Separation of oil–water emulsion from car washes

S. Panpanit, C. Visvanathan and S. Muttamara

Environmental Engineering Program, Asian Institute of Technology, P.O. Box: 4, Klong Luang 12120, Pathumthani, Bangkok, Thailand (E-mail: *visu@ait.ac.th*)

Abstract The potentials of UF and NF membrane processes have been evaluated for separation of oil water emulsion generated from car washing operations. Using membranes, wastewater can be effectively recycled and fresh water usage could be reduced. The parameters studied were membrane type, emulsifier types, pressure and competing compounds. Both an-ionic and non-ionic emulsifiers were used for the experimental runs. The Ca^{2+} and Mg^{2+} were used as the main competitive ions. Results indicate that a polysulfone membrane caused more flux reduction than the cellulose acetate and thin film polyamide membranes. Higher concentrations of emulsifier presented negative flux decline in both UF and NF membranes. However, the presence of nonionic emulsifier in oil emulsion caused more significant flux reduction than an anionic emulsifier. The NF membrane produced higher TOC removal and less fouling than UF. The results indicate that increased competitive Ca^{2+} and Mg^{2+} ions resulted in significant positive NF flux and TOC removal.

Keywords Ultrafiltration; nanofiltration; oil water emulsion; car washes

Introduction

Petrol stations usually consume a large volume of water in many activities such as car washing, floor cleaning, toilet, cafeteria use etc. The average rate of wastewater generated from a petrol station in Thailand is 21 m^3 per day. Most of the wastewater originates from car washing operations and the average water consumption per car is 250–300 l (Suwit, 1997). Car wash wastewater creates crucial problems because it contains soil, emulsifiers, free and emulsifier oil. In general, this wastewater is treated by conventional techniques such as the American Petroleum Institute (API) gravitational oil separator, Parallel Plate Interceptor or Corrugated Plate Interceptor. The main function of these units is to eliminate free oil and removal of suspended solids. However, the oil emulsion and emulsifier were not fully removed and still discharged to the public sewer system. Therefore, the quality of treated water can not attain the existing effluent discharge standard. Aurelle and Verdun (1997) found that oil-water emulsion formed in the presence of emulsifiers are stabilized emulsions. Due to the presence of surface charge, the collision between micro droplets during the Brownian motion is ineffective. It does not lead to coalescence between drops for the separation of emulsions.

Considering the large volume of wastewater generated in the car washing processes, wastewater treatment coupled with recycling could be an attractive alternative. The membrane process has great potential for such recycling options. Among the available physico-chemical treatment methods, ultrafiltration has been found to be most advantageous for treatment of oil-water emulsion (Lipp *et al.*, 1987). Using membranes, the wastewater can be effectively recycled and fresh water usage could be reduced. However, the membrane fouling is considered as the major operational problem in such recycling systems. Lee *et al.*, (1984) showed that fouling was mainly due to adsorption of oil into the membrane structure, which modifies the effective pore diameter resulting in reduction of membrane permeability. In a recycling process, the hardness and emulsifier concentration in recycled water could be increased due to water loss from evaporation. Therefore, the use of recycled water with high hardness for rinsing could cause unpolished appearance problems such as scales and spots on the car body colour.

In many recycling systems, ultrafiltration (UF) has been studied extensively. Ultrafiltration is the typical membrane process for retaining the oil rather than the emulsifier from the oil-emulsion in car wash wastewater. It produces higher flux at lower operating pressure but allows the divalent ions and low molecular weight molecules such as emulsifier to pass through the membrane. Whereas, Nanofiltration (NF) can provide higher flux at lower pressure than reverse osmosis (RO) and has a better rejection of divalent ions and micromolecules than UF. The objective of this research is to examine the potential of UF and NF membranes for recycling of wastewater from car wash as a function of membrane, emulsifier types and the interference due to Ca^{2+} and Mg^{2+} divalent ions which contribute to the hardness.

