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Purification of copper wire drawing emulsion by application of UF and RO

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Abstract

The application of ultrafiltration (UF) and reverse osmosis (RO) membrane technology for the treatment of spent copper wire drawing emulsion to reduce fresh water consumption and environmental pollution has been investigated. The UF pretreatment process was tested on the effluents from copper wire drawing plant that enables further RO purification to process water standards. The tubular membranes used in UF pilot plant were made from polyvinylidene fluoride (PVDF), poly(vinyl chloride) (PVC) and polyacrylonitrile (PAN) with MWCO of 100 kDa, 70 kDa and 50 kDa, respectively. These membranes exhibit 100% rejection of suspended solids and produce the effluents with the content of oil and lubricant of less than 10 ppm. The UF pretreatment generates permeates with Silt Density Index (SDI) of <3 that renders them suitable for RO feed. However, the retention of copper ions and TOC by UF membranes was generally below 10%. The effluent from UF pilot plant was further purified by reverse osmosis using the spiral-wound membranes (BW3040 element, Filmtec). The retention of oil and lubricant in the RO process was 100% and the content of the copper ions in the permeate was generally less than 10 ppm (retention above 99.5%). A combined UF/RO pilot plant system used for the purification of spent copper wire drawing emulsion results in treated water with the conductivity of 40 μS/cm suitable for direct non-potable reuse for emulsion top up.

Keywords: Ultrafiltration; Reverse osmosis; UF pretreatment; Silt Density Index; Copper wire drawing emulsion

1. Introduction

The need for closed water systems, which eventually will lead to zero liquid effluent in copper wire drawing plant originates from the obligations to reduce the effluent volumes as well as minimise the use of fresh water for preparation of emulsion required in the manufacture of cables for the electrical industry. Recycling process waters or effluents can signifi-

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cantly reduce the fresh water consumption of a cable plant. The cable plant utilises emulsion prepared from non-soap emulsifiable lubricant and deionised water (for maximum performance) or soft water for drawing plain and tinned copper wire of intermediate, fine and superfine sizes on single or multi line machines. This emulsion exhibits a low reactivity in the presence of copper, consistent performance over long periods, possesses biostable characteristics in copper rich environments, high temperature stability, pH stability, and provides a low coefficient of friction between copper/ceramic and copper/steel components. The emulsion is semitranslucent initially and becomes blue/green opaque in use with copper. The cable plant produces over 100 m^3/y of such spent emulsion containing copper ions as the principal pollutant with the concentration exceeding 1600 mg/l which creates a considerable problem in the development of suitable treatment technologies to be considered. On the other hand, modern industry is required to operate under increasingly rigorous legislative restriction for the discharge of potentially harmful compounds. Nowadays only a few methods is available to remove heavy metals from wastewater streams produced by metal finishing industries. These include chemical precipitation, ion exchange, electrodialysis, liquid–liquid extraction, evaporation and adsorption. Heavy metals can be chemically transformed by reduction or oxidation in order to facilitate further treatment. The treated effluents may be discharged to a sewer system or be recycled. The obtained sludge can be specially treated by chemical fixation to diminish the mobility of metal ions before final disposal in designed landfills. However, possibilities for recovery of metals should first be evaluated. Hazardous wastewater is frequently disposed by incineration [1]. But to incinerate an aqueous solution with a solid content of less than 10% is not cost effective. In addition, the combustion gas produced contributes to the emission from the process.

A novel process so-called freeze concentration has been recently developed [2] in which wastewater can be concentrated to greatly increase the solids content, thereby significantly reducing the power required in incineration. The use of adsorbents made by attaching metal-ion-specific binding groups to solid polymers, e.g. chitosan, is an important approach to removing heavy metals ions from water and has received considerable attention over last 20 years [3]. The metal-ion-binding sites in the polymers may include ion exchange and chelating functionality or both [4].

The present method for removing copper from wastewater is to precipitate copper hydroxide by a process called "liming" [5]. With this process, however, residual copper is a concern.

