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MICROFILTRATION AND ULTRAFILTRATION OF TANNERY WASTEWATERS

Keywords

Microfiltration (MF), ultrafiltration (UF), tannery wastewaters, fats, proteins.

Summary

The article presents a new pilot scale membrane unit with microfiltration and ultrafiltration modules. The obtained results of the initial investigations confirm the applicability of the MF and UF membranes for proper removal of fats and proteins from tannery wastewaters. The composition of real tannery effluents, the results of the accomplished analyses of microfiltration and ultrafiltration and the evaluation of the possibilities of implementation of this process in a larger scale have been also presented.

Introduction

Tannery industry produces a huge amount of very complex wastewaters containing different organic (fats, organic nitrogen) as well as inorganic (chromium, chlorides, sulphurs) substances [1-2].

Very interesting results, concerning removal of organic substances from tannery wastewaters, can be obtained by the use of microfiltration and ultrafiltration [2-6].

Microfiltration (MF) and ultrafiltration (UF) belong to the mechanical separation processes. They have a common feature – the use of membranes. Pressure difference, on both sides of the membrane, is a driving force of those processes, and it causes that the homogenous components of the separated mix-

ture diffuse, with different velocities, through the membrane [7-8]. The most characteristic microfiltration and ultrafiltration parameters are shown in Table 1.

Table 1. The most characteristic microfiltration and ultrafiltration parameters [7-8]

Parameter	Microfiltration (MF)	Ultrafiltration (UF)
Membrane	Porous - symmetric	Porous - asymmetric
Thickness of membrane	10-150 μm	about 150 μm
Size of pores	0.05-10 μm	1-50 (100) nm
Transmembrane pressure	<0.2 MPa	0.1-1.0 MPa
Separation mechanism	sieve	sieve
Membrane material	polymer, ceramic	polymer, ceramic

1. Experimental

Experimental set up

The microfiltration and ultrafiltration processes were performed in the integrated pilot membrane installation presented in Fig. 1.

a)



Fig. 1. Pilot membrane installation: a) general view, b) scheme: MF - microfiltration module, UF – ultrafiltration module, ZR – retentate tank, ZS – feed tank, ZP – permeate tank, P1 – feed pump, P2 – circulating pump, M – manometer, R – flowmeter, FS – fabric filter

The purified solution is gathered in the feed tank and further pumped via the recycling system (pump P1) with fabric filters, which can be blocked by set of valves, to the membrane module (pump P2). The input pressure of the membrane module is measured by a manometer, and the flowing streams are measured by the set of flowmeters. Permeate and retentate streams leaving the membrane module can be separated in the permeate and retentate tanks (open system) or recycled to the feed tank (closed system).

Membranes

The purification of wastewaters from fats and proteins (organic nitrogen) has been carried out by the use of two kinds of membranes: ceramic and polymer. They are showed in Fig. 2, and their characteristics are presented in Table 2.

Table 2. Characteristics of tested microfiltration and ultrafiltration membranes

	Microfiltra	ation (MF)	Ultrafiltration (UF)		
Manufacturer	Eurosep	Eurosep Eurosep		Eurosep	
Configuration	Capillary	Capillary	Tubular	Capillary	
Material	Polypropylene	polypropylene	TiO ₂ /ZrO ₂	polysulphone	
Active area	0.22 m^2	0.18 m^2	0.175 m^2	1.4 m^2	
Cut-off	0.2 µm	0.3 µm	150 kD	50 kD	
Temp. max.	40°C	40°C	150°C	70°C	
Pressure max.	0.15 MPa	0.15 MPa	0.55 MPa	0.55 MPa	
pH	2-10	2-10	0-14	2-10	



Fig. 2. Investigated microfiltration and ultrafiltration membranes

The separation utilities of the investigated membranes have been checked by the microfiltration and ultrafiltration of the supply-water. The investigations have been performed for different process streams and different transmembrane pressures. The averaged results of hydraulic permeability of the used membranes are given in Fig. 3.



Fig. 3. Hydraulic permeability of tested microfiltration and ultrafiltration membranes

The obtained results for the supply-water fully agreed with those declared by the producers and confirmed the proper separation properties of the used membranes. The investigations show also that both in the case of ceramic and polymer membranes the obtained results are almost the same.

