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REMOVAL OF DETERGENTS FROM INDUSTRIAL WASTEWATER IN ULTRAFILTRATION PROCESS

The aim of the study was to evaluate the suitability of UF membranes for purification and concentration of effluents from detergent production. During preliminary experiments flat-sheet Amicon (the cut-off of 100, 50, 1 and 0.5 kDa) and Intersep (the cut-off of 30, 10 and 4 kDa) membranes were used. Semi-pilot and full-scale cross-flow experiments were performed using Koch/Romicon capillary ultrafiltration modules with polysulfone membranes of the cut-off of 2 and 5 kDa.

The results obtained indicate that a decrease of membrane cut-off value improves the efficiency of effluent treatment. The membrane with a cut-off of 0.5 kDa yields the best separation efficiency: the decrease of COD-Cr value is over 85%, which corresponds to COD-Cr of permeate equal to 8800 g O_2/m^3. It has been found that UF capillary modules made by Koch/Romicon are suitable for concentration of highly polluted effluents containing detergents. The modules applied are characterised by stable transport and separation properties. In the course of a long-term concentration of effluents, an essential drop in a permeability was not observed and the permeate quality remained almost constant, although a systematic increase in pollution load of the concentrate occurred.

Keywords: *ultrafiltration, detergent, surfactant, polysulfone, regenerated cellulose, capillary module, wastewater*

1. INTRODUCTION

Recently a considerable attention has been focused on the problems arising from chemicals coming from detergent production as well as laundry. The environmental risks associated with manufacture, use and disposal of these chemicals is of a great interest. Detergent products are used in large quantities for industrial application such as textiles, food, paints, polymers, cosmetics, pharmaceuticals, mining and paper production. The typical components of detergents are anionic and nonionic surfactants, builders and

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bleachers. Other constituent components are polymers, enzymes, bleaching agent activators (TAED) and perfumes [1]. The consumption of surfactants for both industrial and domestic purposes has resulted in their worldwide production of approximately 17 million tonnes in 2000 (including soap), with expected future growth rates of 3% to 4% per year globally and of 1.5% to 2.0% in the EU. Anionic surfactants are commercially the most important class, and their share in market is about 50% of total production [2].

One of the main consequences of the high level of surfactant production is the increase in the pollution caused by wastewaters coming from manufacturing plants of toiletries and detergents during the washing processes [3]. The high and varied pollution loads of these effluents are mainly due to the residual products in the reactor, which have to be washed away in order to use the same production lines for the manufacture of other products. Most of detergent products reach the environment with domestic and industrial wastewaters. Detergent effluents can cause significant environmental problems because detergent product and its ingredients can be relatively toxic to aquatic life. A direct result of this production is the necessity of the manufacturers to assess the effluent characteristics of their wastewaters and consequently to define pollution control methods. In order to meet more stringent legislative requirements in discharging the wastewaters into the environment or into the sewage system, an effective treatment process must be applied. Because of environmental as well as economic reasons (e.g. increasing water prices) we are forced to look for new methods of wastewater treatment.

Membrane-based separation processes may be an attractive alternative to wastewater treatment which is based on physical-chemical processes, i.e., coagulation [4], foaming [5], advanced oxidation processes [6], [7] and adsorption onto different types of activated carbons [8] and polyelectrolytes [9]. Sometimes the membrane system seems to be the only effective method, as chemical treatment does not work. The processes – because of the selectivity of the membrane – create the possibility of recovering resources and process water as well as of reducing high organic load of the wastewaters.

The aim of the study was to evaluate the suitability of different types of ultrafiltration membranes for treatment of industrial wastewaters containing detergents. The selection of membrane modules for concentration cross-flow tests was an another objective of the research. Finally, the preliminary results were confirmed by operation of the pilot unit with full-size membranes on actual wastewater in a factory.