The conventional wastewater treatment and disposal methods (physical, chemical and biological) do not remove inorganic solutes that contribute to the degradation of surface or groundwater, moreover, they may inhibit the reuse of water. Hence, the advanced wastewater treatment demineralisation processes will play an important role in future. The process that has attracted the most attention recently for the production of potable and process water and also becomes one of the methods for wastewater treatment is reverse osmosis [6]. RO is appropriate to demineralize salty water sources removing all the colloids, and most of organic and ionic species. However, reverse osmosis is susceptible to fouling. Fouling is a major problem in operation of RO plants and can have several negative effects: reduced membrane flux, increased differential pressure, and decreased salt rejection necessitating periodical cleaning. All these effects result in deterioration of plant performance and increased treatment cost. Pretreatment of feed solution is usually needed to prevent significant membrane fouling. Current research and project in membrane fouling are

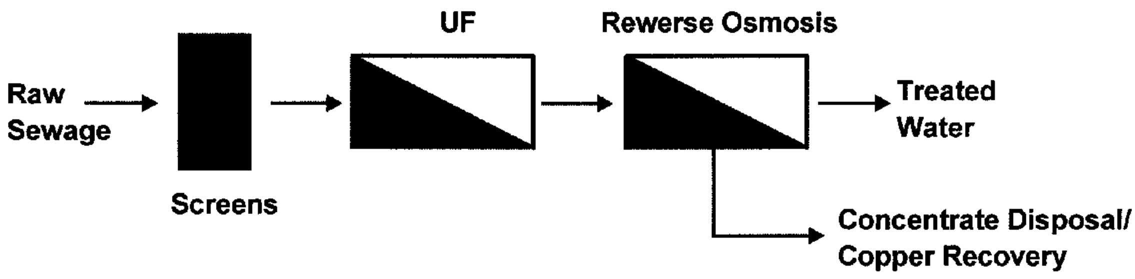

Fig. 1. Purification of spent emulsion using UF pretreatment for RO.

Table 1
Typical parameters of spent emulsion from copper wire drawing plant

Parameter	
Suspended solids, mg/l	54
TOC, mg/l	12,200
Oil and lubricant, mg/l	138
Copper, mg/l	1,610
COD, mg/l	959
Conductivity, µS/cm	1,880
pH	8.34

focussing on fouling control, pretreatment technologies and anti-fouling membranes and modules [7].

The objective of the work presented in this paper was to investigate the possibility of UF pretreatment for RO process with very complex wastewater from copper wire drawing plant. In our previous investigations with treatment of bilge water [8] we found tubular UF membranes suitable for oily wastewater purification since they showed a low fouling behaviour due to the hydrophilic properties, a narrow pore size distribution to form an almost absolute barrier for large particles and oil droplets, and a high surface porosity to maintain high flux rates at low transmembrane pressures. A preliminary estimation and comparison of the tubular membranes made from PVDF, PVC and PAN was performed on the basis of information concerning MWCO, water permeability, flux stability and the SDI values achieved during ultrafiltration of spent copper wire drawing emulsion. A continuous process for purification of spent emulsion was investigated using a combined UF/RO system shown in Fig. 1.

2. Materials and methods

2.1. Spent emulsion characteristics

Raw sewage from copper wire drawing emulsion was collected from Cable Plant located in the northern part of Poland. The only treatment was particle removal by screens. Spent emulsion is a very complex wastewater containing a mixture of many different inorganic ions and organic components. Some of the most important spent emulsion parameters are listed in Table 1.

2.2. Characterization of ultrafiltration membranes

Three different tubular membranes made from PVDF, PVC and PAN and were used for the determination of the water permeability and retention characteristics for dextran solutions. PVDF tubular membranes type FP 100 were purchased from PCI Membrane Systems. The membranes with an internal diameter of 12.5 mm and length of 1.2 m were mounted in B1 module (membrane area 0.9 m^2). Tubular membranes from PVC and PAN with an internal diameter of 25 mm and a length of 2 m (membrane area 0.15 m^2) were prepared in our laboratory by a wet phase inversion method [7]. All ultrafiltration experiments were performed in a laboratory pilot plant shown in Fig. 2. The feed flow rate can be adjusted using a by-pass valve and the throttle valves located downstream of the UF modules.

The water permeability measurements were performed with distilled water as the feed. The flux across the membrane was calculated from $F=V/A*t$ where F is the liquid flow across the membrane (l/m^2-h); A the membrane surface area in contact with the liquid (m^2); t the run time of the experiment (h); and V the volume of permeate collected during time t (l). The transmembrane pressures in the range from 0.5 to 4.0 bar were used. All measurements were performed at 25°C.