Sample analyses

Chemical analyses of the samples coming from the MF and UF experimental runs were determined as follows:

- 1. Chromium by an atomic absorption spectrophotometer.
- 2. Fats by extraction in petroleum ether.
- 3. Total suspended solids by filtration through a 0.45 μ m cellulose acetate membrane.
- 4. Organic nitrogen by Kjeldahl method.
- 5. The conductivity and pH were measured by a conductometer and pH meter (Mettler Toledo).
- 6. The turbidity was measured by a turbidimeter (Hach Lange).

2. Results and discussion

Microfiltration and ultrafiltration of model tannery wastewaters

The model wastewaters were prepared from water coming from the water supply. Microfiltration was used for purification of fats emulsions based on the roksol, and ultrafiltration was applied for the cleaning of water containing animal gelatine. Permeate and retentate streams leaving the MF and UF modules can be recycled to the feed tank. Parameters of both processes (MF and UF) are summarised in Table 3. After 2.5 hours, the analysis of permeates, retentate, and feed samples were performed. Table 4 contains the results of microfiltration and ultrafiltration of model tannery wastewaters.

Process	Microfiltra	ation (MF)	Ultrafiltration (UF)	
	0.2 µm	0.3 µm	150 kD	50 kD
Pressure [MPa]	0.15	0.15	0.45	0.40
Feed flow [dm ³ /h]	1300	2300	1300	1600

Table 3. Parameters of microfiltration and ultrafiltration processes

Table 4. Fats and organic nitrogen in the microfiltration and ultrafiltration process streams for model tannery wastewaters

Stroom	Fats [r	ng/dm ³]	Organic nitrogen [mg/dm ³]		
Sucalli	MF 0.2 μm MF 0.3 μm		UF 150 kD	UF 50 kD	
Permeate	9	17	53	25	
Feed	225	84	307	263	
Retentate	252	119	310	297	
Retention [%]	96	80	83	90	

The retention of the MF and UF membranes is defined as $R = (1 - C_P/C_F) \times 100\%$, where C_P is the concentration of a specific component in the permeate, and C_F is the concentration of the same component in the feed solution.

Analytical determinations on samples coming from the microfiltration and ultrafiltration of model tannery wastewaters showed a marked reduction of fats substances (MF 0.2 μ m – 96%, MF 0.3 μ m – 80%) and organic nitrogen (UF 150 kD – 83%, UF 50 kD – 90%) in the permeate streams compared to the feed solutions (Table 4).

Microfiltration and ultrafiltration of real tannery wastewaters

Microfiltration and ultrafiltration of real tannery wastewaters have been carried out on the MF 0.2 μ m and UF 50 kD modules. The ultrafiltration process was followed by the microfiltration performed at 0.15 MPa. The permeate from microfiltration was used as a feed stream for ultrafiltration carried out at 0.40 MPa (Fig. 4). Every 10 min. permeate, retentate and feed flows as well as permeate volume were registered. After obtaining of 20 dm³ of permeate, the analysis of permeate, retentate and feed flows were performed. Obtained results of the investigations and calculations are given in Table 5 and 6.



Fig. 4. Technological scheme of microfiltration and ultrafiltration processes for real tannery wastewaters

The MF membrane rejected 30% of the fat substances and 3.5% of the organic nitrogen, whereas, the UF membrane rejected 90% of the fats substances and 64% of the organic nitrogen (Table 6). Microfiltration did not give the expected purification results; therefore, this process has been omitted and further purification of tannery wastewaters has been performed using only the ultrafiltration module. The UF 150 kD module was used for the investigation. It gave 83% retention in the case of the model tannery wastewaters.

Domomotor	MF 0.2 μm		UF 50 kD			
Parameter	Permeate	Feed	Retentate	Permeate	Feed	Retentate
pН	4.0	4.0	4.0	4.3	4.0	4.3
Conductivity [mS/cm]	42.8	42.5	42.7	33	42.8	33
Turbidity [mg SiO ₂ /dm ³]	292	373	402	1	292	170
Total suspended solids [mg/dm ³]	336	418.5	406.5	39.0	336	213.5
Chromium [mg/dm ³]	1370	1460	1510	723	1370	1140
Organic nitrogen [mg/dm ³]	2322	2406	1143	828	2322	1135
Fats [mg/dm ³]	75	107	120	7.5	75	37.5

Table 5. Results of analysis of real tannery wastewaters after microfiltration and ultrafiltration processes

Table 6. Results of retention calculation for some wastewaters parameters after microfiltration and ultrafiltration processes