2. MATERIALS AND METHODS

2.1. CHARACTERISTICS OF THE WASTEWATER

The experiments were conducted with the use of wastewater arising from detergent production in a factory producing different kinds of domestic use detergents and washing powders. The characteristics of the effluent treated is given in table 1.

Table 1

Characteristics of effluents from detergent production

Parameter	Value
pH	1.5–3.3
COD-Cr (g O_2/m^3)	40 132–59 072
Anionic surfactants (AS) (g/m^3)	1 552–1 650
TOC (g C/m^3)	11 650

Due to low pH of wastewater, the feeding stream was neutralized by NaOH solution. Prefiltration using a bag filter having pore diameter of 150 μm was applied prior to effluent concentration experiments.

2.2. MEMBRANES

In the preliminary tests aimed at preselecting the ultrafiltration modules for purification and concentration of detergent effluents, flat-sheet Amicon (cut-off of 100, 50, 1 and 0.5 kDa) and Intersep (cut-off of 30, 10 and 4 kDa) membranes were used. The characteristics of the membranes investigated is given in table 2.

Table 2

Characteristics of the membranes investigated

Membrane type	Producer	Description	Cut-off kDa	Mean pore radius, ($\times 10^{-9}$ m) [10]
Regenerated cellulose (YC)	Amicon	Strongly hydrophilic membrane with high water flux	0.5	0.3
Regenerated cellulose (YM)	Amicon	Hydrophilic membrane of high resistance to organic solvents	1 50 100	0.5 15.7
Polyethersulfone (PES)	Intersep	Moderately hydrophilic membrane made of modified polyethersulfone; high resistance to chemical agents	4 10 30	0.6 2.04 8.38

2.3. MEMBRANE MODULES

Cross-flow experiments were performed using Koch/Romicon capillary ultrafiltration modules with polysulfone membranes of the cut-off equal to 2 and 5 kDa. Technical parameters of the experimental modules applied in the semi-pilot tests are given in table 3.

Table 3

Characteristics of Koch/Romicon ultrafiltration modules

Characteristics	Module type	
	Koch/Romicon® PM2	Koch/Romicon® PM5
Cut-off (kDa)	2	5
Membrane area (m^2)	0.09	
Number of capillaries	66	
Internal capillary diameter (m)	1.1×10^{-3}	

Cross-flow pilot tests were made using Koch capillary ultrafiltration modules with polysulfone membranes of the cut-off equal to 5 kDa. The full-size membrane modules were characterised by the surface area of 6.1 m^2.

2.4. EXPERIMENTAL SYSTEMS

2.4.1. EXPERIMENTAL SYSTEM WITH AMICON CELL

The preliminary tests involving evaluation of separation properties of flat-sheet membranes were carried out in a laboratory set-up consisted of an Amicon 8400 UF cell with a total volume of $350\cdot10^{-6}$ m^3 and a diameter of 0.076 m. The transmembrane pressure applied amounted to 0.30 MPa.

2.4.2. SEMI-PILOT EXPERIMENTAL SYSTEM

Effluent concentration experiments, as well as the determination of transport properties of ultrafiltration modules, were carried out using the cross-flow system

