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Waste oil/water emulsion treatment by membrane processes

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Abstract

The present work investigated the treatment of waste drawing oil which is a high-strength waste oil/water emulsion commonly used in the cable and wire industries. Semi-batch ultrafiltration (UF) and reverse osmosis (RO) processes along with prefiltration by a microfilter were employed to treat the waste oil/water emulsion. Experiments were conducted to examine the performances of each of the UF and RO treatment steps. The observed results have clearly shown the excellent performances of the combined UF and RO treatment processes. The water quality of permeate from the combined treatment processes has been consistently excellent which permits direct discharge or can be considered for reuse. © 1998 Elsevier Science B.V.

Keywords: O/W emulsion; UF/RO Treatment; Water quality; Reuse

1. Introduction

Oil/water (O/W) emulsion is an aqueous solution frequently occurring in a wide variety of industrial applications. Drawing oil or cutting machine oil is a typical oil/water emulsion which is commonly used in the precision machining and cable and wire industries. The oil/water emulsion serves the purposes of lubrication, cooling, surface cleaning and corrosion prevention in the manufacturing process. Depending on specific applications, the oil emulsion can consist of up to 97% water, the rest being a complex aqueous mixture which comprises different kinds of oils (mineral, animal,

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vegetable and synthetic), alcohols, sequestrants and surfactants. Even for the same application, the proprietary composition of complex aqueous mixture can vary widely among different suppliers. The temperature of O/W emulsion is usually maintained in the range between 30°C to 90°C in the process because of the heat it removes from the metal surfaces. Hence, some organic components of the complex aqueous mixture could become degraded after a certain period of use. Metal ions and other inorganic contaminants can enter the O/W emulsion during the manufacturing process. Moreover, a serious anaerobic biological growth often occurs in the oil emulsion. Therefore, the waste O/W emulsion needs to be regularly replaced several times every year. A large amount of waste O/W emulsion is thus generated in this fashion worldwide every year by many industries.

Currently, there are no effective methods for dealing with this type of waste oil/water emulsion. Bansal [1] considered oily and latex wastewater treatment using inorganic membrane ultrafiltration (UF). Results from laboratory and pilot plant tests had found such a treatment process efficient and economically attractive. Matz et al. [2] employed ultrafiltration to treat the mineral oil/water emulsions and oily wastewater from oil product refining processes. Very good suspended solids (SS) and COD (chemical oxygen demand) removal was obtained by those authors. Bodzek and Konieczny [3] examined the UF performances of polyacrylonitrile (PAN) and polyvinyl chloride (PVC) membranes for three oil emulsions. Over 90% of COD rejection and over 95% of oil retention were attained by the UF process. Gorzka et al. [4] employed a different approach to deal with oil/water emulsions which were first separated into oil and aqueous phases using inorganic salting-out substances. The two phases were then treated, respectively, by the supercritical air oxidation with cupric oxide catalyst and by an electrochemical process. Very good results were reported by those investigators.

The oil/water emulsion employed in the cable and wire manufacturing processes mentioned earlier is professionally known as the drawing oil. Table 1 compares the properties of typical fresh and waste drawing oils. Treatment of the drawing oil emulsion by the conventional biological and/or chemical methods will be very difficult because of its high oil and copper contents and SS and COD concentrations [5,6]. Good treatment method needs to consistently reduce all these pollutants of the waste drawing oil to acceptable levels. The purpose of this paper is to address this issue by employing the ultrafiltration (UF) and reverse osmosis (RO). Semi-batch experiments were conducted to examine the efficiencies of UF and RO treatment processes in reducing the COD and Cu^{2+} concentrations and suspended solids (SS) and in improving the turbidity and conductivity. Furthermore, emphasis is placed on possible reuse of the treated waste drawing oil.

