Journal of Hazardous Materials 186 (2011) 1667–1671

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Recovery of process water from spent emulsions generated in copper cable factory

K. Karakulski*, A.W. Morawski

Institute of Inorganic Chemical Technology and Environment Engineering, West Pomeranian University of Technology in Szczecin, ul. Pułaskiego 10, 70-322 Szczecin, Poland

ARTICLE INFO

Article history:
Received 12 February 2010
Received in revised form
24 September 2010
Accepted 10 December 2010
Available online 17 December 2010

Keywords:
Ultrafiltration
Nanofiltration
Pretreatment
Emulsion
Copper ions

ABSTRACT

Treatment of waste emulsions generated in the cable factory from copper wire drawing was investigated using the integrated membrane processes: ultrafiltration (UF) and nanofiltration (NF). The application of UF tubular membranes (MWCO 100 kDa) resulted in 98% retention of oil and lubricants, whereas the degree of passage of copper ions (the major component of effluents from cable factory) was 99%. The average permeate flux amounted to 45 l/m^2 h for the transmembrane pressure of 3.5 bar during the UF pretreatment of waste emulsions. The Silt Density Index (SDI) values of UF permeates were appropriate for the application of spiral wound membranes in the NF process. The complete removal of oil and lubricants was achieved in NF process and the content of TOC was reduced by more than 90%. The rejection of copper ions in the NF process was 90% and 98% for NF270 and NF90 membranes (FILMTEC), respectively. The quality of NF permeates allows a direct reuse of treated water for the preparation of fresh emulsion.

1. Introduction

Emulsions with special formulations are used in copper wire drawing operations in the cable factory to control friction between the workpiece and drawing die, to dissipate heat generated during the drawing procedure, and to improve the surface quality of the workpiece [1]. These fluids are generally oil-in-water (O/W) emulsions that contain additives such as surfactants, antimicrobial agents, and antifoaming agents to exhibit a low reactivity in the presence of copper and a consistence performance. After a period of time, these emulsions become less effective because of their thermal degradation and a gradual contamination by suspended solid, therefore, they must be replaced periodically. These emulsions must be treated before their disposal, due to the detrimental effects on aquatic life and their interference with conventional wastewater treatment processes. Because of their diverse composition, concentration of oil and the content of copper ions, it is difficult to find an effective method of their treatment [2,3]. Oil and grease can exist in such wastewaters in several forms: free, dispersed or emulsified. The differences are based primarily on the droplet size. In an oil–water mixture, free oil is characterized with droplet sizes greater than 150 μm in size, dispersed oil has the droplet sizes in the range from 20 μm to 150 μm, whereas emulsified oil has droplets typically less than 20 μm [4]. Waste emulsions are treated using a number of different techniques. Technologies such as dissolved air floatation, acid, salt or heat cracking, and gravity separation are commonly used for the treatment of waste emulsions [4,5]. The application of cross-flow membrane separation techniques such as microfiltration, ultrafiltration and nanofiltration enables to maintain an acceptable permeate flux due to tangential fluid flow in the module which induces the hydraulic turbulence necessary to scour the membrane surface of accumulated solute molecules [6]. Concerns on the occurrence of metal ions in the aquatic environment have been a subject of importance because of their toxicity and accumulation may pose various hazards for human health and environment. Therefore, the removal of metal ions from numerous industrial wastewaters has stimulated vigorous research activities in the development of advanced treatment technologies [2]. The membrane separation processes have been determined to be a feasible option for the removal of heavy metal from aqueous solution because of its relative ease of construction and control, and the feasible recovery of valuable metals. Nanofiltration is a relatively new membrane process which is considered to be intermediate between ultrafiltration and reverse osmosis. NF membranes are mainly utilized for softening surface water and brackish water. They are usually polyamide based thin film composite (TFC), which are relatively close to RO membranes in chemical structure. However, RO membranes are characterized by higher rejection to monovalent and divalent ions while NF mem-

