

Green Technology Contribution in Development of Coolant Wastewater Filtration

By Erna Yuliwati

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Abstract

The cross-flow membranes has been performed for treating wastewater emulsion of oil derived from the automotive industry on the metal cutting section. The objective of this study is to treat liquid waste from machining process using membrane technology. The mechanism of ultrafiltration process is flow of small molecules pass through pore of membrane. The performance of the cellulose acetate hydrophilic membrane is determined by the permeate and rejection flux. The operation of this two-stage ultrafiltration membrane involves a 12% composite cellulose acetate membrane (CA-12) in phase I and 15% (15%) cellulose acetate membrane (CA-15) in phase II with a 90 minute operating time with pressure of 3.5 bar. Flux of phase I, without pretreatment and with pretreatment are 17,03 L / m².h and 59,05 L / m².h respectively. In phase II, the flux of treatment without and with preteatment are 22.08 L / m².h and 24.86 L / m².h , respectively. COD and surfactant rejection for both membrane without pretreatment of 96.57% and 96.35%, whereas for waste feed with COD rejection of 98.56% and surfactant rejection of 97.44 %.

Keywords: Cutting oil; Ultrafiltration; cellulose acetate; COD rejection; surfactant rejection

1. Introduction

The environment is becoming more polluted due to the various wastes discharged from a wide range of machining process from industrial applications. The use of coolants are essential component of machining process as its cools the cutting zone, lubricates the tool chip contact thereby reducing the friction and temperature generated. Meanwhile, the metal working industries saw the limitation of the use of conventional coolant and coolant strategies. Among the alternative ways of conventional coolant usage reduction, dry machining and minimum quantity lubrication (MQL) technique is effective in machining proses in order to foster the sustainability environment. MQL in comparison with flood cooling and dry machining drastically minimize (1/300,000 times) the negative effect on the environment, resulting the reduce of cutting force and usage of coolant [1]. However, the lubricating oil tends to evaporates as it strikes the already heated cutting tool at high temperature. The need of thermal conductivity nanoparticles in cutting fluids are explored to eliminate or reduce drastically the shortcomings of conventional coolants in MQL technique.

Nanofluids (NFs) are new classes of fluids engineered by dispersing nanomaterials in based fluids that could be deionized water, esters or vegetable oils (e.g coconut oils) [2]. Nanomaterials are defined as the materials whose its structural have dimensions in the

range between 1 and 100 nanometer. In nanomaterials due to the increase of surface area to the volume, some physical and chemical properties such as thermal, electrical, mechanical, chemical, optical and magnetic property of the materials can be changed significantly. The nanomaterials exhibit different and unique properties as compared to the bulk materials with the same compositions [3]. NFs are class of solid/liquid mixtures engineered by dispersing nanoparticles in conventional base liquids. Common nanoparticles could be metallic/intermetallic compounds namely, Ag, Cu, Ni Fe ceramic compounds namely oxides, sulfides, carbides, Al₂O₃, Fe₂O₃, TiO₂, SiO₂, ZnO₂ are some nanostructured materials [4]. Base liquids of NFs are vegetable oil, coconut oil, gear oil, and pump oil. NFs were applied in different areas such as thermal application, fuel additives, lubricant, surface coating, environmental remediation, inkjet printing, biomedical, petroleum industry. Example of the NFs thermal applications is cooling system in different industries, such as metal cutting operation. Cooling is most potential scientific challenges in different industries for heat transfer applications [5]. NFs can be used in metal processing and could also be used as efficient coolant in data centers and electronics cooling systems, as shown in Figure 1. NFs were applied also in environmental remediation as an additive in membrane composition in order to produced nanofiltration membrane.