Table 1
Properties of fresh and waste drawing oils and tap water

	pH	COD (mg/l)	Cu^{2+} (mg/l)	Conductivity (μmho/cm)	Specific weight
Waste drawing oil	7.65	61,150	287	2219	1.013
Fresh drawing oil	8.55	62,100	–	1410	1.015

2. Materials and methods

The semi-batch UF/RO experimental apparatus is shown in Fig. 1. The system primarily consisted of a prefilter and UF and RO cells. The prefilter was made of woven cotton threads and capable of retaining all particulates larger than 5 μm. The UF unit had a hydrophillic, spiral-wound tube of polyether sulfone (PES) membrane. It had a 1.8 cm inside diameter and was 24-cm long with a 137.5 cm^2 effective filtration surface area. The membrane cartridges considered for the RO units were polyamide (PA) membranes. The RO membranes were also of spiral-wound form and had the same size of the UF unit. All filtration cartridges were obtained from Nanopore Technologies, Hsin Chu, Taiwan.

The waste drawing oil for the present experimental study was supplied by a major copper cable and wire manufacturer in northern Taiwan. Fresh drawing oil, also supplied by the same manufacturer contained 3% of complex aqueous mixture and 97% tap water. The complex aqueous mixture has been known to comprise various oils (animal, vegetable, mineral and synthetic), surfactants and sequestrant, etc. and the exact composition is proprietary and not known. After about 6 months of usage, the copper content of the drawing oil became excessive, leading to high conductivity. Some of the oils and other organic components in the oil emulsion might be decomposed during that period. In addition, there could be significant microbial growth of anaerobic nature due to very low dissolved oxygen (DO) concentration in the oil emulsion. High copper content, oil degradation and microbial growth in the drawing oil emulsion would adversely affect the quality of final copper wire products. Hence, the drawing oil needed to be discarded and replaced by a new batch. The properties of the original waste drawing oil obtained for the present experiments are listed in Table 1. It should be noted that the properties of waste drawing oil could change from batch to batch due to variations of operating conditions in the manufacturing process.

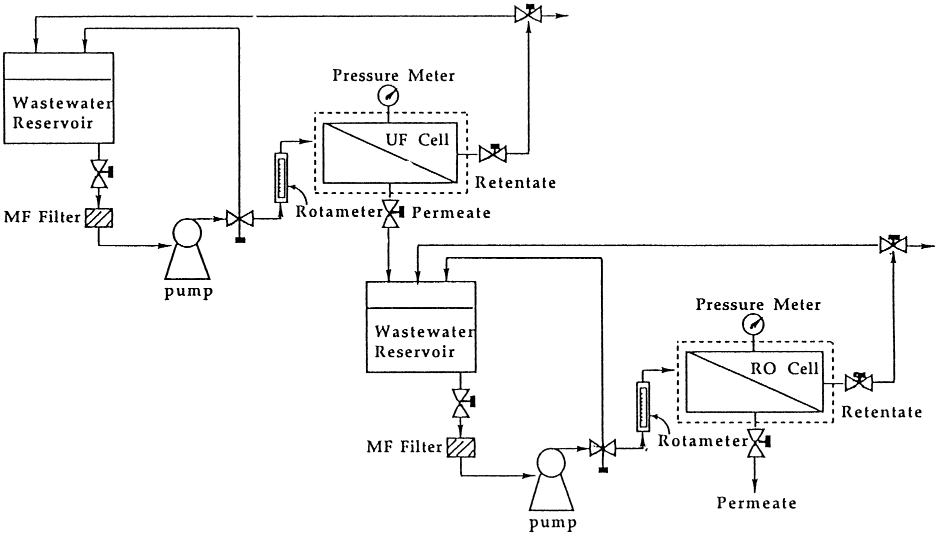

Fig. 1. Experimental schematic.

The waste drawing oil obtained from the cable and wire mill was put in the O/W emulsion reservoir. It went through the prefilter first to remove coarse suspended particles. Then the UF treatment was started with an appropriate set of operating variables. The volume of permeate was regularly registered. Periodically, small permeate samples were taken for measurements of the COD concentration, turbidity, conductivity and copper concentration. The COD concentration, turbidity (NTU) and bacterial count were measured by the standard methods [7]. The copper concentration was determined using a GBC 932 atomic absorption spectrophotometer (GBC Scientific Equipment, Victoria, Australia). The conductivity and pH were measured by a Suntex SC-12 conductivity meter (Suntex Industrial, Taiwan).