The retention characteristic of ultrafiltration membranes is usually presented in the form of a molecular weight cut-off (MWCO). The cut-off is identical with the molecular weight of a tested substance that has a predefined retention, e.g. 90%. During such characterization test it is necessary to choose proper operating conditions in order to minimize polarization phenomena. The best operating conditions are low pressure, high recirculation rate (high turbulence), and very low solute concentration. The choice of a solute with good chemical and conformational stability, without any physical or chemical

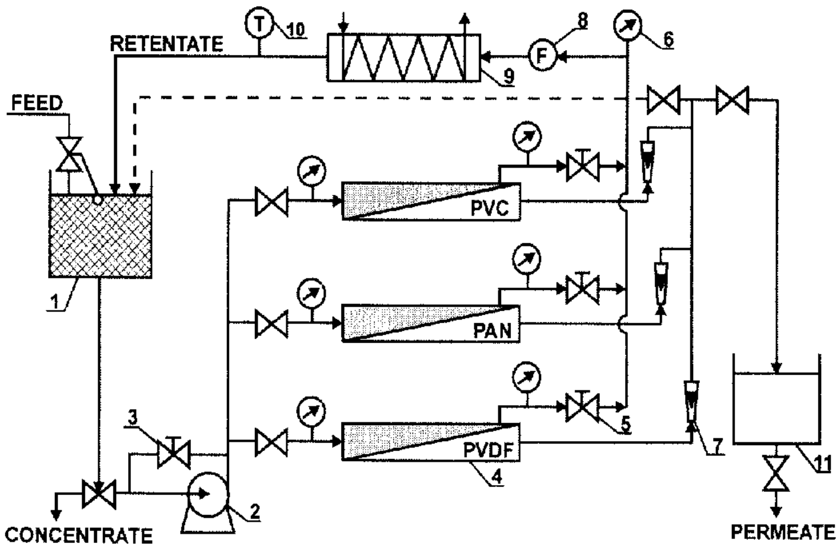

Fig. 2. Schematic diagram of UF pilot plant.

interaction with the membrane, is another important factor. However, the membrane manufactures use a wide range of test substances (dextrans, polyethylene glycols, proteins, etc.), as well as different test conditions. Detailed information regarding test substances, test conditions or definition of MWCO are not found in manufacturer specification sheets. These missing or differing specifications make a reliable membrane comparison on the basis of manufacturer information impossible.

The test solutions used in our laboratory for the determination of MWCO had the following compositions: distilled water 98.8 wt. %, dextran 1.0 wt. %, and sodium azide 0.2 wt. % which was added to the water to prevent bacterial growth. Industrial grade dextrans (Polfa, Poland) with molecular weights in the range of 2–100 kDa were employed without further purification. The measurements were performed at transmembrane pressure of 1 bar, the other conditions were the same as for the permeability tests.

The ultrafiltration of a testing solution with the lowest molecular weight dextran was run for 4 h in zero recovery (the retentate and the permeate were recirculated), then the feed and permeate samples were collected for analysis. After accomplishing this test, the UF installation was flushed with distilled water, and a subsequent solution of dextran with a higher molecular weight was tested in the same manner. The testing procedure was repeated for the consecutive dextran solutions.

The reduction of different components were calculated by comparing the concentration of the substance in the permeate and in the feed, as follows:

$$R = (1 - C_P/C_F) \times 100 \quad (1)$$

where R is the reduction (%), C_P is the concentration in the permeate, and C_F is the concentration in the feed.