Materials and method

Five types of flat sheet membranes GM, PS-100, C-100 and C-30 for ultrafiltration and flat sheet nanofiltration membrane type DK were used in this study. Characteristics of the membrane are shown in Table 1. The GM ultrafiltration and DK nanofiltration membrane were from Desalination System Asia. Celgard manufactured the remaining ultrafiltration membranes. A schematic diagram of the ultrafiltration and nanofiltration experiment unit is illustrated in Figure1 and Figure 2. The ultrafiltration system consists of a 15 l stainless steel feed tank, installed with a stainless steel coil of 10 mm diameter for controlling feed temperature at 30ºC. The inlet and outlet of the cooling coil was connected to a chilling system. The acrylic resin plate and frame membrane module type C10-T (NITTO DENKO) with effective area 6.0×10^{-3} m^2 was used as test UF module. The nanofiltration system consists of a 3 l stainless steel feed tank installed with a stainless steel coil of 10 mm diameter for cooling the feed emulsion. Here, the stainless steel plate and frame membrane module with effective area 1.15×10^{-3} m^2 was tested. The feed emulsion investigated in this study consists of lubricant oil with distilled water and emulsifier. A Philip's blender was used for blending 100 mg/l of lubricant oil type PTT V-120 manufactured by Petroleum Authority of Thailand with distilled water. A lubricant was added to the distilled water and emulsions generated by mixing with blender. The mixture was stabilized by adding emulsifier at 0.1% by weight. The two types of emulsifiers used were an-ionic emulsifier $CH_3(CH_2)_{11}$–OSO_3–Na and non-ionic emulsifier $C_{11}H_{23}CH_2O(CH_2CH_2O)_8$–H. The concentrations of oil and emulsifier as well as emulsifier type are similar to those generated in actual car wash wastewater. The characteristics of emulsifiers are listed in Table 2. The hardness of water is caused by the presence of polyvalent metallic ions, principally Ca^{2+} and Mg^{2+}. In this study, $CaCl_2$ and $MgCl_2$ at a concentration range from 100 to 400 mg/l were selected as representative of Ca^{2+} and Mg^{2+} in hard water. The membrane permeate was basically measured in terms of permeate flux, percentage of TOC removal and divalent ion removal. Permeate Flux was obtained by weighing permeate with an electronic balance. TOC was analyzed by TOC analyzer type TOC-500, while Ca^{2+} and Mg^{2+} were

Table 1 Characteristics of membrane

Type	Material	MWCO (kDalton)	Water flux (l/m²–h)
PS-100*	Polysulfone	100	635
C-100*	Cellulose acetate	100	580
C-30*	Cellulose acetate	30	515
GM*	TFM polyamide	8	94
DK**	TFM polyamide	150–300 Dalton	58

Note   * Pressure 400 kPa for UF
      ** Pressure 1000 kPa for NF and 98% rejection of Ca^{2+}

Table 2 Emulsifier characteristics

Emulsifier type	Molecular structure	Mw.
Anionic	$CH_3(CH_2)_{11}$–OSO_3–Na	288
Nonionic	$C_{11}H_{23}CH_2O(CH_2CH_2O)_8$–H	538
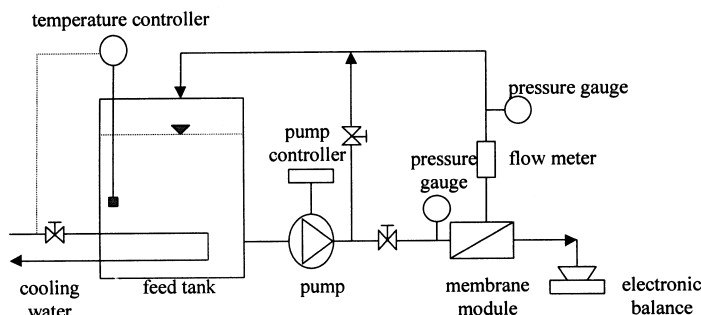
Figure 1 Ultrafiltration experimental set-up
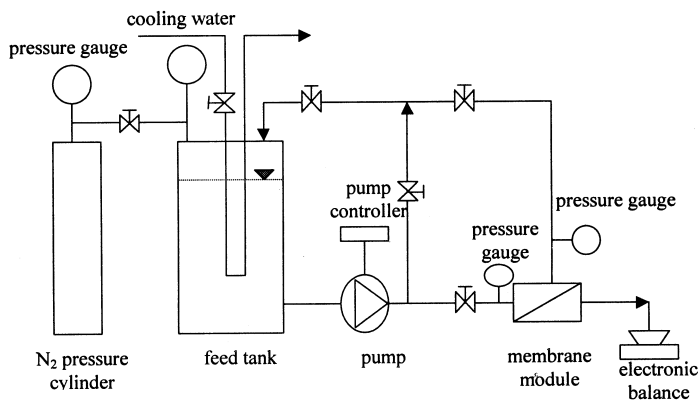
Figure 2 Nanofiltration experimental set-up