* Corresponding author at: Institute of Inorganic Chemical Technology and Environment Engineering, Faculty of Chemical Engineering, West Pomeranian University of Technology in Szczecin, ul. Pułaskiego 10, 70-322 Szczecin, Poland.
Tel.: +48 91 449 4682; fax: +48 91 449 4686.
E-mail address: krzysztof.karakulski@zut.edu.pl (K. Karakulski).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.12.041

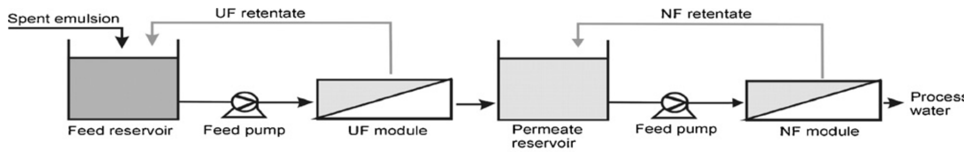

Fig. 1. Flow diagram UF/NF integrated membrane system for treatment of waste emulsions from cable factory.

branes are characterized by lower rejection to monovalent ions and higher rejection to divalent ions as well as higher flux than RO [7]. The NF process is carried out under lower operating pressures than reverse osmosis (RO), and with lower molecular weight cut-offs (MWCO) than ultrafiltration [8]. Therefore, this process would be ideal when integrated with either RO or UF membrane products as either a primary or secondary treatment for these types of applications. Fouling is a major problem in operation of membrane plants and can have several negative effects: reduced membrane flux, increased differential pressure, and decreased salt rejection necessitating periodical cleaning. Pretreatment of feed solution is usually needed to prevent a significant membrane fouling. Current research projects in membrane fouling are focussing on fouling control, pretreatment technologies and anti-fouling membranes and modules [9,10].

The application of UF process as a pretreatment step for industrial effluents replaces the conventional methods of pretreatment for NF, results in a longer membrane life, and the ability to operate the NF system at higher flux rates [11]. The objective of these studies was to investigate the possibility of purification of complex oily wastewater generated in the copper wire drawing factory utilizing the integrated membrane systems based on ultrafiltration and nanofiltration processes to recover process water.

2. Experimental procedure

The studies on the treatment of waste emulsions from cable factory and model emulsion were carried out with the application of pilot plants for UF and NF processes with the utilization of commercially available modules for UF process (tubular membranes) and two types of spiral elements for NF process.

2.1. Composition of waste emulsions

The industrial effluents for the treatment by UF/NF integrated membrane system were obtained from cable factory located in the northern part of Poland. These effluents comprise a complex wastewater containing suspended solids, oil and lubricants and copper ions as the major components with various distributions of oil droplets size (Table 1).

Table 1
Characteristics of original waste emulsions from cable factory.

Parameter	Waste emulsions	
	DRAWLUB	WIROL 5000
Content of oil and lubricants (mg/dm^3)	257	147
Concentration of Cu^{2+} ions (mg/dm^3)	988	1587
TOC (mg/dm^3)	1832	1173
TDS (mg/dm^3)	2123	2874
Electrical conductivity ($\mu S/cm$)	3076	3987
NTU	5145	8108
Suspended solids (mg/dm^3)	64	57
Average oil droplets size (μm)	0.4	0.1
pH	7.35	7.65