2.3. Purification of spent emulsion in a combined UF/RO system

A combined UF/RO system for purification of spent copper wire drawing emulsion is illustrated in Fig. 1. The effluent from cable plant was pretreated by UF process using the pilot plant shown in Fig. 2. The performance of UF membranes during pretreatment was studied in terms of flux, removal efficiency in relation to membrane characteristics, and the SDI values achieved for permeate. Two modes of spent emulsion treatment with ultrafiltration were evaluated in the presented studies. Tests for the determination of flux stability during 50 h of spent emulsion treatment were carried out at the transmembrane pressure of 2 bar with constant feed concentration (the streams of both retentate and permeate were returned to the feed tank (Fig. 2, broken line). The other test was performed with permeate further purified by reverse osmosis. On the basis of dissolved solids concentration and conductivity of raw sewage (Table 1) the RO process was performed with spiral-wound element BW 3040 (purchased from Filmtec) for brackish water desalination. According to recommendation of the manufacturer the feed should posses the SDI value lower than 5 to prevent excessive fouling and the increase of differential pressure. RO process was run on the pilot unit (PCI Membrane Systems) designed for pilot scale work. The permeate flux from PVDF membrane (FP 100) during the UF pretreatment was at the same level as RO permeate flux (at 30 bar), hence, these two processes were run in a continuous mode. During these tests, the permeate flux for each type of membrane was measured using a rotameter, and the samples of permeate and feed were collected for the analysis

The pollution parameter reductions were calculated from Eq. (1).

2.4. Methods of analysis

The original raw sewage as well as the resulting permeates and retentates were analysed for their ionic content (pH, conductivity – Ultrameter 6P MYRON L, emission mass spectroscopy AES-ICP Ultrace 238JY, Jobin Yvon), total organic carbon (TOC Analyzer multi N/C, Analytic Jena), oil and lubricant (OCMA 310 Horiba analyser), chemical oxygen demand (COD) and suspended solids by the procedure outlined in standard methods [9]. The measurement of the SDI has been carried out with a filtration cell, which was connected to a pressure vessel such that the cell can be filled during filtration by keeping the pressure at 2 bar. Membrane filters used were 0.45 μm Millipore filters of type HAWPO4700. For each measurement the pressure vessel and the filtration cell were filled with the water to be investigated. Both were sealed, and the pressure was applied and continuously adjusted to maintain 2 bar required for the total filtration time. First 500 ml of filtrate was collected, and the time t_1 for this task was taken. The filtration was then continued for another 15 min (T), and after this another 500 ml of filtrate were collected and the time t_2 was taken. The SDI is defined as:

$$SDI = (1 - t_1/t_2)/T \times 100 \qquad (2)$$

3. Results and discussion

3.1. Separation and transport properties of PVDF, PVC and PAN membranes

The characterization of the ultrafiltration membranes made from PVDF, PVC and PAN was performed by the measurements of the retention of dextrans. The resulting retention curves for dextrans with different molecular weights are presented in Fig. 3. The slope of the curves for both PVC and PAN indicates that these membranes possess a diffusive cut-off corresponding to a wide pore size distribution. However, the commercial membrane FP 100 exhibits a rather narrow pore size distribution which is reflected by a low retention of dextran 10 kDa and a high retention of dextran 40 kDa. MWCO determined from retention curves amount 50, 70 and 100 kDa for PAN PVC and PVDF membranes, respectively. Moreover, the higher is MWCO the larger is the permeate flux of respective membrane.

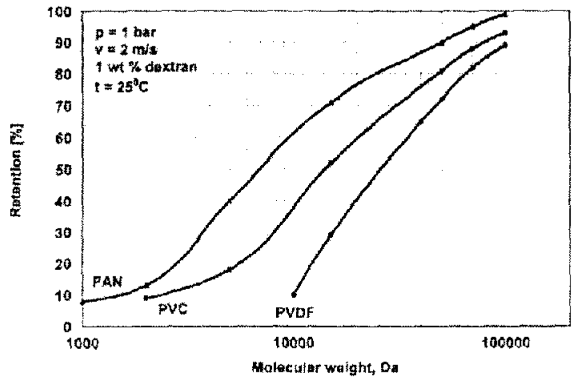

Fig. 3. Retention curves of UF membranes made from PVDF, PVC and PAN.