measured by Atomic Absorption. All experiments were operated for three hours in order to obtain steady state flux.

Results and discussion

Permeate flux as function of time and membrane type

The membranes and emulsion interaction were initially tested with five types of ultrafiltration GM, PS-100, C-100, C-30 and nanofiltration membrane type DK with anionic emulsion. Figure 3 presents the effect of membrane material on flux at a pressure of 400 KPa and oil emulsion 100 mg/l. A sharp decrease in the initial flux from 635 to 270 l/m²–h of PS-100 was observed when pure water is replaced by emulsion. The initial flux of C-100 and C-30 declined from 580 to 290 l/m²–h and 515 to 400 l/m²–h within one hour respectively. This is due to the interaction between the membrane material and hydrophobic part of the oil emulsion leading to adsorption on the membrane surface. As the emulsifier molecules are much smaller than the membrane pores, it leads to internal membrane pore fouling. This phenomenon modifies the effective pore diameter, resulting in reduced membrane flux. The polysulfone membrane is more hydrophobic than cellulose acetate and has a relatively higher
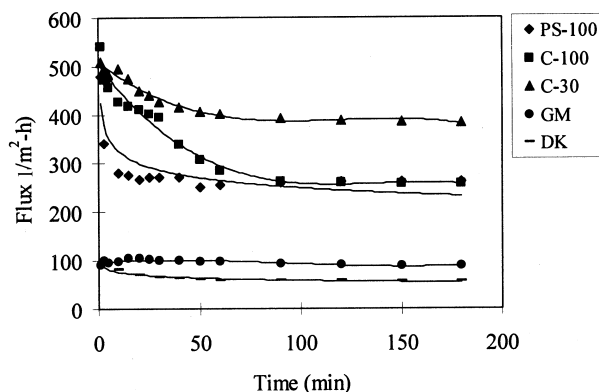
Figure 3 Flux comparison with different membrane types
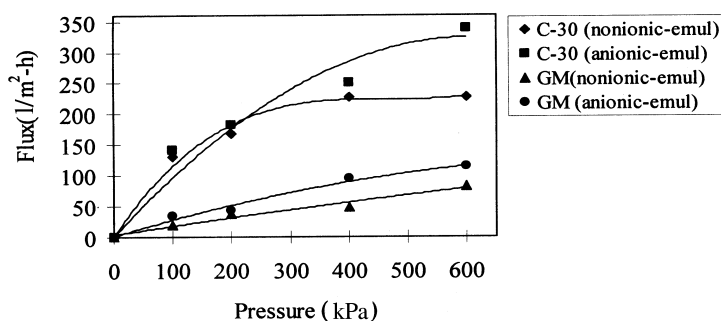

Figure 4 Variation of permeate flux as function of pressure, UF membrane (C-30, GM) and emulsifier type

adsorption tendency with the membrane material. Therefore, the PS-100 shows more flux reduction than C-100 and C-30. The above results are in agreement with observations of others. Richard *et al*. (1977) also found that in treating the oil-emulsion, membrane fouling led to reduced ultrafiltration rate over time. Danae *et al*. (1992) showed this using a nonionic emulsifier tested with the polysulfone and cellulose acetate membranes. The reason for the sharp decrease in flux of the polysulphone membrane is most likely the interaction between the membrane material and the hydrophobic part of the emulsifier molecule. The GM and DK are thin film polyamide membranes that have hydrophilic stability. The permeate flux of GM and DK membranes do not show the predominant reduction. This is due to surface membrane charge characteristics. The polyamide exhibits a moderate to strong anionic surface charge. For this reason, the surface of the polyamide will repel the anionic emulsifier. Therefore, membrane flux is not decreased significantly due to less adsorption of the emulsifier on the membrane surface.