Paramatar	Retention [%]		
I arameter	MF 0.2 μm	UF 50 kD	
Total suspended solids [mg/dm ³]	20	88	
Chromium [mg/dm ³]	6.2	47	
Organic nitrogen [mg/dm ³]	3.5	64	
Fats [mg/dm ³]	30	90	

The ultrafiltration process was carried out in the open system (the permeate was continuously taken out to the second reservoir) at a pressure 0.50 MPa. Every 10 minutes permeate, retentate and feed flows, as well as the permeate volume were registered. After obtaining of 20 dm³ of permeate, the analysis of permeate, retentate and feed flows were performed. The results are summarised in Table 7.

The UF 150 kD module rejected 88% of the fat substances and 63% of the organic nitrogen (Table 7). A comparison of the retention values obtained in the two-steps MF/UF process (Table 6) and values of direct filtration, presented in Table 7, confirm our conclusion concerning the substitution of this two-step process by the ultrafiltration process, proceeded by the conventional, mechanical purification.

Deremeter		Retention		
Falameter	Permeate	Feed	Retentate	[%]
рН	4.4	4.3	4.3	-
Conductivity [mS/cm]	35.1	41.1	42.2	-
Turbidity [mg SiO ₂ /dm ³]	1	261	294	-
Total suspended solids [mg/dm ³]	18	528	366	93
Chromium [mg/dm ³]	1230	1630	1700	25
Organic nitrogen [mg/dm ³]	927	2512	1156	63
Fats [mg/dm ³]	12	103	82	88

Table 7. Results of analysis of real tannery wastewaters after ultrafiltration process

Fig. 5 shows the dependence of permeate flux and Volume Reduction Factor (VRF) on filtration times. VRF is defined as the ratio between the initial feed volume and the volume of the resulting retentate (VRF = V_0/V_R).



Fig. 5. Microfiltration and ultrafiltration of real tannery wastewaters: a) permeate flux versus filtration time, b) Volume Reduction Factor versus filtration time

The experiment shows that the permeate flux and the VRF are strongly dependent on filtration time (Fig. 5.). The result shows that the permeate flux decreased with operating times by increasing the VRF due to the fouling phenomena. Membrane fouling can be caused by specific physical and/or chemical interactions between the membrane and various components present in the process stream, e.g. fats and proteins.

Conclusions

Application of microfiltration and ultrafiltration for the retention of fat substances and organic nitrogen from tannery wastewaters was studied. The microfiltration and ultrafiltration of model tannery wastewaters showed a marked reduction of fat substances (MF 0.2 μ m – 96%, MF 0.3 μ m – 80%) and organic nitrogen (UF 150 kD – 83%, UF 50 kD – 90%). An integrated MF/UF process of real tannery wastewaters provided a marked retention of fat substances (90%) and organic nitrogen (64%). The UF process of real tannery wastewaters rejected 88% of the fat substances and 63% of the organic nitrogen. The obtained results of the investigations show that the ultrafiltration process is responsible for proper removal of fats and proteins from tannery wastewaters. That is why, in the purification process, the microfiltration module can be omitted or substituted by the conventional filtration.

The experiment shows that the main drawback of the application the microfiltration and ultrafiltration in tannery wastewaters treatment is the decrease of the permeate flux due to the fouling phenomena. The low permeate flux causes that, for effluent purification, a large membrane area is needed, which in consequence, produces high investment costs.

Moreover, application of ultrafiltration for chromium tannery wastewaters would be allowed for obtaining of pure chromium regenerated stream. The regenerated stream could be then recycled for further tannery processes (Fig. 4). It is important, because the traditional regeneration stream contains a lot of proteins and fats, which makes the tannery process much more difficult.

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Mikrofiltracja i ultrafiltracja ścieków garbarskich

Słowa kluczowe

Mikrofiltracja (MF), ultrafiltracja (UF), ścieki garbarskie, tłuszcze, białka.

Streszczenie

W artykule zaprezentowano półtechniczną instalację membranową wraz z testowanymi modułami mikro- i ultrafiltracyjnymi oraz metodykę usuwania z ich pomocą emulsji tłuszczowych i białek zwierzęcych ze ścieków garbarskich. Przedstawiony został skład przebadanych ścieków garbarskich, wyniki przeprowadzonych badań mikro- i ultrafiltracji, a także ocena możliwości i celowość zastosowania tego procesu w większej skali.