2.2. UF and NF pilot plants

The UF process was carried out with tubular module B1 (PCI Membrane Systems) equipped with PVDF membrane (FP100), whereas the NF process was carried out with the spiral modules equipped with NF-270-2540 and NF-90-2540 membrane elements (FILMTEC). The performance of UF membranes during the pretreatment was studied in terms of flux, removal efficiency in relation to membrane characteristics, and the SDI values determined for the UF permeates. Two modes of emulsions treatment with ultrafiltration process were performed. Tests for the determination of flux as a function of the transmembrane pressure and the operation time were carried out at constant feed concentration (the streams of both retentate and permeate were returned to the feed tank). The other tests were performed with permeate further purified by nanofiltration. After accomplishing the UF process with spent emulsions originated from copper cable factory, the tubular membranes were subjected to cleaning in order to determine the degree of flux recovery. The cleaning procedure of UF membranes consisted in a first rinsing step with tap water (30 min), then a cleaning step with a 0.5 wt.% solution of cleaning agent (Impurex) prepared in deionized water (2 h) and finally, the UF membranes were rinsed with tap water (40 min). Every cleaning step was performed at a temperature of 45 °C, transmembrane pressure of 1 bar and a crossflow velocity of 3 m/s. After cleaning the flux of UF membranes was restored in 95%. Because the flux was stable in the NF experiments (operation time for NF modules was 16 h), the spiral membrane elements were only rinsed with deionized water after accomplishing the NF process carried out with the UF permeates. A combined UF/NF system for the treatment of waste emulsions from copper cable factory is shown in Fig. 1.

2.3. Analytical procedure

The waste emulsions from cable factory and model emulsion ($400\,mg/dm^3$ of oil with the content of copper ions of $1000\,mg/dm^3$) and the resulting UF and NF permeates were analysed for their ionic content (emission mass spectroscopy AES-ICP Ultrace 238JY, Jobin Yvon; TDS and conductivity (Ultrameter 6P MYRON L), oil and lubricant (OCMA 310 Horiba analyser), total organic carbon (TOC Analyzer multi N/C Analytic Jena) and turbidity (Hach Model 2100AN IS Laboratory Turbidimeter). The content of suspended solids was determined according to the procedure outlined in standard methods. The Silt Density Index (SDI) was determined according to an ASTM method out using the equipment purchased from Millipore. The distribution of size of the oil droplets in waste emulsions from the cable factory was determined using a Malvern Instrument Mastersizer 2000MU. The reduction of different pollutants was calculated by comparison of the pollutant concentration in the permeate and in the feed. The rejection (R_i) for species *i* was calculated as:

$$R_i = \left[1 - \frac{C_{ip}}{C_{if}}\right] \tag{1}$$

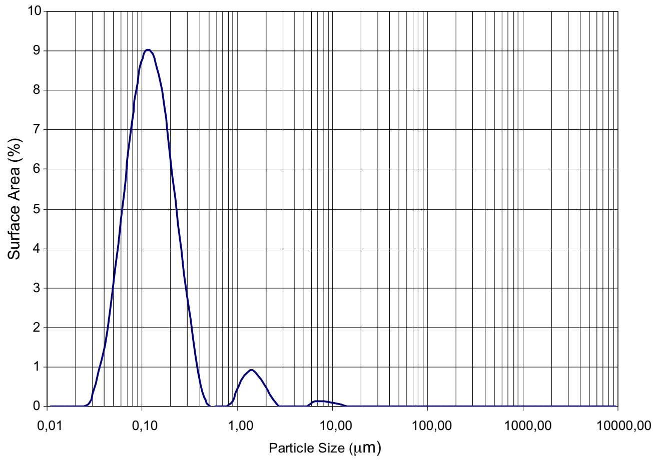

Fig. 2. The size distribution of oil droplets in waste emulsion WIROL 5000.

where C_{ip} is the permeate concentration and C_{if} is the concentration of species i in the feed.

3. Results and discussion

3.1. Determination of oil droplets size for waste emulsions from cable factory

The distribution of size of the oil droplets in spent emulsions from the cable factory was determined using a Malvern Instrument Mastersizer 2000MU. The results of the size distribution of oil droplets in the form presented by the software of Malvern Mastersizer 2000MU are shown in Figs. 2 and 3. The spent emulsions from cable factory (WIROL 5000 and DRAWLUB) exhibit a different character of oil droplet size distribution, namely, the emulsion WIROL 5000 has a bimodal distribution of oil droplets: the main fraction of droplets having the average size of 0.1 μm and a small fraction of oil droplets having the average size of 1 μm (Fig. 2), whereas the emulsion DRAWLUB exhibits a monomodal distribution of oil droplets size (Fig. 3), but the average size of oil droplets is four times larger than that for emulsion WIROL 5000.