Permeate flux as a function of pressure and emulsifier type
The C-30 and GM ultrafiltration membrane types were selected and tested by varying emulsifier type and pressure from 100 to 600 kPa. Figure 4 illustrates an increase of applied pressure induced higher driving forces through the membrane resulting in increase of membrane flux. Generally, the concentration polarization is a significant factor in ultrafiltration membrane due to the relatively low diffusivity of macromolecules of emulsion. In addition, the occurrence of a gel layer on the membrane surface causes the additional fouling. As the applied pressure difference is increased, the flux of C-30 does not increase linearly in both types of emulsifier due to the concentration polarization and gel layer
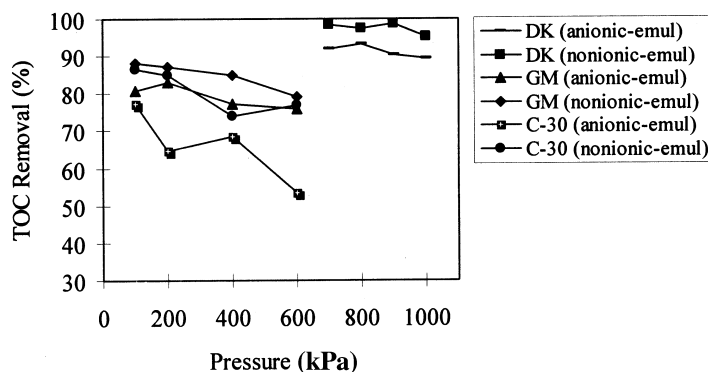
Figure 5 Rejection as a function of pressure and two types of emulsifier
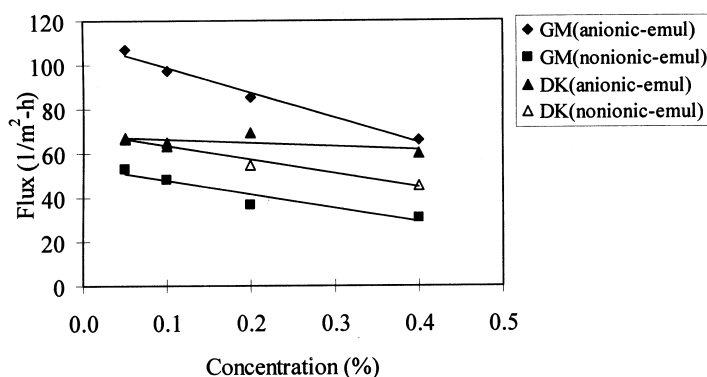
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Figure 6 Effect of emulsifier on UF and NF membrane flux

formation, since the nonionic emulsifier has a higher hydrophobic degree and molecular weight than anionic emulsifier. If there was concentration polarization under the use of non-ionic emulsifier it should also affect GM membrane. However, on increase of applied pressure, no significant flux reduction was observed in GM membrane in both types of emulsifier. The results support that cellulose acetate membrane can cause more fouling due to concentration polarization than TFM polyamide membrane.

Figure 5 shows that the reduction of TOC removal efficiency increases significantly in C-30 and GM ultrafiltration membrane, but not in NF with increase of pressure. TOC removal is in the range of 95–98% and 60–85% for NF and UF respectively. The possible reason for UF is that the small molecular weight of the emulsifier allows easy penetration through the membrane pores. However, rejection by NF membranes is constant with increasing pressure. This is due to larger molecular weight material of emulsifier diffusing through the membrane at a slower rate, leading to lower concentrations in the membrane permeate.

