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Green Technology Contribution in Development of Coolant Wastewater Filtration

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Abstract

The aim of this study is to treat liquid waste from machining process using membrane technology. The cross-flow membranes has been performed for treating wastewater emulsion of oil derived from the automotive industry on the metal cutting section. 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 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. COD and surfactant rejection were resulted for both membrane with and without pretreatment process. In phase I, flux of CA-12 without pretreatment and with pretreatment were 67.03 L / m2.h and 81.05 L / m2.h respectively. The values of COD and surfactant rejection with pretreatment process are 86.57% and 86.35%, respectively. In phase II, the flux of CA-15 without and with pretreatment were 82.08 L / m2.h and 84.16 L / m2.h , respectively. Meanwhile, these values of COD and surfactant with pretreatment are 92.56% and 97.44 %. It concluded that CA-15 membrane with pre treatment produced better results in filtration the machining fluids due to the effect of nanoparticles that added to the membrane composition.

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

1. Introduction

The environment was became 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 quality 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, Al2O3, Fe2O3, TiO2, SiO2, ZnO2 are some nanostructured materials [4]. Base liquids of NFs is vegetable oil, coconut oil, gear oil, and pump oil. NFs was 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.

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 coolants usually based on the recommendations of coolants suppliers and machine tool manufactures. Substances used in machining for cooling and/or lubrication can defined as cutting fluids, gas-based coolants/lubricants and solid lubricants. It has been used 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 in organic contaminants. Membrane filtration was used for water separation in order to separate liquid/liquid or liquid/solid mixtures. Moreover, membrane filtration is also used to separate insoluble components from the aqueous phase. One of the uses that demonstrate the usefulness of membrane filtration is a separation of oil in an emulsion from water, such as coolant wastewater.

Figure 1 shows the membrane filtration applications, which were applied in environmental remediation in order to produced high value of rejection.

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]. Table 1 showed the component of coolant wastewater from machining process.from machining process.

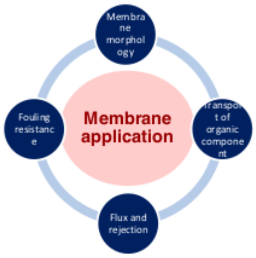

Figure 1 NFs thermal applications

Table 1. 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 membrane filtration 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 could not 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. Advantages and disadvantages of vegetable oils as lubricants [13]

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

Table 2 showed the advantages and disadvantages of vegetable oils as coolant. 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 conducted of membrane fabrication, membran The flux declined 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:

$$J = \frac{Q}{A} \tag{1}$$

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

$$\text{Permeability} = \frac{Q}{A\Delta P} = \frac{Q}{N\Delta P dl\pi} \tag{2}$$

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:

$$R\ (\%) = \left[1 - \left(\frac{C_p}{C_f}\right)\right] \times 100 \tag{3}$$

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 Figure 2. The system consists of rapid mix continuous feed supply that controlled by a buoyant water level controller. A bubbling system controlled by adjustable airflow 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.min applied to exert shear stress to suppress potential particles deposition on the membrane surface.

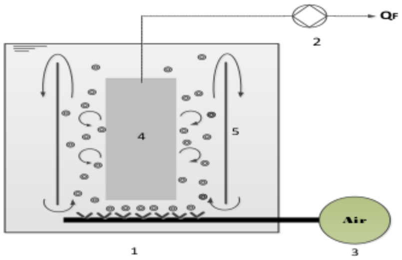

Figure 2 Schematic diagram of waste coolant ultrafiltration: (1) membrane reservoir; (2) peristaltic pump; (3) aerator; (4) membrane bundles; (5) partitioned glass.

The experimental set-up 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 μL was deposited on the dry membrane using a micro-syringe. A microscope with a long working distance 6.5x objectives 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 calculated using the following equation,

$$\varepsilon = \frac{(w_1 - w_2)/\rho_w}{(w_1 - w_2)/\rho_w + w_2/\rho_P} \times 100 \tag{4}$$

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 40 fibers with the length of 40 cm was used to determine water permeability.

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q}{\varepsilon \times A \times \Delta P}} \tag{5}$$

where η is water viscosity (8.9 x 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 (m^3 s^{-1}), A is effective area of membrane (m^2).

2.3. *Permeation flux and rejection*

An in-house produced fiber module, with a filtration area of 12.48 cm^2, was submerged in prepared suspension in membrane reservoir with a volume of 16

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 1.6 L/min to maintain proper turbulence. The filtration pressure at 0.5 bars was supplied by vacuum pump and controlled by needle valve. Permeate flow rates were continually recorded using flow meter respectively.