3.2. Pretreatment of model and waste emulsions by UF process

A membrane-based pretreatment of the feed for NF process should allow to maintain a high permeate flux, an appropriate retention characteristics with regard to the components responsible for the membrane fouling and SDI values appropriate for spiral wound modules. Therefore, all UF experiments were performed using the tubular membranes taking into account the composition of waste emulsions from cable factory (Table 1). One of the major benefits of tubular membrane design is its ability to cope with high levels of suspended solids, without the need for any prefiltration. The UF pretreatment with the application of the PVDF membranes with MWCO of 100 kDa effectively reduced the content of colloids, oil and lubricants in the treated emulsions and allowed to completely remove suspended solids, hence, the obtained UF permeates had the values of SDI below 5 (Fig. 4) which is recommended by the manufacturers of the spiral wound membrane elements.

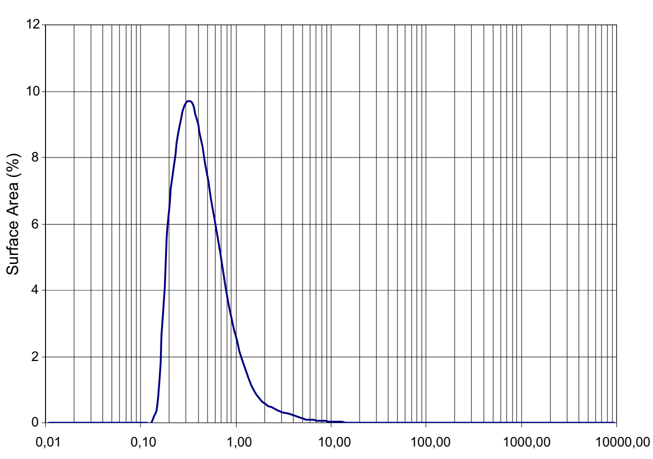

Fig. 3. The size distribution of oil droplets in waste emulsion DRAWLUB.

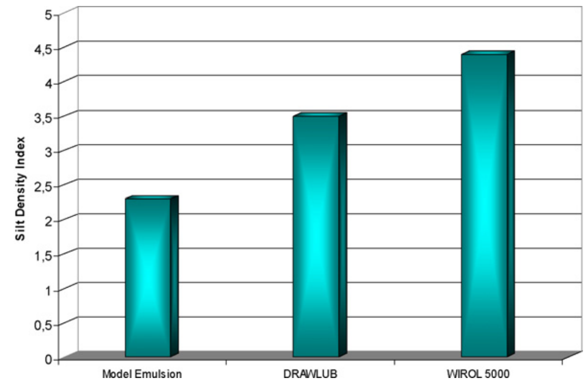

Fig. 4. SDI values of UF permeates obtained from model emulsion and waste emulsions from cable factory.

3.3. Effect of operation parameters on performance of UF membrane

The effect of transmembrane pressure on the permeate flux during the UF process carried out with tap water, model emulsion and waste emulsions DRAWLUB and WIROL 5000 used as the feed was presented in Fig. 5. The permeate flux increases linearly with an increase of the transmembrane pressure up to 3 bar, subsequently, a deviation from a linear dependence was observed for studied emulsions, which indicated that the permeate flux is affected by the concentration polarization. The highest flux at the transmembrane pressure of 3 bar was obtained for model emulsion (60 m^3/m^2 h) whereas in the case of waste emulsions from cable factory the obtained flux amounted to 52 and 44 dm^3/m^2 h) for DRAWLUB and WIROL 5000, respectively. The differences in the permeate flux were mainly associated with the differences in the composition