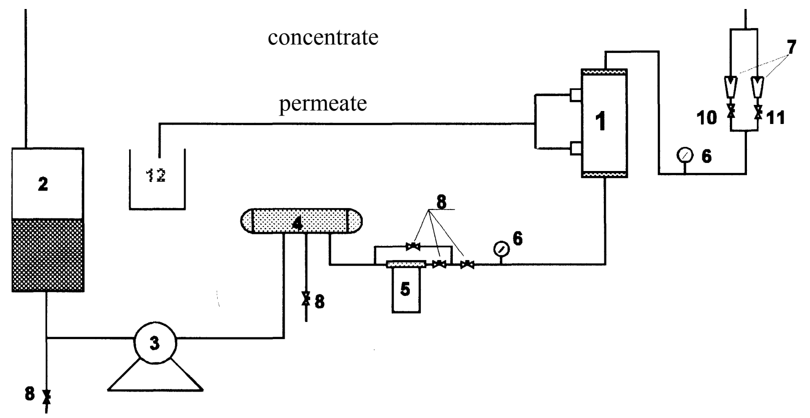

Fig. 1. Semi-pilot UF set-up: 1 – membrane module, 2 – feeding tank, 3 – hydraulic membrane pump of Milroyal C-Dosapro Milton Roy type, 4 – pressure accumulator, 5 – preliminary 25 µm filter, 6 – manometer, 7 – rotameter, 8–10 – control valves, 11 – drain valves, 12 – permeate tank

presented in figure 1. Due to high concentration of suspended solids, effluents were passed through a 150 µm filter bag prior to membrane filtration. The effective volume of the set-up amounted to 0.08 m^3.

2.4.3. FULL-SCALE PILOT SYSTEM

The concentration ratio experiments together with the evaluation of membrane stability were performed in the full-scale pilot system. The scheme of the UF pilot system flow is shown in figure 2.

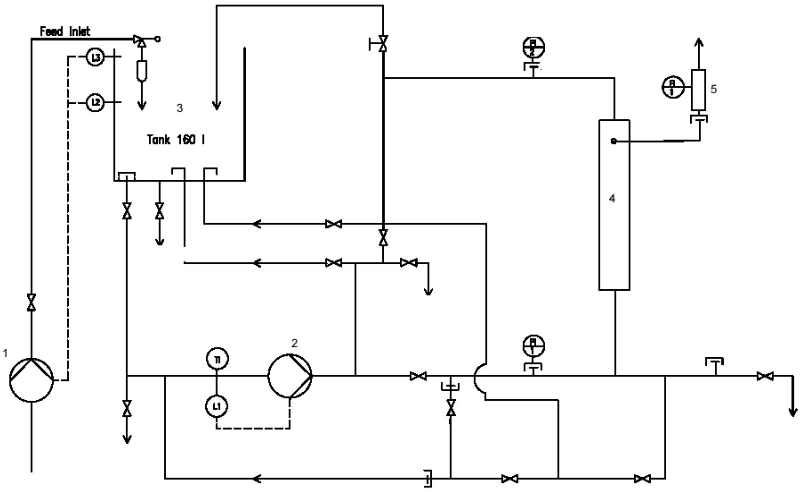

Fig. 2. Pilot UF set-up: 1 – feed pump, 2 – main pump, 3 – process tank, 4 – membrane module, 5 – rotameter

The unit consisted of the following major parts: ultrafiltration modules (4), centrifugal feed pump (1), centrifugal circulation pump (2) and process tank (3). Additionally, due to high concentration of suspended solids, effluents were passed through a 100 µm filter bag prior to membrane filtration. The volume of the process tank was 0.16 m^3.

2.5. ANALYTICAL METHODS

In order to evaluate the effectiveness of membrane separation, anionic detergents and COD-Cr were determined in the feed and permeate.

The concentration of anionic surfactant (AS) was measured spectrophotometrically (the indicator Rhodamine G6, the absorbance at a 565 nm wavelength).

2.6. DETERMINATION OF TRANSPORT AND SEPARATION PROPERTIES OF THE MEMBRANES

2.6.1. PRELIMINARY TESTS

Preliminary tests designed to determine the suitability of chosen membranes for the treatment of industrial wastewaters were performed in a laboratory system with Amicon cell. Prior to membrane filtration wastewater was neutralised and prefiltered through filter cloth, filter paper and Watman 17 filter.

Ultrafiltration of distilled water and pretreated wastewater was carried out at the transmembrane pressure of 0.30 MPa. In order to maintain a constant concentration of the substances in the feed solution, the permeate was recirculated to UF cell. At this stage of research only separation effectiveness of membranes was determined (the value of COD-Cr in the permeate was measured).