The obtained water permeability results for studied membranes as a function of transmembrane pressure are shown in Fig. 4. The linear relationship between water flux and the transmembrane pressures was obtained for PAN and PVDF membrane. PVC membrane exhibits a deviation from linearity, at higher pressures, namely the increase of pressure from 3 to 4 bar results in the increase of flux amounting half of that for the same gradient of pressure but from a lower region of pressures. This decline of water permeability for PVC membranes can be explained by the compression of larger pores that

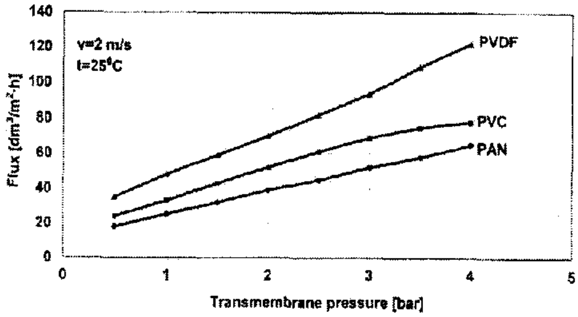

Fig. 4. Effect of transmembrane pressure on water permeability of PVDF, PVC and PAN membranes.

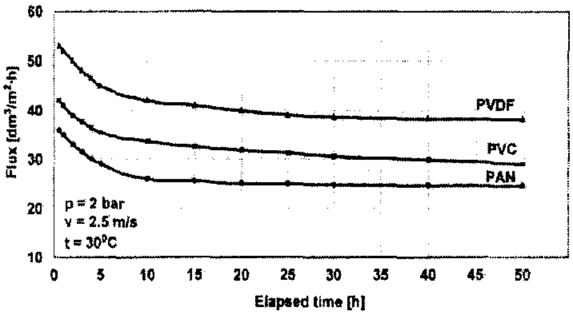

Fig. 5. Permeate flux stability during UF pretreatment of spent copper wire drawing emulsion (oil and lubricant content 133 ppm).

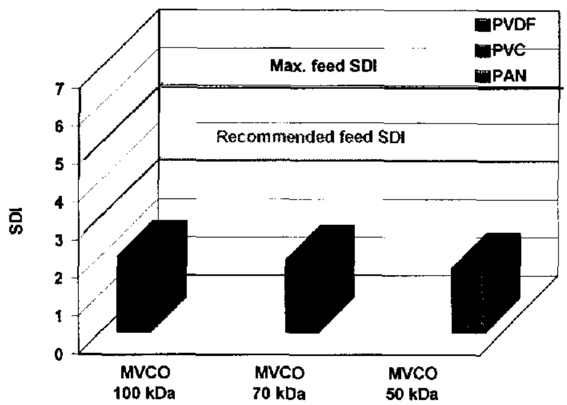

Fig. 6. Average Silt Density Index of UF permeates from PVDF, PAN ans PVC membranes.

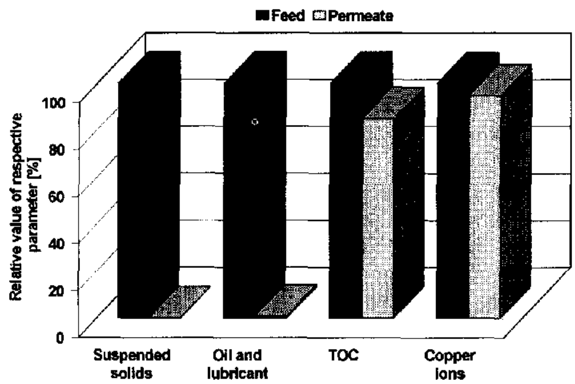

Fig. 7. Reduction of respective parameters achieved by PVDF membrane in UF pretreatment of spent copper wire drawing emulsion (temp. 25°C, p = 2 bar).

have the major contribution to membrane permeability at pressures exceeding 2 bar.

3.2. *Effectiveness of UF pretreatment for spent emulsion*

A membrane-based pretreatment for RO feed should allow to maintain a high permeate flux, an appropriate retention characteristics with regard to certain components in the raw sewage and a SDI value which is recommended by spiral-wound elements. The ultrafiltration process was carried out within the range of process parameters recommended for oil emulsions. All UF experiments were performed using tubular membranes. One of the major benefits of tubular membrane design is its ability to cope with high levels of dissolved solids, without the need for any prefiltration. Therefore, UF pretreatment should effectively reduce such parameters as

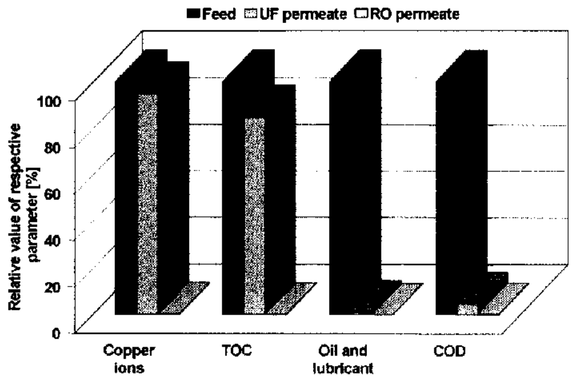

Fig. 8. Reduction of respective parameters achieved by treatment of spent copper wire drawing emulsion in UF/RO system.