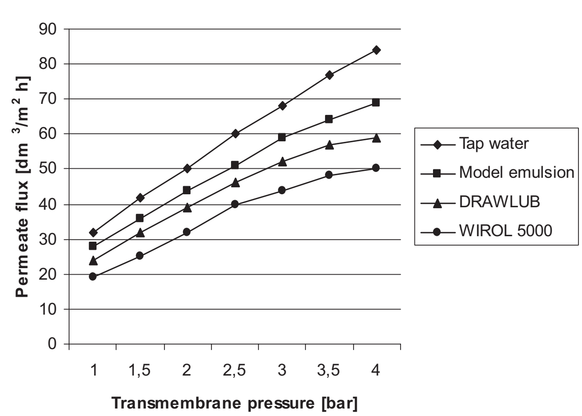

Fig. 5. The effect of transmembrane pressure on the permeate flux in UF process of model emulsion and waste emulsions DRAWLUB and WIROL 5000 (v = 2 m/s, T = 30 °C).

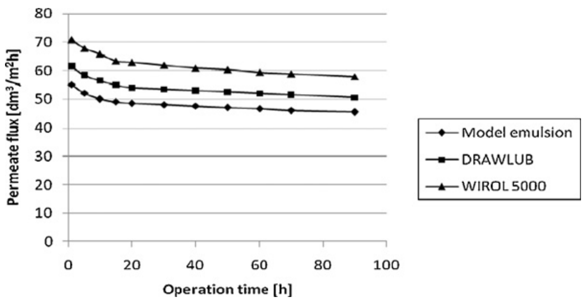

Fig. 6. The changes of permeate flux as a function of operation time for model emulsion and waste emulsions DRAWLUB and WIROL 5000 (P = 3 bar, v = 2.5 m/s, T = 30 °C).

of waste emulsions DRAWLUB and WIROL 5000 (different oil contents – Table 1 and oil droplets size distribution – Figs. 2 and 3). Moreover, the permeate fluxes obtained during the pretreatment of waste emulsions from cable factory were significantly lower than that for the model emulsion although the model emulsion had a higher content of oil and lubricants. The application of UF membranes with MWCO of 100 kDa results in the complete rejection of suspended solids and the retention of oil and lubricants was at a level of 99%. The UF membranes employed exhibit a 99% passage of copper ions, which is the major component of spent emulsion.

The performance of UF membranes was evaluated by the changes of the permeate flux during a continuous operation of UF process for 90 h at the transmembrane pressure of 3 bar and a constant concentration of the feed (the permeate was recycled to the feed tank) using the model emulsion and waste emulsions originated from the cable factory. It was observed that the flux demonstrated an exponential decrease with time over a period of 20 h, than the flux was practically stable during the course of the experiment lasting 90 h (Fig. 6). An initial decline in the permeate flux was associated with the formation of a layer of the rejected matter on the membrane surface which acts as a secondary filtration element. This layer undergoes the compaction with increasing operating time, so the flux drop was caused by the increased resistance offered by the compressed secondary layer.

The changes of the permeate flux as a function of volume concentration ratio (VCR) were determined at the transmembrane pressure of 3.5 bar and a constant temperature of 35 °C using the model emulsion and waste emulsions originated from the cable factory. VCR was calculated as the ratio of the initial volume of feed solution to the volume of the retentate. The results presented in Fig. 7 indicated that the permeate flux was gradually decreasing along with an increase in the value of VCR which is a typical relationship for the course of ultrafiltration process during the concentration of treated wastewater. The degree of water removal from concentrated emulsions was 90% for the value of VCR = 10 and the content of oil and lubricants in the feed was enhanced 10 times, whereas the content of oil and lubricants in the UF permeates was maintained at the same level (below 10 mg/dm^3). The permeate flux decreased by 30% for VCR = 10, which indicates that the UF process of emulsions concentration can be run to higher values of VCR determined by acceptable flux decline which is in industrial practice assumed to be at a level of 50%.

