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Technical performances of ultrafiltration applied to municipal wastewater treatment plant effluents

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ABSTRACT

The use of membrane separation like ultrafiltration for reuse of reclaimed water has become an increasingly attractive option, especially nowadays when water quality and water scarcity are stringent issues. In this study, a secondary effluent from Iasi municipal wastewater treatment plant (MWWTP) was treated in a laboratory-scale ultrafiltration equipment with 4 and 6 kDa membranes, in cross-flow operating mode, with complete recirculation of the concentrate, under various pressure conditions (1–2.5 bar) and time periods (1–4 h). Considering the technical performances of the ultrafiltration process, two main directions were followed: firstly, the assessment of membrane productivity in terms of permeate flux, volume reduction factor (VRF), and fouling index (I_t) and secondly, the evaluation of permeate quality, calculated by the removal efficiencies calculated for various water quality indicators: turbidity, Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Phenols, Total Nitrogen, Total Phosphorous (TP), Total Fe, Total Cr, Cu^{2+}, Zn^{2+}. The best results obtained on the EM006 membrane, (1 h test, pressure $p = 1.5$ bar) show removal efficiencies up to 50% in terms of organic compounds removal (COD and TOC indicators), 100% in terms of solids presence (measured by turbidity) and phenolic compounds, up to 30% reduction of TP. The permeate quality was compared with different limits of pollutants concentration, specified in the existing legislative framework for reclaimed water, in United States (US) and Spain (EU). The study indicates that ultrafiltration of the secondary municipal effluent from Iasi MWWTP, in an advanced treatment step, is a feasible option for water reclamation, but special attention is required to the compounds containing nitrogen and especially nitrates concentration which exceed the maximum admissible concentration.

Keywords: Ultrafiltration; Secondary municipal effluent; Technical performances; Advanced treatment

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1. Introduction

The conventional municipal wastewater treatment plants (MWWTP) generally include the mechanical and biological treatment stages and discharge the final effluents into surface waters. In the recent years, the water scarcity issues as well as the impacts of insufficiently treated effluents and the stringent guidelines for wastewater discharges imposed the need for wastewater recycling and reuse, many studies being directed toward finding new technologies or optimizing existing process configurations for municipal wastewater treatment with the scope of water reclamation. The treatment of municipal wastewaters has to be designed, implemented, and controlled by taking into consideration the possibilities of recycling or reusing applications of the resulted effluent [1,2]. Unfortunately, even though some US and EU states have already established regulations regarding the safety quality standards of reclaimed water, in Romania, there is still a lack of legislation regarding this aspect.

There are many available processes that may be considered in advanced treatment stages for municipal and industrial effluents, efficient in removing the pollutant loads to a certain quality as required by the subsequent use of water. On one hand there are the degradation processes, in which the pollutants are transformed into harmless or at least less toxic compounds i.e. all types of advanced oxidation processes such as: catalytical oxidations [3–6], photocatalytical processes [7], ultrasonication [8], coagulation, and electrocoagulation [9]. On the other hand, there are separation processes, in which pollutants are eliminated from the effluents, as it is the case with membrane processes [8,10–12]. Both categories of processes have advantages and disadvantages and the selection of alternatives for the process integration has to be taken by evaluating each individual case, considering criteria like wastewater quality and quantity, technical performances and financial costs of the technology, simplicity in integrating advanced treatment stages with conventional wastewater treatment, etc. [13,14].

Within the separation processes applied for the removal of pollutants from wastewaters, membrane separation processes and especially ultrafiltration (UF) has been successfully applied either as the main polishing step of the effluent, in some cases, replacing the biological treatment [15] or partially concentrate the effluent with two exiting streams: the permeate with a very good quality and the concentrate which can be sent back to the sewer or can undergo further treatment. The advantages of ultrafiltration, used in the treatment of wastewater, are maintenance of water quality and availability for integration and expansion in various configurations, together with the simplicity of design and control. The main problem associated with membrane processes is the frequent membrane fouling and/or blocking of the membrane pores, leading to high costs related to the consumption of water and chemicals for cleaning or the acquisition of the new membranes [13].