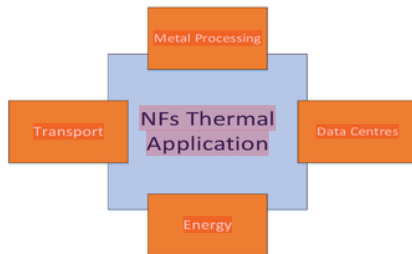


Figure 1 NFs thermal applications

Proper selection of coolants is particularly important as it could affect the tool life, cutting forces, power consumption, machining accuracy and surface integrity [6]. Despite the significant effects of coolants in machining process, the selection of the type and delivery system of the coolants are usually based on the recommendations of coolants suppliers and machine tool manufactures. Substances used in machining for cooling and/or lubrication can be defined as cutting fluids, gas-based coolants/lubricants and solid lubricants. It has been widely accepted characteristics of the coolants is their miscibility in water. Then, it has been used in order to categorize the coolants into water-soluble or non-water soluble, also known as oil-based coolants [8]. Oil-based fluids are one of alternative coolant used in machining operations. They are classified into two basic categories such as naphthenic mineral oils and paraffinic mineral oils. Based on the limitation of mineral oils, some studies develop the use of vegetable oils as coolants in machining operations [9]. Moreover, vegetable oils is classified as nanofluids that potential to enhance the performance of conventional heat transfer fluids and also potential treatment of its waste before delivered to the environment.

As known, several common treatment methods have been improved for disposing and pre-treatment alternatives available for non-hazardous water miscible machine coolant wastewater, such as chemical treatment, membrane technology, evaporators to remove soluble and insoluble of organic and inorganic contaminants. Membrane ultrafiltration has been greatly used in water separation in order to separate liquid/liquid or liquid/solid mixtures. Ultrafiltration is most commonly used to separate insoluble components from the aqueous phase. One of the uses that demonstrate the usefulness of ultrafiltration is a separation of oil in an emulsion from water, such as coolant wastewater. In this study, machining coolant emulsions can have the oil separated and concentrated, with the water phase being discharged to sanitary sewer, and the concentrated oil phase being disposed of at a lower cost. However, these methods would lead

to a huge production of sludge and complicated operations problems [10-12]. (Galil and Levinsky, 2007); (Judd, 2011); (Kalyandurg, 2003). Table 1 showed the component of coolant wastewater from machining process.

Table Error! No text of specified style in document. Component of wastewater of nanofluids machining process.

No	Component	Percentage, %
1.	Titanium	0.03
2.	Aluminum	0.001
3.	Cobalt	0.018
4.	Coconut oil	94

Based on those data, the ultrafiltration was used to remove the inorganic contaminant which soluble in coolant wastewater. Coconut oil has a long shelf life compared to other oils, lasting up to two years due to its resilience to high temperatures. Coconut oil is best stored in solid form, at temperatures lower than 24.5 °C (76°F) to extend shelf life. However, unlike most oils, coconut oil will not be damaged by warmer temperatures. Fractionated coconut oil "is a fraction of the whole oil, in which most of the long-chain triglycerides are removed so that only saturated fats remain. It may also refer to as "caprylic/capric triglycerides" or medium-chain triglyceride (MCT) oil because mostly the medium-chain triglycerides caprylic and capric acid are left in the oil. Table 2 showed the advantages and disadvantages of vegetable oils as coolant.

Table Error! No text of specified style in document. Advantages and disadvantages of vegetable oils as lubricants [13] (Shashidhara and Jayaram, 2010).

Advantages	Disadvantages
High biodegradability	Low thermal stability
Low pollution of the environment	Oxidative stability
Compatibility with additive	High freezing points
Low production cost	Poor corrosion protection
Wide production possibilities	
Low toxicity	
High flash points	

Vegetable oils do display many desirable characteristics, which make them very attractive lubricants for many practical applications.

2. Experimental Section

2.1. Materials and methods

This study has been conducted of wastewater analysis, the flocculated water from the outside to the inside of the membrane fibers. The flux decline will be expected to increase in the course of time due to membrane fouling. Thus operational permeate flux is monitored over the time to determine the degree of membrane fouling to membrane permeability. Parameters used to quantify the efficiency of membrane processes are flux (J), permeability and solute rejection (R), where the flux is defined as:

$$J = \frac{Q}{A} \quad (2.1)$$

where Q is the permeate flow rate ($L \cdot hr^{-1}$) and A is the effective membrane area (m^2), and permeability as:

$$\text{Permeability} = \frac{Q}{A\Delta P} = \frac{Q}{N\Delta P d l \pi} \quad (2.2)$$

where ΔP is the transmembrane pressure (Pa), N is the fiber quantity, d is the outer membrane diameter (OD), and l is the effective membrane length (m), the rejection (R %) as:

$$R (\%) = \left[1 - \left(\frac{C_p}{C_f} \right) \right] \times 100 \quad (2.3)$$

where C_p is the permeate concentration in mg/L and C_f is the feed dissolved organic compound (DOC) concentration (mg/L) measured by DOC analyzers (Shidmadzu TOC-VE).