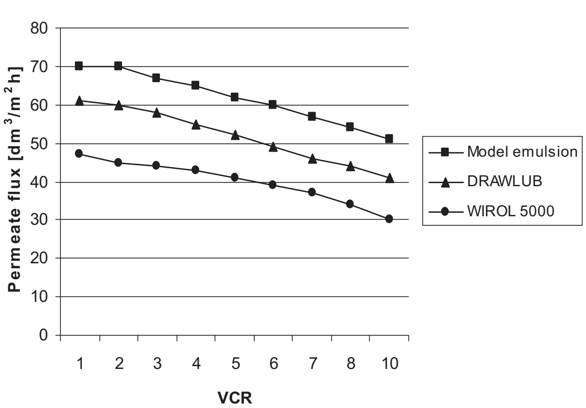

Fig. 7. The changes of permeate flux during the concentration of model emulsion and waste emulsions DRAWLUB and WIROL 5000 (P = 3.5 bar, v = 2 m/s, T = 35 °C).

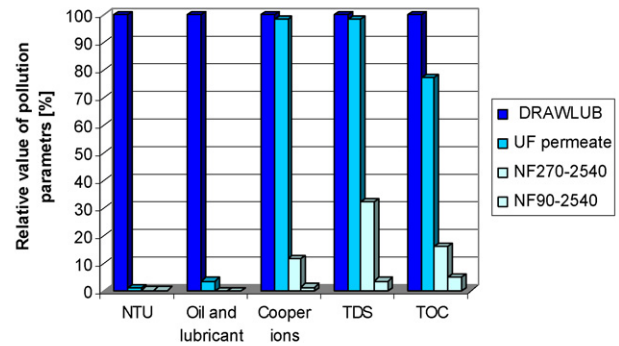

Fig. 8. Reduction of pollution parameters in the permeates UF and NF after treatments of waste emulsion DRAWLUB by UF/NF integrated membrane systems (spiral modules NF270 and NF90, transmembrane pressure 15 bar, T = 25 °C).

3.4. *Treatment of waste emulsions from cable factory by UF/NF integrated membrane system.*

The application of UF process as pretreatment of the feed for the NF process allowed to achieve the values of SDI appropriate for the spiral modules (Fig. 4). The spiral wound modules were equipped with NF-270-2540 and NF-90-2540 membrane elements (FILMTEC) in order to evaluate their performance in the preparation of process water from obtained UF permeates. The primary objective of NF process was to achieve the complete retention of oil and lubricants and to reduce the content of copper ions and total organic carbon (TOC) to a level corresponding to the specification of process water used for the preparation of fresh emulsions DRAWLUB and WIROL 5000. The performance of the NF membranes using the effluent pretreated by UF was shown in Figs. 8 and 9. The increase of transmembrane pressure in the NF process results in higher flux, but the retention of solute (copper ions) was at the same level for the pressure range used in NF process. The rejection of copper ions obtained with NF270 membrane was at a level of 90%, whereas the application of NF90 membrane resulted in 99% rejection of copper ions. The latter membrane also exhibited a very high degree of removal of TOC (99%) in a comparison with the NF270 membrane element which had the rejection of TOC at a level of 90%.

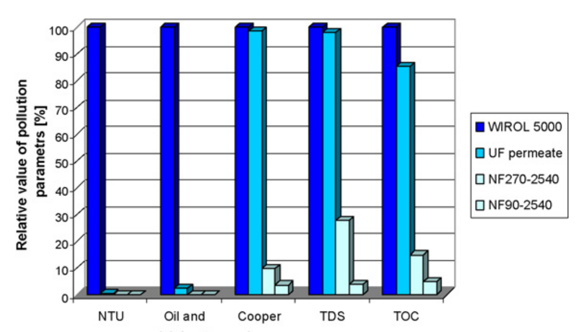

Fig. 9. Reduction of pollution parameters in the permeates UF and NF after treatment of waste emulsion WIROL 5000 by UF/NF integrated membrane systems (spiral modules NF270 and NF90, transmembrane pressure 15 bar, T = 25 °C).

Table 2
Typical parameters of NF permeates (process water) after treatment of waste emulsion WIROL 5000 by UF/NF integrated membrane systems.