2.6.2. EXPERIMENTS IN A SEMI-PILOT SYSTEM

Prior to each cycle, the membrane module has been treated with water at 0.10 MPa, until the constant permeate volume flux was established. Transport properties with respect to water and industrial effluents were investigated at the transmembrane pressure equal to 0.05, 0.10 and 0.15 MPa and cross-flow rate of 2 m/s.

The stability of membrane modules in the wastewater from detergent production was tested at the transmembrane pressure of 0.10 MPa and initial volume of 0.055 m^3. After each hour of the test the permeate flux was measured. Periodically, concentration of anionic surfactants and COD-Cr was analysed in the permeate and concentrate.

The degree of effluent concentration was determined according to the following formula:

$$CF = \frac{V_0}{V_t},$$

where CF is the concentration factor, V_0 and V_t denote the initial volume of feed and the volume of concentrate after time t, respectively.

2.6.3. EXPERIMENTS IN A FULL-SCALE PILOT SYSTEM

A full-scale pilot test was performed according to semi-pilot procedure, i.e. before each cycle the membrane module has been treated with water at 0.10 MPa, until the constant permeate volume flux was established. The response of membrane to industrial effluents was investigated at the transmembrane pressure equal to 0.10 MPa and the cross-flow rate of 2 m/s. Permeate volume flux (J) was calculated from equation given in Chapter 2.6.2.

The stability of membrane modules was tested in pilot experiments in the wastewater from detergent production at the transmembrane pressure of 0.10 MPa and an initial volume of 0.16 m^3. The system was permanently fed with wastewater, so a constant level of liquid in the process tank was kept (semi-continuous process). After each hour of the test the permeate flux was measured. At the end of the cycle, when the concentration factor estimated was reached, the concentrate was discharged from the system which was flushed out with water. The value of COD-Cr in the wastewater (concentrate) and in the permeate was determined at the beginning and at the end of each UF cycle.

The effluent concentration was determined according to the following formula:

$$CF = \frac{V_c}{V},$$

where CF is the concentration factor, V_c denotes the cumulative volume of wastewater fed to the process tank after the time t, and V is the concentrate volume (equal to 0.16 m^3).

3. RESULTS AND DISCUSSION

3.1. PRELIMINARY EVALUATION OF THE UF PROCESS IN THE WASTEWATER TREATMENT

The results of wastewater treatment experiments with the use of membranes that differ in the molecular weight cut-off are shown in figure 3. The aim of the preliminary tests was to assess the usability of ultrafiltration process for the treatment of industrial wastewater arising from detergent production. In the light of this aim, only separation efficiency of several flat membranes was verified in the first stage of investigation. The membranes tested were characterised by different cut-off values (from 0.5 kDa to 100 kDa).

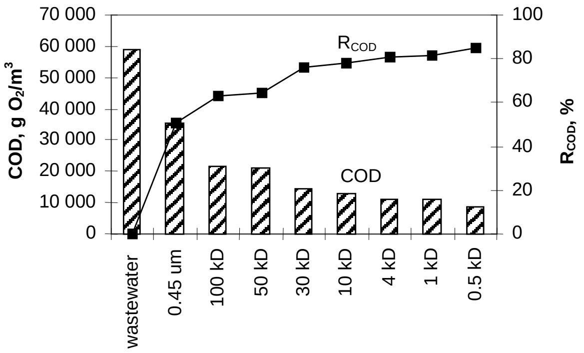

Fig. 3. Efficiency of detergent wastewater treatment by various UF membranes (ΔP = 0.30 MPa)

The results obtained (figure 3) indicate that a decrease in the membrane cut-off value improves the efficiency of effluent treatment. Ultrafiltration membranes of high cut-off values enable 63–76% decrease in COD-Cr of the treated wastewaters. The reduction of COD-Cr by more than 80% can be reached in UF process for the membranes of a cut-off lower than 10 kDa. The membrane with a cut-off of 0.5 kDa yields the best separation efficiency: a decrease in COD-Cr value is over 85%, which corresponds to COD-Cr permeate equal to 8800 g O_2/m^3.