After the UF experiments were completed, the permeate entered the RO filtration process. The RO treatment was conducted to determine its efficiencies in improving further the water quality of the UF permeate. The parameters monitored from the permeate samples of the RO filtration were similar to those of the UF operations.

3. Results and discussion

3.1. Ultrafiltration process

Transmembrane pressure is a generally regarded as a very operating parameter of the UF system [8,9]. An increase in the transmembrane pressure tends to increase the UF filtration, but as demonstrated in Fig. 2, it is not always so. A maximum permeate flux

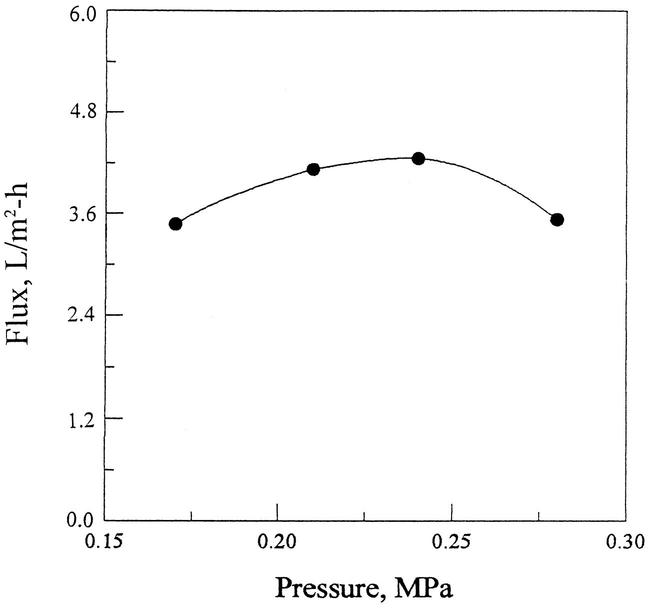

Fig. 2. Effect of UF transmembrane pressure on the accumulated permeate volume and permeate flux with 0.4 l/min feed rate.

was attained at 0.24 MPa as seen in Fig. 2 and beyond that, further increase in the transmembrane pressure reduced the permeate flux. A reasonable explanation for this is that beyond the optimum transmembrane pressure, the solute concentration near the membrane on the retentate side might cause sufficient pore clogging and/or membrane polarization, resulting in a reduced permeate passage and flux. According to Cheryan [8] and Persson and Nilsson [10], the total membrane resistance (R_t) is defined as the ratio of the transmembrane pressure (ΔP) to the permeate flux (J_v). Fig. 3 shows the total membrane resistance as a function of the transmembrane pressure. The total membrane resistance is seen to increase fairly rapidly as the transmembrane pressure becomes larger than 0.21 MPa. At 0.24 MPa, the total membrane resistance is about 13.9% higher than that at 0.21 MPa while at 0.28 MPa, the percentage increase grows to 58.3%. The rapid increase in the total membrane resistance beyond 0.24 MPa is apparently due to reduced permeate flux at high transmembrane pressure as shown in Fig. 2. Hence, considering the decrease in permeate flux and the increase in total membrane resistance, the transmembrane pressure at 0.24 MPa is deemed as optimum and recommended for efficient UF treatment of the present O/W emulsion.

The permeate COD concentrations pertaining to Fig. 2 are demonstrated in Fig. 4a. It is apparent that there is a significant drop in the permeate COD concentration by about 500 mg/l as the transmembrane pressure is increased from 0.17 MPa to 0.21 MPa. However, the decrease in the permeate COD concentration becomes less significant as the transmembrane pressure is further increased beyond 0.21 MPa. It is noted that the initial COD concentration of the waste drawing oil emulsion used here was 61,150