Parameter of NF permeate	FILMTEC nanofiltration elements for commercial systems	
	NF270-2540	NF90-2540
Concentration of Cu^{2+} (mg/dm^3)	147	27
TOC (mg/dm^3)	73	14
TDS (mg/dm^3)	671	137
Electrical conductivity (μS/cm)	987	223
Turbidity (NTU)	0.63	0.54

The treatment of UF permeates obtained from waste emulsion WIROL 5000 with NF90 membrane element resulted in process water with the parameters shown in Table 2. The quality of the permeate obtained by the application of UF/NF integrated membrane system for industrial effluent from cable factory allows the direct reuse of treated wastewater for fresh emulsion top up.

4. Conclusions

The treated waste emulsions from cable factory are characterized by a very small size of oil droplets (0.1 μm, and 0.4 μm for WIROOL 5000 and DRAWLUB, respectively) being approximately one order of magnitude smaller than typical oil-in-water emulsions. The application of UF membranes made from PVDF with MWCO of 100 kDa results in the rejection of oil and lubricant at a level of 99% and the complete reduction of suspended solids. The UF membranes demonstrate good flux stability during the pretreatment of spent copper wire drawing emulsion. These membranes allow to produce the permeate with the SDI value (below 5) recommended by manufacturers of spiral wound modules. An outstanding advantage of the proposed combination of the membrane processes is the complete rejection of suspended solids, oil and lubricants. The content of organic compounds determined as TOC in the NF permeate was below 100 mg/dm^3, and the rejection of copper ions obtained with NF90 membrane was at a level of 99%, whereas for the NF270 membrane the rejection of copper ions was at a level of 90%. Purification of UF permeate in the NF process with the application of NF90 membrane elements results in the recovery of process water which can be directly reused for fresh emulsion top up.

Acknowledgement

Financial support by the Polish State Committee for Scientific Research by means of project 1 T09B 115 30 is gratefully acknowledged.

References

[1] K. Karakulski, A.W. Morawski, Purification of copper wire drawing emulsion by application of UF and RO, Desalination 131 (2000) 87–95.
[2] M. Šćiban, M. Klaśnja, B. Škrbić, Adsorption of copper ions from water by modified agricultural by-products, Desalination 229 (2008) 170–180.
[3] T. Mohammadi, A. Esmaeelifar, Wastewater treatment using ultrafiltration at a vegetable oil factory, Desalination 166 (2004) 329–337.
[4] M. Cheryan, N. Rajagopalan, Membrane processing of oily streams. Wastewater treatment and waste reduction, J. Membr. Sci. 151 (1998) 13–28.
[5] A. Hong, A.G. Fane, R. Burford, Factors affecting membrane coalescence of stable oil-in-water emulsions, J. Membr. Sci. 222 (2003) 19–39.
[6] J. Lindau, A.S. Jonsson, Cleaning of ultrafiltration membranes after treatment of oily waste water, J. Membr. Sci. 87 (1994) 71–78.
[7] Y. Xu, R.E. Leburn, Investigation of the solute separation by charged nanofiltration membrane: effect of pH, ionic strength and solute type, J. Membr. Sci. 158 (1999) 93–104.
[8] K. Mehiguene, S. Taha, N. Gondrexon, J. Cabon, G. Dorange, Copper transfer modeling through a nanofiltration membrane in the case of ternary aqueous solution, Desalination 127 (2000) 135–143.
[9] K. Boussu, A. Belpaire, A. Volodin, C. Van Haesendonck, P. Van der Meeren, C. Vandecasteele, B. Van der Bruggen, Influence of membrane and colloid characteristics on fouling of nanofiltration membranes, J. Membr. Sci. 289 (2007) 220–230.
[10] Q. Li, M. Elimelech, Organic fouling and chemical of nanofiltration membranes: measurements and mechanisms, Environ. Sci. Technol. 38 (2004) 4683–4693.
[11] L. Wang, X. Wang, K. Fukushi, Effects of operational conditions on ultrafiltration membrane fouling, Desalination 229 (2008) 181–191.