Permeate flux as function of emulsifier concentration

Experiments were conducted with concentrations ranging from 0.05% to 0.4% for both anionic and nonionic emulsifier in oil emulsion 100 mg l^{-1}. The effect of feed concentration on flux is presented in Figure 6. The reductions of permeate flux of DK membrane is less than GM membrane with increasing feed concentration for both emulsifier types. Figure 6 shows that the increase in feed concentration of nonionic emulsion causes more significant GM flux reduction than the anionic emulsion. It could be that the anionic emulsifier

increases the negative charges on oil droplets and membrane surface and reduces membrane fouling (Richard *et al.,* 1977). However, DK membrane shows less flux reduction than GM membrane when the nonionic emulsifier replaces the anionic emulsifier.

Effect of competing compounds on NF membrane

In this study, $CaCl_2$ and $MgCl_2$ were used as competing compounds, because car wash wastewater always contains divalent ions, especially Ca^{2+} and Mg^{2+}. The nonionic emulsifier was selected instead of the use of anionic emulsifier to avoid the precipitation of salts on membrane surface. It was observed that an anionic emulsifier reacts with Ca^{2+} and Mg^{2+} result in the scaling formation, which blocks and reduces the membrane productivity. The results in Figure 7 show that NF flux increases slightly with increases of both $CaCl_2$ and $MgCl_2$ concentrations in order to maintain electroneutrality on both sides of the nanofiltration membrane. This is because at higher concentrations, higher Donnan potential allows more solvent to pass through the membrane. In addition, the higher charge, such as Ca^{2+} and Mg^{2+} will result in a greater decrease in charge with distance from the particle interface, resulting in a decrease of potential barrier. However, Figure 8 shows that the TOC in permeate reduces significantly with increases of competing compound concentrations. As reported by Schirg and Widmer (1992), flux increases with increasing feed concentration of divalent ions. In addition, the solution diffusion models in Eqs. (1) and (2) show that the differential in concentration and pressure gradient drives the solute and solvent flux through the membrane. It diffuses across the membrane due to the chemical potential which is the result of both concentration and pressure differences across the membrane. This solution diffusion equation shows how the chemical potential plays an important role in allowing the solvent to pass through the membrane. The total flux (J_T) is a summation of solvent flux (J_W) and solute flux (J_S). Under higher Ca^{2+}, Mg^{2+} concentrations and constant applied pressure, more solvent and solute pass through the membrane resulting in an increase of total flux (J_T) and divalent ions in the permeate. However, the TOC in permeate remains constant with increase of pressure according to the results from Figure 5. Therefore, the ratio of TOC in permeate per total flux (J_T) declines, which means a reduction of TOC concentration in permeate with an increase of divalent ion concentration.

The solution diffusion equations associated with Figures 7 and 8 are as follows:

$$J_W = K_W (\Delta p - \Delta \pi) \qquad (1)$$

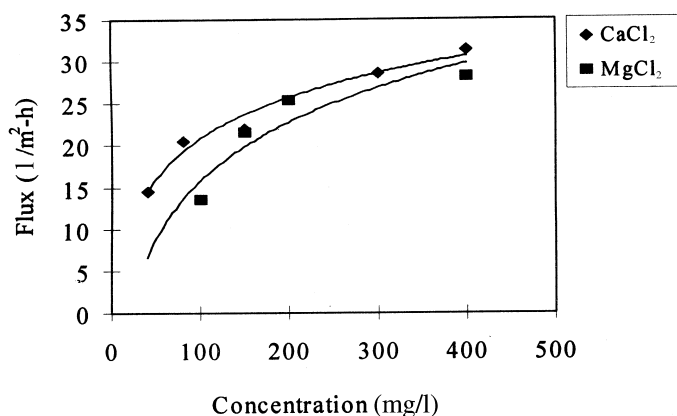$$J_S = K_S (C_M - C_P) \qquad (2)$$
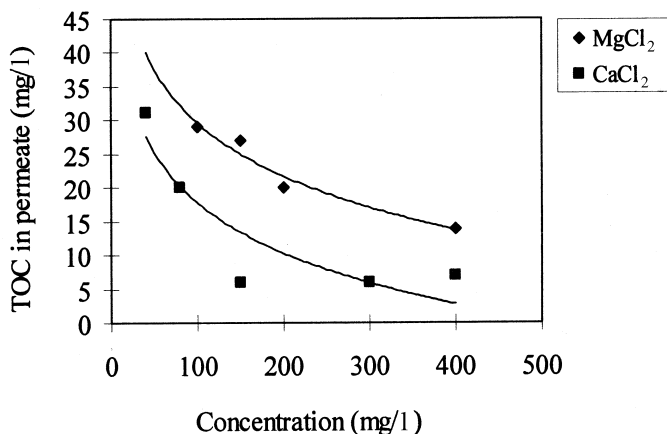