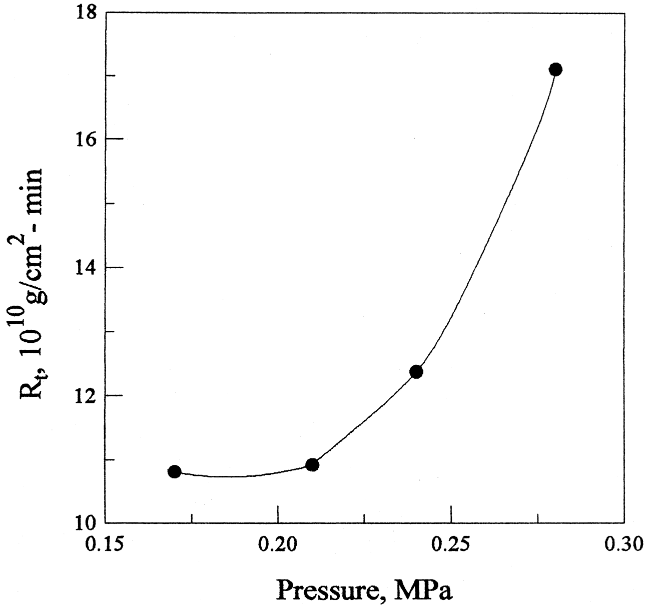

Fig. 3. Effect of UF transmembrane pressure on the total membrane resistance with 0.4 l/min feed rate.

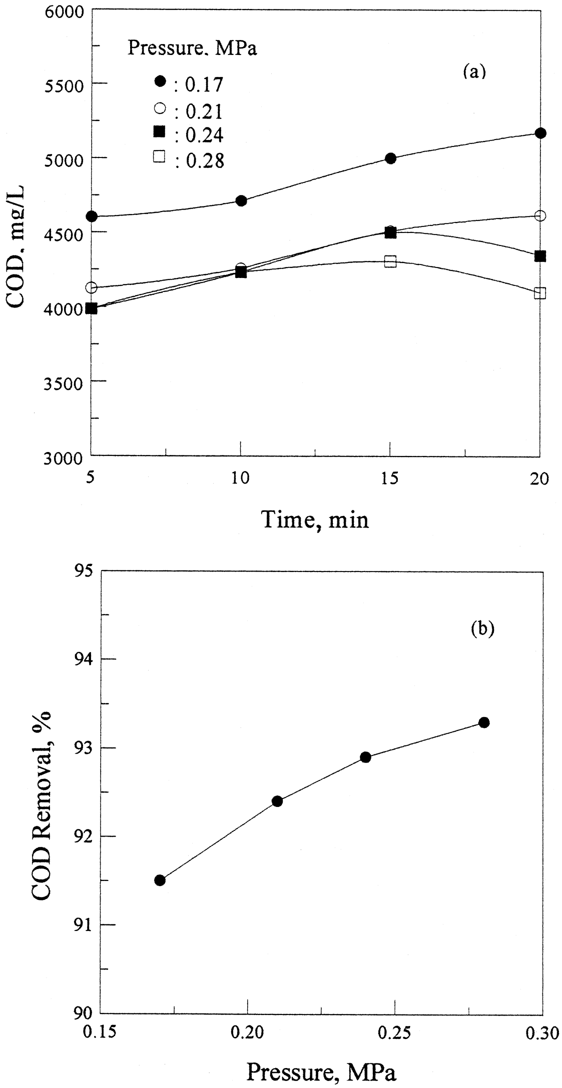

Fig. 4. Effect of UF transmembrane pressure on the permeate COD concentration and its removal with 0.4 l/min feed rate.

mg/l. With this high initial COD concentration, the COD removal by UF operation at 0.24 MPa transmembrane pressure was approximately 93%, as seen in Fig. 4b. Even operated at a lower transmembrane pressure of 0.17 MPa, a very good COD removal was still retained (at 91.5%), demonstrating the high efficiency of UF treatment in removing COD.