The experimental set-up is schematically illustrated in **Error! Reference source not found.** The system consists of rapid mix continuous feed supply that controlled by a buoyant water level controller. A bubbling system controlled by adjustable air flow regulator continuously supplied air bubbles within the fibers network at the bottom of the membrane module to provide a continuous up-flow circulation of micro-flocs suspension for hindering any micro-particles settlement. In particular, a constant air scouring bubble of $200 L/(m^2 \cdot min)$ was applied to exert shear stress to suppress potential particles deposition on the membrane surface.

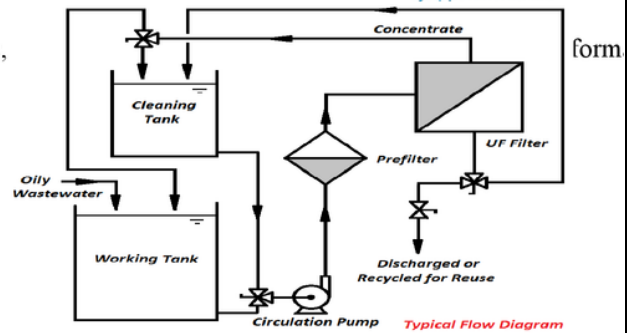


Figure 2 Schematic diagram of waste coolant ultrafiltration

The experimental set-up is schematically illustrated in Figure 2. The unit was designed from high-quality PVC materials, glass and stainless steel for all wetted parts to prevent corrosion contamination as well as to establish high equipment practicality and reliability.

2.2. Membrane morphology

The morphology of the membrane was observed by field emission scanning electron microscope (FESEM) (JEOL JSM-6700F). The FESEM micrographs were taken at certain magnifications. It produced photographs at the analytical working distance of 10 nm. Surface composition analysis was carried out on energy dispersive X-ray (EDX) (JEOL JSM-6380LA).

The static contact angle of the membrane was measured by the sessile drop method using a Drop Meter A-100 contact angle system (Maist Vision Inspection & Measurement Co. Ltd.) to characterize the membrane wetting behavior. A water droplet at $3 \mu L$ was deposited on the dry membrane using a micro-syringe. A microscope with a long working distance 6.5x objectives was used to capture micrographs.

Asymmetric porous membranes were characterized by determination of porosity and average pore radius. The membrane porosity, ϵ , was defined as the volume of the pores divided by the total volume of the porous membrane. The membrane porosity was calculated using the following equation,

$$\varepsilon = \frac{(w_1 - w_2)/\rho_w}{(w_1 - w_2)/\rho_w + w_2/\rho_p} \times 100 \quad (2.4)$$

where ε is the porosity of the membrane (%), w_1 the weight of wet membrane (g), w_2 the weight of dry membrane (g), ρ_p the density of the polymer (g/cm³) and ρ_w is the density of water (g/cm³).

Average pore radius, r_m , was investigated by filtration velocity method, which a measurement of the ultrafiltration flux of the wet membrane applied on pure water in limited time (20 h) under 0.1 MPa pressure. It represents the average pore size of the membrane thickness (l), which was measured by the difference value between the external radius and an inner radius of the hollow fiber membrane. The test module containing 60 fibers with the length of 35 cm was used to determine water permeability. According to Guerout-Elford-Ferry equation, r_m could be calculated:

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q}{\varepsilon \times A \times \Delta P}} \quad (\text{Error! No text of specified style in document.5})$$

where η is water viscosity (8.9×10^{-4} Pa s), l is the membrane thickness (m), ΔP is the operation pressure (0.1MPa), ε is the porosity of the membrane (%), Q is volume of permeate water per unit time (m³ s⁻¹), A is effective area of membrane (m²).

