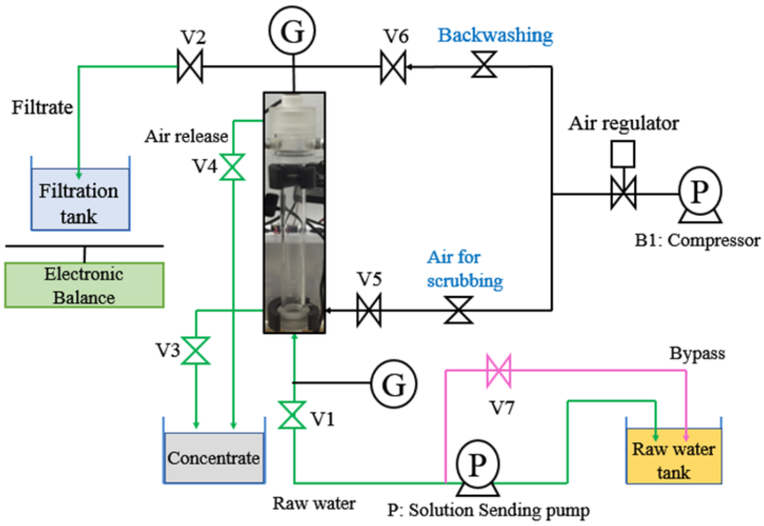

Figure 1 Diagram of the membrane filtration experiments

For the physical cleaning method, backwashing and air scrubbing were applied. Backwashing method applied air pressure of 0.2 MPa from the treated water side for 10 seconds, then performed air scrubbing while keeping the treated water side in the pressurized state. Air scrubbing was done with an air flow rate of 60 NL/hr from the bottom of the housing for 60 seconds. After that, drained the solution from the housing, restarted filtration.

Feed solution

In this study, synthetic wastewater was prepared into two types of wastewater as shown in Table 1 that summarizes the components of raw water. Water A refers to organic compounds (tannic acid, Wako pure chemical industries, Ltd.) and Water B refers to organic and inorganic compounds which is added by iron oxide (Fe_2O_3, ACROS Organic, Belgium).

Analytical methods

In order to analyze the characteristics of wastewater and membrane properties, the following method was used to verify the result. The operational parameters that affect membrane characteristic was trans membrane pressure (TMP). When TMP reached 75 kPa, physical cleaning (backwashing) and air scouring were applied to the membrane in every cycle. When pressure was more than 25% of initial pressure, it required maintenance cleaning by chemical regimes (future study). The TMP was measured in every 1 minute by Data logger. Temperature was measured by using glass tube thermometer 0-100°C. Chemical oxygen demand (COD) was measured by collecting sample from feed and permeate water in each batch every day and followed the Standard Method 5220C closed reflux titrimetric [6]. Total organic carbon (TOC) concentrations of permeate and feed samples

Table 1 Characteristic of synthetic wastewater

Parameter	Organic wastewater (Water A)	Organic and inorganic wastewater (Water B)
TSS* (mg/l)	240	250
TDS* (mg/l)	3,200	3,200
COD* (mg/l)	4,000	4,000
Tannic acid (mg/l)	100	100
pH (buffered)	7.50	7.50
Iron oxide (mg/l)	-	10

Note: ** TSS adjusted by adding Kaolin,*
** TDS adjusted by adding NaCl,*
** COD adjusted by adding glucose*

were measured by Total organic carbon analyzer (TOC-L Shimadzu Co., Ltd. Japan) to determine the TOC rejection by the membrane. The rejection was calculated using a following equation (1). TSS (Total Suspended Solids) in feed and permeate water was measured following Standard Method (2540D) [6]. Turbidity was measured using HI98703 HANNA Instrument. pH and TDS were measured by using HI98131 HANNA Instrument.

$$\Re = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad (1)$$

where $\Re$ is the rejection, C_p (mg/l) is the TOC concentration in the permeate, and C_f (mg/l) is the TOC concentration in the feed.

The permeate from each sample was collected in a 3L beaker on an electronic balance. Change in volume was recorded as a function of time, and the permeate flux was calculated by a following equation (2).

$$J = \frac{\Delta V}{A\Delta t} \qquad (2)$$

where J is the flux (L/m^{2}h), $\Delta V\ (L)$ is the volume of permeate collected during a time period of Δt (h), and A is the filtration area (0.0864 m^2).