As was shown by preliminary tests, the concentration of detergent wastewaters can be performed by applying membranes of relatively low cut-off values (0.5–4 kDa). These membranes are characterised by high COD-Cr reduction.

3.2. TRANSPORT PROPERTIES OF MEMBRANE MODULES

The hollow fibre modules made by Koch/Romicon have been chosen on the basis of preliminary tests. The modules of this type were characterised by an internal fibre diameter equal to 1.1×10^{-3} m. It was anticipated that fibre size was large enough to avoid intensive fouling and membrane clogging. The modules with the cut-off values equal to 2 and 5 kDa were applied.

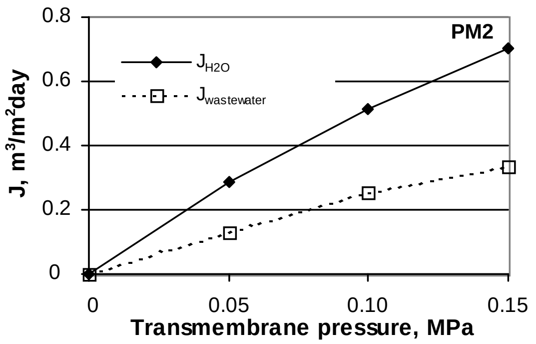

Fig. 4. Transport properties of the PM2 module in relation to water and detergent effluents

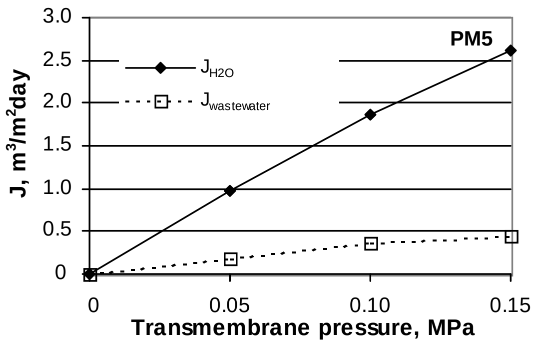

Fig. 5. Transport properties of the PM5 module in relation to water and detergent effluents

The transport properties of the PM2 and PM5 modules were determined at the following transmembrane pressures: 0.05, 0.10 and 0.15 MPa. Distilled water and detergent effluents were passed through the modules. The results obtained are shown in figures 4 and 5.

The permeate volume flux versus the pressure applied was represented by a linear relationship. During effluent tests carried out in both modules an essential drop in membrane permeability was observed. The effluent volume flux exhibited only 50% and 20% of water volume flux for PM2 and PM5 modules, respectively (at the pressure of 0.10 MPa).

Taking into account the results obtained, it can be concluded that treated wastewaters showed a close affinity with the membrane material. The five-fold and two-fold decrease in membrane permeability (in comparison to water flux) observed for PM5 and PM2 modules, respectively, was probably caused by sorption of contaminants in the membrane pores. The shape of the curves representing the relationship between effluent volume flux and the pressure applied indicates that further increase in the transmembrane pressure is not economically justified. A slight increase in membrane permeability will not compensate the increment of energy demand.

3.3. WASTEWATER CONCENTRATION IN THE SEMI-PILOT SYSTEM

The suitability of PM2 and PM5 modules for the concentration of detergent effluents was verified. The results obtained are shown in figures 6–9.