The rejection test was carried out with distilled water and syhthetic coolant wastewater with mixed liquor suspended solid (MLSS) concentration of 6 g/L. All experiments were conducted at 25^{0}C.

3. Results and Discussion

3.1 Membrane properties

Properties and performance of membrane tabulated in Table 3. 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 Cellulose Acetat had modified the nanoporous membrane poresize.

Table 3. Membrane properties

Parameter	Membrane	
Membrane configuration	Hollow fiber	Hollow fiber
Membrane material	PVDF/CA12	PVDF/CA15
Outer diameter (mm)	1.2	1.2
Inner diameter (mm)	0.6	0.6
Poresize (nm)	35.2	39.6
Membrane area (dm^2)	12.48	12.48
Flux, L/m^3.h		
Without pre treatment	67.03	82.08
With pre tretment	81.05	84.16
COD removal (%) (with treatment)	86.57	92.56
Surfactan removal (%) (without treatnent)	86.35	97.44

Improvement of membrane morphology is observed with adding of CA, as shown in Table 3. The result shows that the flux of the CA-15 membrane with treatment was better (84.16 L/m^3.h) as compraed with CA-12 with treatment of 81.05 L/m^3.h. These values tend to similar trend of CA-15 and CA-12 without treatment. COD and surfactant removal resulted better values by using CA-15 than CA-12. This improvement was caused by the change of membrane morphology of PVDF/CA membrane with adding the CA particles. It is observed that adding CA particles affected the interaction between CA particles and PVDF chains. Generally, the addition of nanofillers into PVDF is due to the agglomeration phenomena [14-16]. This phenomenon shows 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 cellulose acetate [17]. 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 shows the FESEM micrographs of modified PVDF nanomembranes. Improvement of membrane morphology is observed for addition of a small amount of cellulose acetate (CA). CA particles have high specific areas and hydrophilicity, which will affect the mass transfer during the spinning process. The cross-sectional images of nanomembranes consist of finger-like macrovoids extending from both inner and outer wall of the membranes, and an intermediate sponge-like layer.

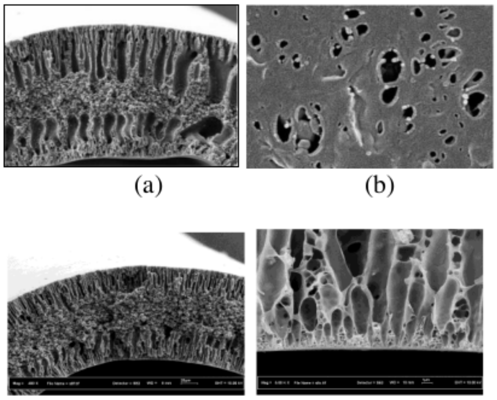
(a) (b)
(c) (d)

Figure 3. FESEM image of (a) cross section and (b) outer wall of PVDF/CA-15 membrane; (c) cross-section and (d) outerwall of PVDF/CA-12.

This phenomenon can explained by the kinetic effect on the rate of solvent-nonsolvent exchange in the phase inversion process [18]. At lower CA concentration (12%), an increase of CA 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.

This phenomenon can be explained by the kinetic effect on the rate of solvent-nonsolvent exchange in the phase inversion process. At lower CA concentration, an increase in the amount of hydrophilic. CA 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. Whereas at higher concentrations of CA-15, an increase in CA-15 concentration increases the viscosity of the polymer dope, decreasing the rate of water intrusion into the polymer dope, which results in the shorter finger-like macrovoids and thicker intermediate sponge-like layer. The decrease of fingerlike in CA-12 effect the sponge-like structure, which decrease the flux and removal process.

4. Conclusion

Experimental results showed that a submerged ultrafiltration process using modified PVDF membranes has a great potential for machining filtration process. flux of CA-12 without pretreatment and with pretreatment were 17.03 L / m^2.h and 19.05 L / m^2.h respectively. The values of COD and surfactant rejection with pretreatment process are 86.57% and 86.35%, respectively. In phase II, the flux of CA-15 without and with pretreatment were 22.08 L / m^2.h and 24.86 L / m^2.h , respectively. Meanwhile, these values of COD and surfactant with pretreatment are 92.56% and 97.44 %. It concluded that CA-15 membrane with pretreatment produced better results in filtration the machining fluids due to the effect of nanoparticles that added to the membrane composition.

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