The permeate flux through a porous membrane is described as the applied transmembrane pressure driving force, TMP (Pa), divided by the resistance to mass transfer, *R* (m^{-1}), and the permeate viscosity, μ (Pa.s) [7]

$$J = \frac{\text{TMP}}{\mu R} \qquad (3)$$

For the pure water filtration, *R* represents the resistance to mass transfer associated with the clean membrane. During a fouling experiment, the resistance to permeation increases due to various mechanisms, such as pore plugging, cake layer formation, concentration polarization, etc. [8]. Thus, R comprises the intrinsic resistances of the membrane itself and resistance borne to fouling.

RESULT AND DISCUSSION

To determine the susceptibility of the membrane to fouling by organics and mixture of organic and inorganic colloid, filtration experiments were conducted using raw water containing tannic acid for organics and tannic acid with iron oxide.

Organic Fouling

During 10-day operation (22 cycles of filtration with physical cleaning), foulants increase gradually and were not reduced by physical cleaning. As presented in Figure 2, TMP gradually increased from one cycle to next cycle until the last cycle where its TMP was higher than the first cycle about 36% (compared with the protocol set at 25% of maximum TMP). It is defined that MF membrane was fouled since physical cleaning was ineffective in removing suspended solids and organics from the membrane surface. Then, it is defined as "irremovable fouling". Table 2 shows that MF membrane cannot remove organics from water thus TOC of feed water and permeate were nearly same.

Table 2 Characteristic of feed and permeate wastewater for MF membrane for 10 days operation with 22 cycles of physical cleaning of Water A.

	Turbidity (NTU)	TSS (mgl^{-1})	TOC (mgl^{-1})	pH (-)	Temperature (^{o}C)
Feed water	208.3 ± 19	271 ± 102	1387 ± 13.4	7.46 ± 0.1	25.3 ± 1.0
Permeate water	0.25 ± 0.04	-	1383 ± 2.8	7.23 ± 0.18	25 ± 0.9

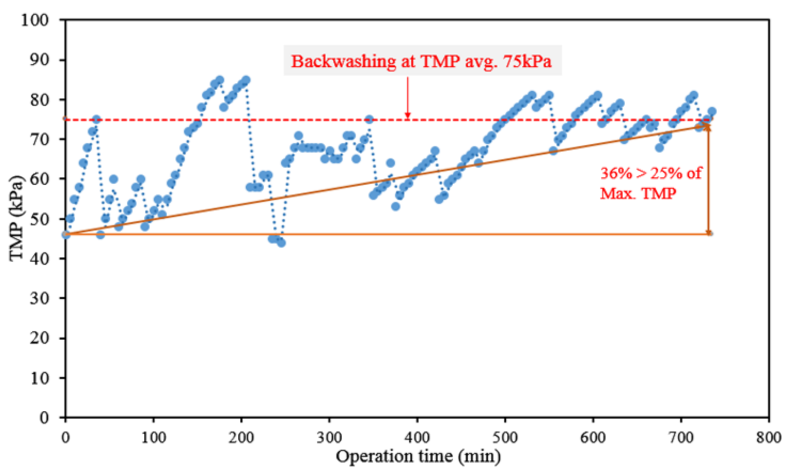

Figure 2 Transmembrane pressure development at filtration of tannic acid water (Water A) during 10 days with 22 cycle operation

The irremovable fouling is evident as shown in Figure 3. The permeate flux of tannic acid water was steadily declined from first day to the last day about 63% of the DI water flux attained with a new membrane. This would probably explain by the fact that hydrodynamic conditions of membrane surface was changed by clogging with some organic matter in the pores of membrane and a cake layer of colloids formed on the membrane surface which caused membrane fouling, although physical cleaning was applied in each cycle [9].

Organic and inorganic fouling

According to Figure 4, TMP increases with Water A and Water B were greatly different. The slopes of the graphs for Water A without Fe_2O_3 is markedly lower than that for Water B with Fe_2O_3 about 5-folds. It is because Water B contained Fe_2O_3, which could be rejected by the MF membrane. Then, Water B caused the MF membrane to be fouled faster than water A.