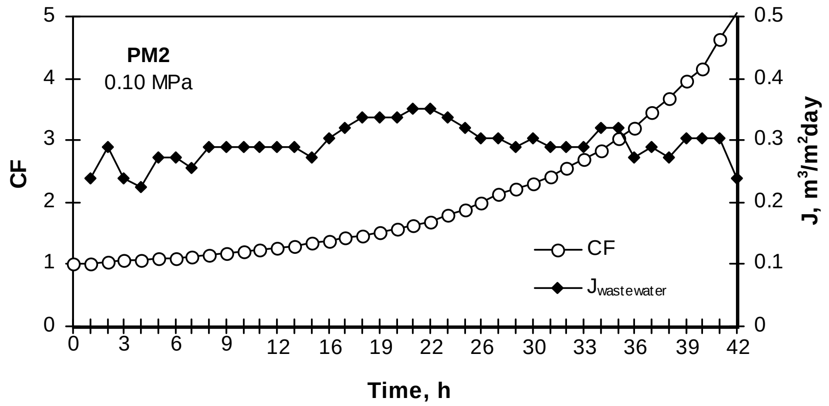

Fig. 6. Concentration factor and volume flux versus time of wastewater concentration in PM2 module

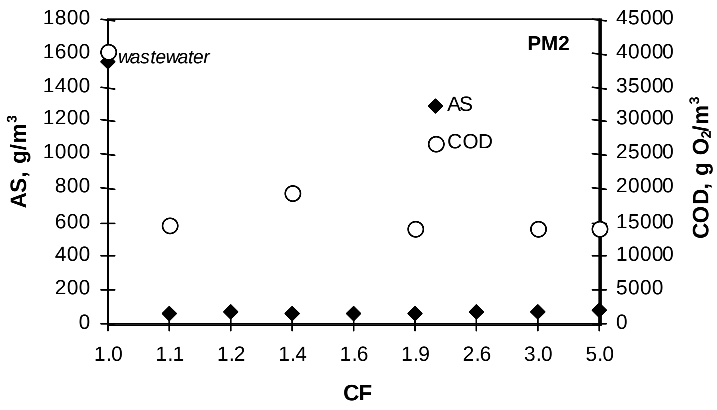

Fig. 7. Permeate quality in the course of wastewater concentration in PM2 module

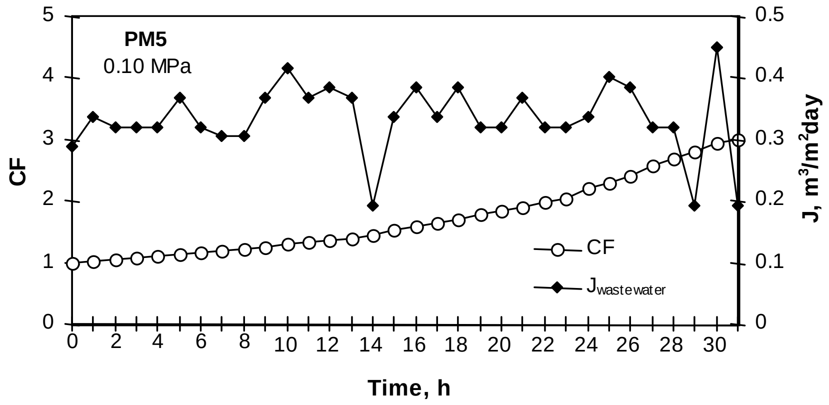

Fig. 8. Concentration factor and volume flux versus time of wastewater concentration in PM5 module