The transmembrane pressure not only affects the permeate flux and COD concentration, as demonstrated above, it also influences the copper removal. Fig. 5 illustrates such

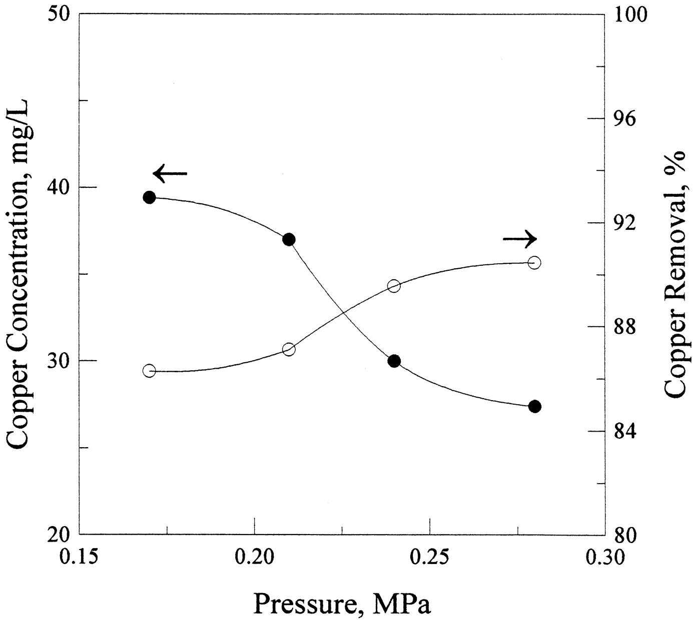

Fig. 5. Effect of UF transmembrane pressure on the permeate copper concentration and its removal with 0.4 l/min feed rate.

an effect. It is of interest to note that there is relatively little change in both the permeate copper concentration and its removal below 0.21 MPa and above 0.24 MPa, but there appears to be a significant transition between 0.21 MPa and 0.24 MPa. The reason for such a beneficial transition is not exactly known. It may be due to the pore blockage and/or polarization caused by the pollutants at a higher transmembrane pressure as noted earlier. But it should be noted that in terms of copper removal, the effect of transmembrane pressure is not really that large. As the transmembrane pressure increases from 0.17 to 0.28 MPa, the copper removal increases from 86.2 to 92.3%. Considering that 39.7 mg/l permeate copper concentration is sufficiently low, the small improvement in the copper removal due to a 64.6% increase in the transmembrane pressure might be difficult to justify economically.

3.2. Reverse osmosis process

The RO process is usually operated at a much higher transmembrane pressure because of smaller pore size. The effect of transmembrane pressure on the permeate flux is displayed in Fig. 6. The permeate volume was observed in the test runs to increase monotonously with the transmembrane pressure and time. The permeate flux obtained from the volume–time relation is demonstrated in Fig. 6 which shows a higher permeate flux for an increasing transmembrane pressure. The results obtained from the test runs revealed that the permeate volume and flux will taper off at a sufficiently high

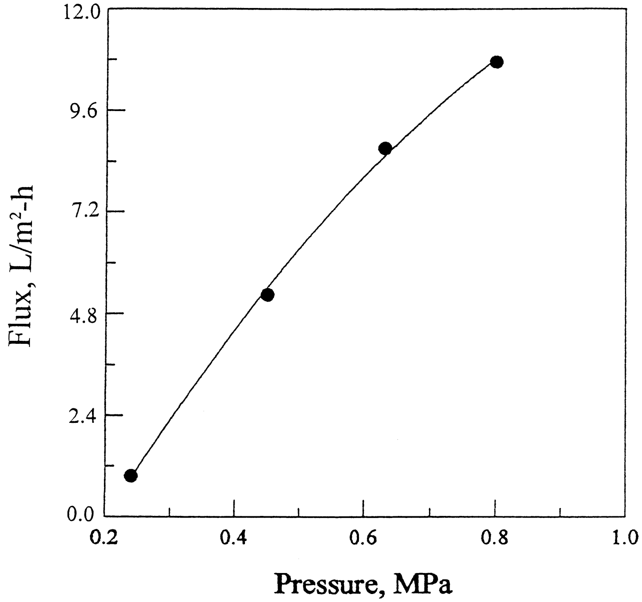

Fig. 6. Effect of RO transmembrane pressure on the accumulated permeate volume and permeate flux with 0.4 l/min feed rate.