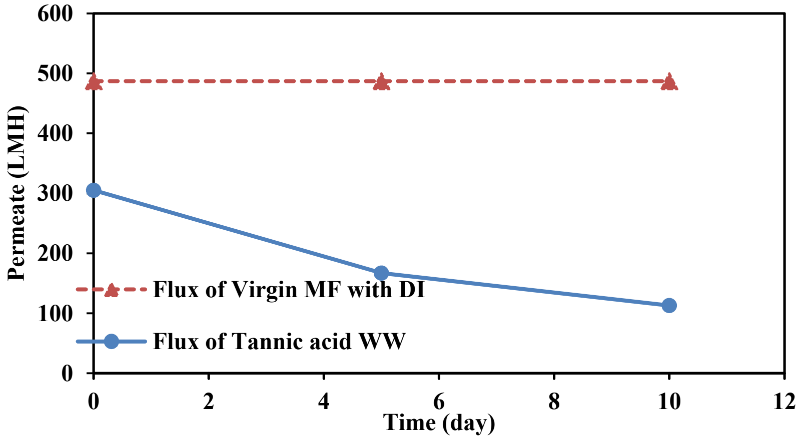

Figure 3 Flux of tannic acid water (Water A) on Day 1, 5, and 10 compared with new membrane flux with DI water

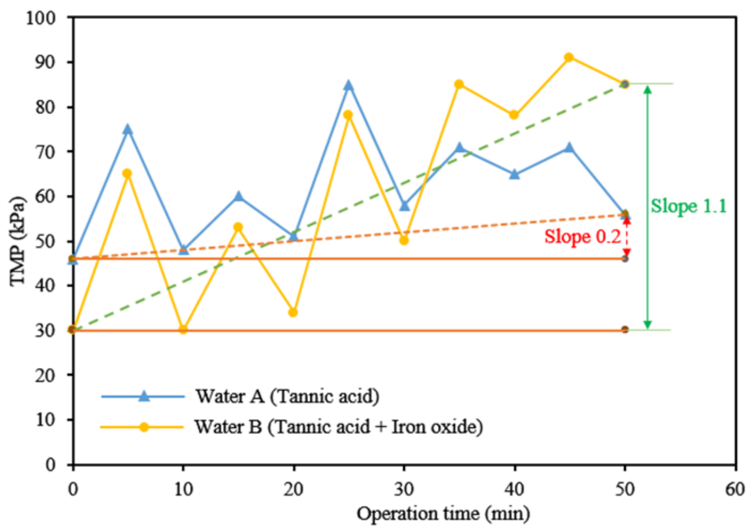

Figure 4 Comparison on TMP increases between Water A (tannic acid) and Water B (Tannic acid + Iron oxide) during initial 3 days with 5 cycle operation

As expected, the fouling caused by iron oxide occurred very quickly. The permeate flux of the first day is 382 L/m^2h dropped to 70 L/m^2h of the last day, which accounted for about 83% decline, compared with flux across new membrane. As shown in Figure 5, it was evident that of tannic acid with iron oxide made membrane fouled faster than tannic acid alone, since the particle size of iron oxide is bigger than tannic acid and pore of the MF membrane. After finishing filtration for each batch, the membrane was soaked in the NaOCl solution with 25 mg/l Cl_2 for preservation. This resulted in removal of some attached foulants which brought down TMP before starting new cycle, i.e. TMP recovery (Figure 6). Apparently, TMP recovery gradually declined with increasing filtration cycles, suggesting strongly attached foulants.