Figure 7 Effect of $CaCl_2$ and $MgCl_2$ on NF flux

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Figure 8 Effect of CaCl$_2$ and MgCl$_2$ on TOC in permeate

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where:

J_W = solvent flux (l/m^2–h)

K_W = solvent mass transfer coefficient (1/h)

Δp = pressure difference across the membrane (m)

$\Delta \pi$ = osmotic pressure difference across the membrane (m)

J_S = solute flux (mg/m^2–h)

K_S = solute mass transfer coefficient (m/h)

C_M = solute concentration at the membrane surface (mg/l)

C_P = solute concentration in permeate (mg/l)

Conclusions

With the nanofiltration, TOC removal is significantly higher than UF membrane. The average of TOC removal was 75% for membrane types PS-100, C-100, C-30, GM and 98% for DK respectively. The improvement of TOC removal and permeate flux are presented with increasing Ca^{2+} and Mg^{2+} concentration in emulsion due to the solution diffusion model and Donnan effect behaviors. The parameters such as membrane material, pressure, emulsifier types and concentrations are the significant parameters influencing permeate flux. By selecting the polysulfone membrane, the effect of membrane fouling is higher than cellulose acetate and TFM polyamide membrane, because the hydrophobicity degree of polysulfone membrane is higher than the cellulose acetate and polyamide membrane. The increase of pressure does not affect the permeate quality of DK. In contrast, it shows dramatically a decrease in permeate quality of all UF membranes. The nonionic emulsifier predominates in significant flux reduction in UF membrane rather than the anionic emulsifier. However, using both emulsifier types, they do not show the considerable flux reduction in DK. Due to the better membrane performance of DK in terms of flux, divalent ion rejection and TOC removal, the DK membrane is recommend for recycling wastewater from car wash.

Acknowledgement

References

Aurelle, Y. and Verdun, P. (1997). New Advances in Oily Wastewater Treatments, *Franco-Thai Symposium on New Water and Wastewater Treatment*, Bangkok, Thailand.

Danae, D., Vassilis, G. and Gun, T. (1992). Interaction behavior in ultrafiltration of nonionic surfactant: Part 1 Flux Behavior, *Membrane Science*, **69**, 251–258.

Lipp, P., Lee, C.H., Fane, A.G. and Fell, C.J.D. (1987). A fundamental study of the ultrafiltration of oil-water emulsion, *Membrane Science*, **36**, 161–177.

Lee, S.B., Aurelle, Y. and Roques. (1984). Concentration polarization, membrane fouling and cleaning in ultrafiltration of soluble oil, *Membrane Science*, **19**, 23–38.

Suwit, C. (1997). The study of the improvement of wastewater quality in gas station. Unpublished Report, *Petroleum Institution*, Bangkok, Thailand.

Richard, G., Luthy., R.E., Selleck. and Terry, R. (1977). Surface properties of petroleum refinery waste oil emulsion, *Environmental Science and Technology*, **11**(13), 1211–1217.

Schirg, P. and Widmer, F. (1992). Characterization of nanofiltration membrane for separation of aqueous dye-salt solution, *Desalination*. **89**, 89–107.