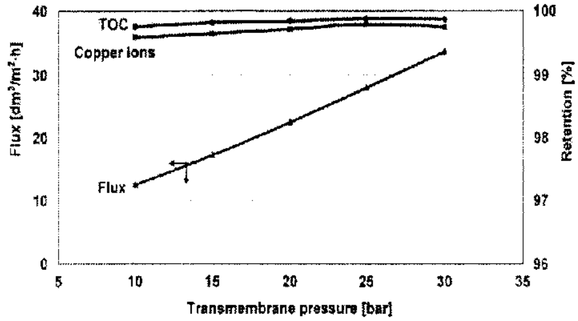

Fig. 9. Effect of transmembrane pressure on permeate flux and retention of TOC and copper ions in RO process (BW 3040 element – Filmtec, temp. 25°C).

suspended solids, oil and lubricant that the resultant permeate will reach the level of SDI required for spiral-wound elements. The performance of UF pretreatment obtained with spent copper wire drawing emulsion illustrated in Figs. 5–7 allows to conclude that UF process with properly selected membranes (FP 100) is very effective for the preparation of RO feed suitable to run the process with spiral-wound element without a serious membrane fouling. The retention of suspended solids and oil and lubricant is higher than 99%, however, the principal ionic component (copper) is rejected by UF membrane in lees than 10% over the entire pressure range used in UF process. The use of membranes with lower MWCO (50 and 70 kDa) does not result in a significantly lower value of SDI (Fig. 6) which is probably caused by a rather wide pore size distribution for these membranes.

The performance of BW 3040 element with the feed pretreated by UF is shown in Figs. 8 and 9. The increase of transmembrane pressure results in both higher flux and higher retention of rejected components, which is characteristic relationship of reverse osmosis without severe membrane fouling. This dependence confirms that the proposed treatment of very complex wastewater from cable plant is effective and allows obtaining the treated water for direct reuse for emulsion top up.

4. Conclusion

The application of UF membranes with MWCO in the range of 70–100 kDa results in complete reduction of suspended solids and very high retention of oil and lubricant. These membranes allow obtaining the SDI below a value recommended by manufacturers of spiral-wound elements. The UF membranes demonstrate good flux stability during the pretreatment of spent copper wire drawing emulsion The obtained UF permeates are suitable for further purification in RO process with spiral-wound elements. An outstanding advantage of the proposed combination of membrane processes is the complete elimination of suspended solids in the UF permeate as well as 99% retention of oil and lubricant. Purification of UF permeate in RO process results in treated water which can be directly reused for fresh emulsion top up.

References

[1] R. Waite, Household Waste Recycling. Earthscan Publications, London, 1995, pp. 32–77.

[2] The Role of Freeze Concentration in Waste Water Disposal, Filtration & Separation, 10 (1999) 34.

[3] A. Findon, G. McKay and H.S. Blair, J. Environ. Sci. Health, A28 (1) (1993) 173.

[4] R.S. Juang, F.C. Wu and R.L. Tseng, Water Res., 10 (1999) 2403.

[5] R.A. Conway and R.P. Ross, Handbook of Industrial Waste Disposal. Van Nostrand-Reinhold Environmental Engineering Series, Van Nostrand, New York, London, 1980.

[6] J. Nuortila-Jokinen, A. Kuparinen and M. Nyström, Desalination, 119 (1998) 11.

[7] R. Scheikholeslami, Desalination, 123 (1999) 45.

[8] K. Karakulski, A. Kozlowski and A.W. Morawski, Sep. Technology, 5 (1995) 197.

[9] Standard Methods for the Examination of Water and Wastewater, 13th Ed. American Public Health Association, Washington, DC, 1971.