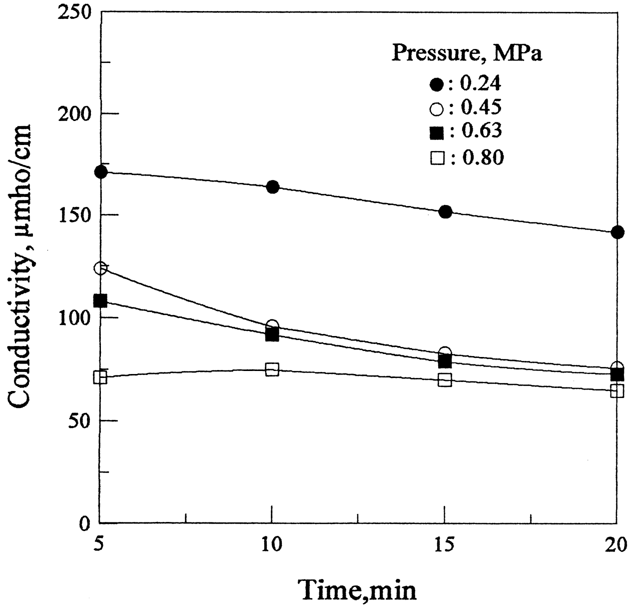

Fig. 7. Effect of RO transmembrane pressure on the permeate conductivity with 0.4 l/min feed rate.

transmembrane pressure. The diminishing benefit of higher transmembrane pressure would be significantly negated by an increased operating cost.

The conductivity of the waste drawing oil emulsion was rather high due to the presence of various types of ions. Although the UF treatment was demonstrated above to be capable of removing significant amounts of COD and copper from the waste drawing

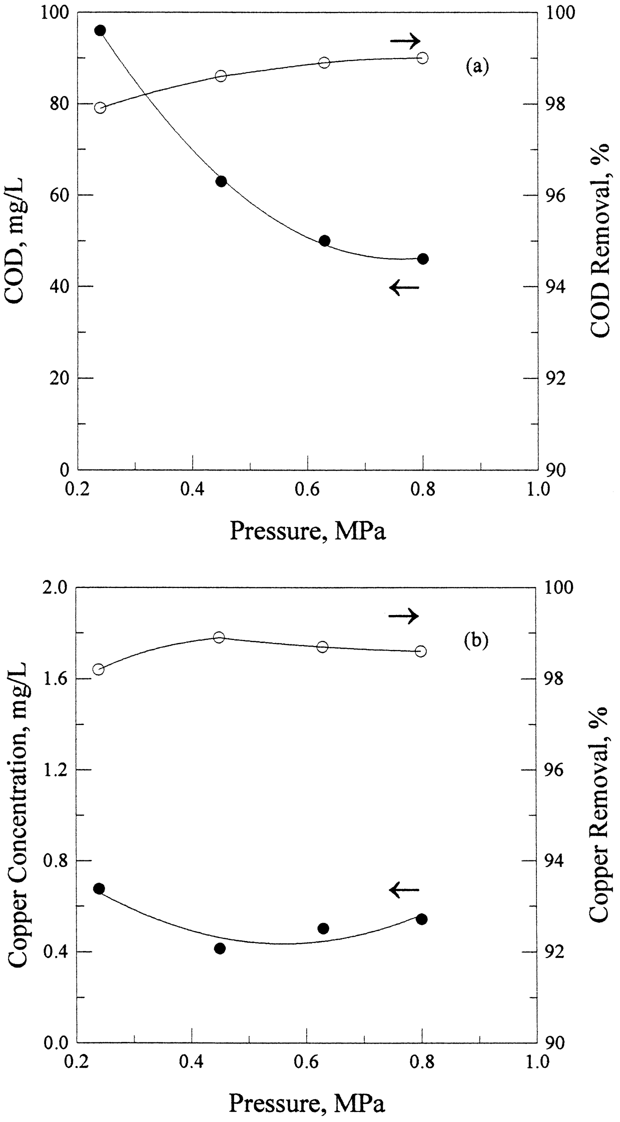

Fig. 8. Effect of RO transmembrane pressure on the permeate COD and copper concentrations and their removal with 0.4 l/min feed rate.