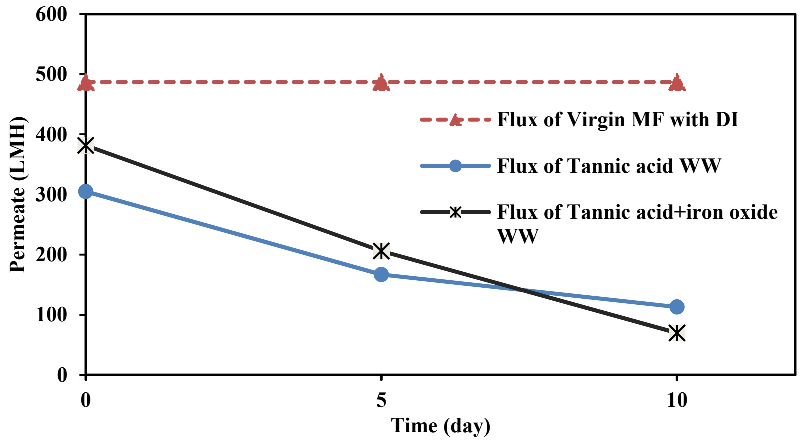

Figure 5 Flux of tannic acid + iron oxide water (Water B) on Day 1, 5, and 10 compared with tannic acid alone and new membrane filtrates with DI water

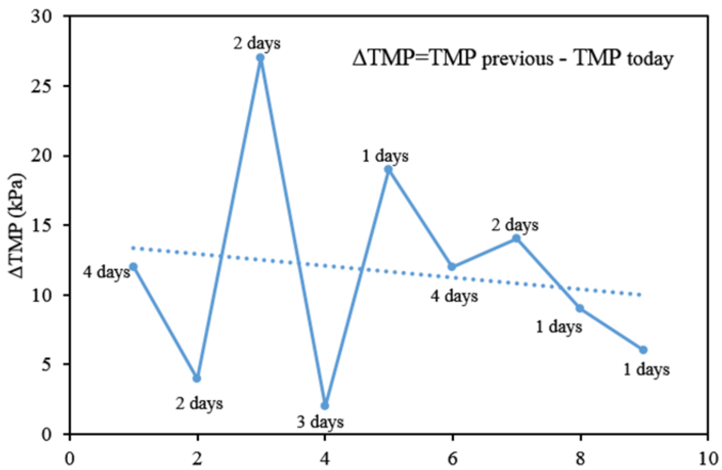

Figure 6 Comparison of Water A (without iron oxide) and Water B (Iron oxide) initial 3 days of operation

CONCLUSION

The following conclusion can be drawn from this study.

- Tannic acid with iron oxide caused more severe fouling than tannic acid alone.
- Although the MF membrane did not significantly reject tannic acid, a small amount that attached to the membrane caused a gradual increase of irremovable fouling, up to 36% of the maximum TMP after 22 filtration cycles.
- The overall results demonstrate that feed water composition, i.e. organics and inorganic colloid, greatly affected fouling in MF membrane. In real wastewater treatment of food and beverage industries, to prolong the filtration time, pre-treatment to remove these compounds is recommended.

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REFERENCE

[1] Pendergast, M. and E.M. M Hoek. 2011. A review of water treatment membrane nanotechnologies. Energ. Environ. Sci. 4(6): 1946-1971.

[2] Cassano, A., C. Conidi, and R. Castro-Muñoz. 2019. Current and Future Applications of Nanofiltration in Food Processing, in Separation of Functional Molecules in Food by Membrane Technology. Elsevier. 305-348.

[3] Hashino, M., et al. 2011. Effect of kinds of membrane materials on membrane fouling with BSA. J. Membrane Sci. 384 (1-2): 157-165.

[4] Ravereau, J., et al. 2016. Ageing of polyvinylidene fluoride hollow fiber membranes in sodium hypochlorite solutions. J. Membrane Sci. 505: 174-184.

[5] Woo, Y.C., et al. 2013. Effect of chemical cleaning conditions on the flux recovery of fouled membrane. Desalin. Water Treat. 51(25-27): 5268-5274.

[6] Apha, A. 2005. WEF, 2005. Standard methods for the examination of water and wastewater. 21: 258-259.

[7] Field, R.W. and G.K. Pearce. 2011. Critical, sustainable and threshold fluxes for membrane filtration with water industry applications. Adv. Colloid Interface. 164(1-2): 38-44.

[8] Taniguchi, M., J.E. Kilduff, and G. Belfort. 2003. Modes of natural organic matter fouling during ultrafiltration. Environ. Sci. Technol. 37(8): 1676-1683.

[9] Louie, J.S., et al. 2006. Effects of polyether–polyamide block copolymer coating on performance and fouling of reverse osmosis membranes. J. Membrane Sci. 280(1-2): 762-770.