2.2. Permeation flux and rejection

An in-house produced fiber module, with a filtration area of 11.42 cm², was submerged in prepared suspension in membrane reservoir with a volume of 14 L. A cross-flow stream was produced by air bubbling generated by a diffuser situated underneath the submerged membrane module for mechanical cleaning of the membrane module. The air bubbling flow rates per unit projection membrane area was constantly set at 1.8 L/min to maintain proper turbulence. The filtration pressure was supplied by a vacuum pump and controlled by a needle valve at 0.5 bars. Permeate flow rates were continually recorded using flow meter respectively.

The rejection test was carried out with distilled water and sythetic coolant wastewater with mixed liquor suspended solid (MLSS) concentration of 3-8-g/L. All experiments were conducted at 25^oC.

3. Results and Discussion

3.1 Membrane properties

Properties of membrane can be shown in Table 7.1. Based on analysis of structural and characterization of PVDF membrane. The membranes were obtained based on size of outer and inner diameter, average poresize and membrane surface area. It showed that SiO₂ had modified the nanoporous membrane poresize. Improvement of membrane morphology is observed with adding of SiO₂. The result shows that the permeate flux of the membrane was better (flux value of 92.4%) as compared to the neat PVDF membrane (flux value of 84.3%). The result shows that the permeate flux of the membrane was better (flux value of 92.4%) as compared to the neat PVDF membrane (flux value of 84.3%). This improvement was caused by the change of membrane morphology of PVDF membrane. It is observed for adding SiO₂ particles, may affect the interaction between SiO₂ particles and PVDF chains.

Table 3. Membrane properties

Parameter	Membrane
Membrane configuration	Hollow fiber
Membrane material	PVDF/SiO ₂
Outer diameter (mm)	1.2
Inner diameter (mm)	0.6
Poresize (nm)	35.2
Membrane area (dm ²)	10.48

Generally, the addition of nanofillers into PVDF matrix is due to the agglomeration phenomena. This phenomena is owing the the nature characteristic of the nanofillers (such as small size and high surface energy) and the poor compatibility with hydrophobic PVDF bulk. At present, the dispersion of nanofillers for the preparation of PVDF-inorganic composite membrane usually achieved by strong mechanical stirring. They have unique ability to bond polymers with dissimilar materials such as silica. The bond thus formed has good initial strength as demonstrated by failure of the composite by polymer rupture and the bond exhibits excellent retention of strength even after severe environmental aging.

3.2 FESEM analysis

Figure 3 illustrated that SiO₂ affects the mass transfer during the phase inversion process. The cross-sectional images for hollow fibers consist of finger-like macrovoids extending from both inner and outer wall

of the hollow fiber, and an intermediate sponge-like layer. This phenomenon can be explained by the kinetic effect on the rate of solvent-nonsolvent exchange in the phase inversion process. At lower SiO₂ concentration (1%), an increase in the amount of SiO₂ tends to draw more water into the polymer dope, resulting in an increase in the length of finger-like macrovoids and decrease in the thickness of the intermediate sponge-like layer.

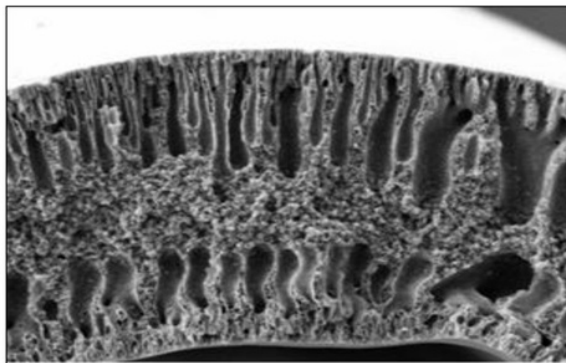


Figure 3 FESEM image of cross section of PVDF/SiO₂ membrane

4. Conclusion

Experimental results showed that a submerged ultrafiltration process using modified PVDF membranes has a great potential for refinery produced wastewater treatment. The quartic equation developed in this study shows the presence of a high correlation between observed and predicted values. Interestingly, 3-dimension response surfaces plots can be a good driven approach for visualizing the parameter interaction. The optimum factor conditions were satisfied at ABRF of 2.25 ml/min, HRT of 276.93 min, MLSS concentration of 4.50 g/L, and pH of 6.50 to resulted COD removal of 90.28 %.

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