oil emulsion, it is relatively ineffective in removing other inorganic ions [8,9]. The experimental data for various test runs performed in this study consistently showed that less than 20% reduction of conductivity was realized and the conductivity of the permeate remained above 1800 μmho/cm. However, as seen in Fig. 7, the RO treatment is able to lower the conductivity from that level to below 200 μmho/cm which is about the conductivity of tap water employed for preparing the fresh drawing oil emulsion. It is also observed in Fig. 7 that the permeate conductivity after RO operation at a transmembrane pressure larger than 0.45 MPa tends to cluster together around 75 μmho/cm. Further increase in the transmembrane pressure does not improve the permeate conductivity.

The effect of transmembrane pressure on the COD and copper concentrations and their removal are shown in Fig. 8a,b. Apparently in Fig. 8a, the COD concentration was lowered from 97 mg/l to 46 mg/l as the transmembrane pressure was increased from 0.24 MPa to 0.8 MPa. But in terms of COD removal, the improvement appears to be small primarily due to high permeate COD concentration (around 4500 mg/l) after the UF treatment. The effect of transmembrane pressure on the copper concentration is relatively small, as shown in Fig. 8b, noting that the copper concentration after the RO operation was consistently excellent.

To put the results of the present study in better perspective, the quality of the original waste drawing oil emulsion and those after the UF and RO treatments are listed in Table 2. The aqueous solution had relatively little change in pH. However, there are drastic improvements in other permeate quality after the UF and RO treatments. The most apparent visual change of the drawing oil emulsion is its transparency. The original O/W emulsion was milky and opaque. After the UF treatment, the permeate became completely transparent with faint yellowish color which turned into crystal clear after the RO treatment. This is reflected by the NTU change in each treatment stage. The COD and copper removal is seen to be superior, exceeding 99%. The bacterial count removal is excellent also. According to the technical personnel of the cable and wire company that supplied the original waste oil emulsion for the present test, at the bacterial count level after the RO treatment in Table 2, there won't be any concern about bacterial growth for quite a while, implying a very safe margin being achieved.

Table 2
Water quality of original waste oil emulsion and permeates after UF and RO treatments

Quality parameter	Original waste oil emulsion	After UF treatment	After RO treatment
pH	7.65	7.92	7.36
COD, mg/l	61,150	4347	46
COD removal, %	–	92.9	99.9
Conductivity	2219	1907	65
Copper concentration	287	30.1	0.5
Copper removal, %	–	89.5	99.8
NTU	19,600	2.5	0.4
Bacterial count	10^5–10^6	10^3	10^2

1. Conductivity in mho/cm and copper concentration in mg/l.
2. UF and RO treatments operated at 0.24 MPa and 0.8 MPa, respectively.

4. Conclusions

The present study conducted treatment tests of waste drawing oil emulsion derived from a large copper wire and cable company by combined ultrafiltration and reverse osmosis. The fresh O/W emulsion comprises 97% water and 3% of highly complex aqueous mixture containing various kinds of oils, sequestrants and surfactants. The waste drawing oil emulsion obtained for the present tests had rather high COD and copper concentrations and strong milky color. The experimental tests were performed in a semi-batch fashion. It employed spiral wound polyether sulfone (PES) UF and polyamide (PA) RO cartridges.

The UF test results indicate that an optimum transmembrane pressure of 0.24 MPa exists for the present UF treatment system. Under this transmembrane pressure, the accumulated permeate volume, permeate flux and total membrane resistance are in very good combination. The test results also show that the UF treatment is very effective in reducing the COD and copper concentrations and in improving the turbidity (NTU), but it is relatively ineffective in reducing the conductivity of the UF permeate. In conjunction with the RO treatment, the final permeate quality is found to be excellent with over 99% improvements in the COD, copper, conductivity and turbidity. The bacterial count after the RO treatment has also been found to be below 10^2 which is very good in freeing the oil emulsion from concern of anaerobic growth.

Acknowledgements

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