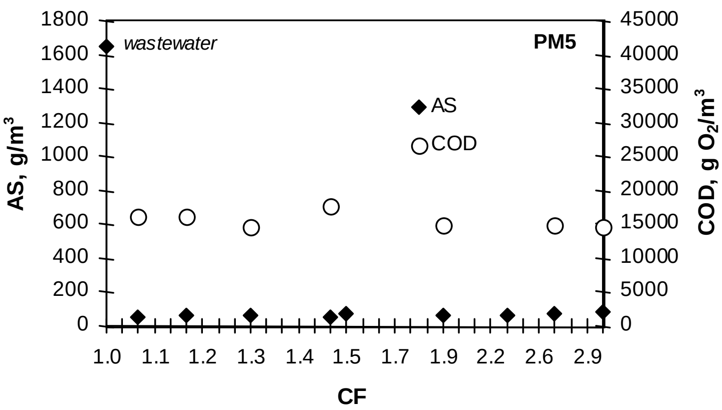

Fig. 9. Permeate quality in the course of wastewater concentration in PM5 module

The modules applied were characterised by a stable properties during long-term concentration process. The PM5 module enabled over three-fold concentration of the initial volume of the detergent wastewaters, whereas for PM5 module concentration factor amounted to 5. The membrane permeability remained almost on a constant level approaching 0.20–0.30 m^3/m^2day (PM2 module) and 0.25–0.40 m^3/m^2day (PM5 module). The permeate quality was also satisfactory in the course of wastewater concentration. The permeate COD-Cr value was maintained in the range of 10000–20000 g O_2/m^3 for both modules.

Effluent permeate is characterised by low detergent concentration. High rejection of detergents is probably caused by agglomeration of surfactant particles and, in consequence, by creation of premicelles and micelles. These particles of high-molecular weight are efficiently separated by UF membranes. However, it seems that not only the molecular sieve effect is dominant, influencing the permeate quality. The interactions between contaminant particles and membrane material can be regarded as a factor supporting the efficiency of the detergent wastewater treatment by ultrafiltration.

3.4. WASTEWATER CONCENTRATION IN THE PILOT FULL-SCALE SYSTEM

Pilot system was used to confirm the results expected to occur in the actual operating conditions. The results obtained are shown in figure 10.

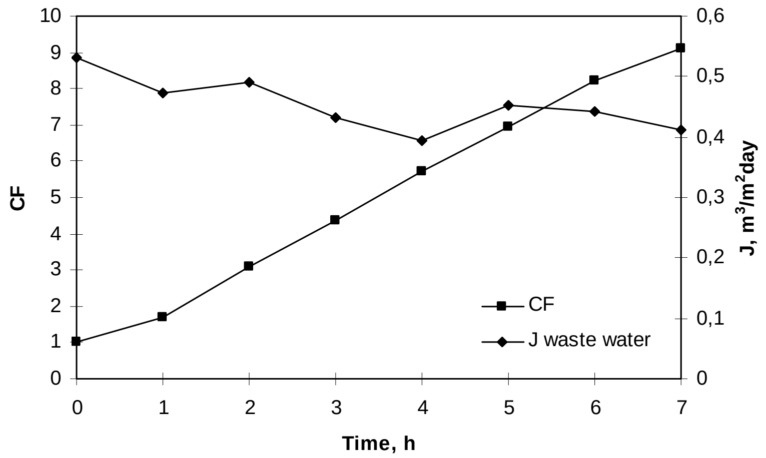

Fig. 10. Concentration factor and volume flux versus time of wastewater concentration in pilot module

The full-size modules applied were characterised by a stable properties during long-term concentration process. The tests showed that it was possible to achieve concentration factor values higher than 9, i.e. less than 10% of the initial volume of the treated wastewater remained as a concentrate. The membrane permeability was kept almost on a constant level approaching 0.25–0.40 m^3/m^2day. The permeate quality was also satisfactory in the course of wastewater concentration. The permeate COD-Cr value was maintained in the range of 8000–12000 g O_2/m^3.

4. CONCLUSIONS

Taking into account the results presented, it can be concluded that ultrafiltration low-pressure membrane process enables efficient treatment of industrial wastewaters arising from detergent production.

The results obtained indicate that UF hollow fibre modules made by Koch are suitable for concentration of highly-polluted effluents containing detergents. The modules applied are characterised by stable transport and separation properties. In the course of long-term effluent concentration, an essential drop in permeability was not observed and the permeate quality remained almost constant despite a systematic increase in pollution load of the concentrate. The separation efficiency of both modules tested was similar: the modules yielded 65–85% reduction in COD-Cr value and over 95% retention of anionic detergents.

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