Based on these aspects, many studies have reported encouraging results on the application of ultrafiltration on municipal and industrial effluents with the scope of reuse or recycling application. With respect to industrial effluents treatment by UF or other membrane processes, authors [16–20] have reported the performances of the process for wastewaters coming from fruit juice and milk processing industry, cork process, tanneries, dairy industry, and car wash effluent.

Discussing the treatment of municipal wastewater, Ravazzini et al. [15] have studied the possibilities of using direct ultrafiltration on tubular polymeric membranes for raw sewage and primary effluents and found out that the filtration of primary effluents shows smaller cleaning resistance increase and higher permeate production, even though the same fouling mechanism was proved. Delgado Diaz et al. [21] have used also a primary settled municipal effluent (MWWTP Santa Cruz de Tenerife, Spain) for a combined coagulation–ultrafiltration process, with the scope of replacing biological treatment. Their results indicated that the quality of the obtained permeate meets the Spanish Standards for reclaimed water reuse. Another case of membrane treatment applied for a primary sedimentation effluent (MWTP Soseigawa, Japan) was reported by Lateef et al. [22] and the results indicate that the process could be installed and performed without extra space requirements, but further treatment of the concentrate is needed.

Dialynas and Diamadopoulos [23] have integrated a pilot-scale hollow-fiber UF equipment in the MWWTP Rethymno, Greece applied for the biologically treated effluent. The single direct UF process, operated at low pressures (max. 0.5 bar) has managed to achieve removal efficiencies of 19% expressed as Chemical Oxygen Demand (COD), 25% expressed as Dissolved Organic Carbon (DOC), and over 99% expressed as fecal and total coliforms. Nanotubular ceramic UF membranes used on a secondary effluent resulting from Ponte Rosarolo, Italy registered good results in terms of removal efficiencies for the main quality indicators: Biological Oxygen Demand (BOD), COD, Total Nitrogen (TKN), Total Phosphorous (TP), and Total Dissolved Solids [24]. The secondary effluent of Mostoles MWWTP, Spain has been ultrafiltered by flat sheet commercial membranes with molecular weight cut-off (MWCO) of 1, 2, 5, and 20 kDa, made of thin-film composite and polymeric materials. The removal efficiencies found in the permeate were: 52–67% for COD, 48–59% for Total Organic Carbon (TOC), 83–89% turbidity, 14.7–36% for TN, and 57–62% for TP [25]. The performance of ultrafiltration in eliminating emerging pollutants (selected pharmaceuticals and pesticides) was demonstrated on a secondary effluent (MWWTP Alcala, Spain) by Acero et al. [26].

Similar studies were performed by Blst'akova et al. [27] for domestic wastewater of the MWWTP Bratislava, Slovenia, with removal efficiencies of 91% in terms of organic matter and 97% in terms of $N–NH_4^+$ and Falsanisi et al. [28] for the effluent from MWWTP Taranto, Italy and obtained a permeate that complies with the Italian agriculture wastewater reuse guidelines and State of California Title 22 regulation.

Other studies have demonstrated that coupling ultrafiltration with other membrane processes, adsorption or coagulation are feasible options to consider, when permeate is used for example in agriculture: irrigation and aquifer recharging [29–32].

The main objective of this study is to evaluate the technical performances of an UF process, performed on a laboratory-scale equipment, for the treatment of secondary effluents coming from the Iasi MWWTP, Romania. In this case, ultrafiltration is a polishing step, after mechanical, biological treatment, and secondary sedimentation, with the scope of producing a permeate of such quality that would allow the reuse and recycling applications or *e.g.* for irrigation within MWWTP perimeter, at the Dancu greenhouses, but also for screens, grids, and platforms cleaning, respectively. The quality of the resulting effluent is assessed by the removal efficiency of the pollutants, associated with the following water quality indicators: Suspended Solids (SS) and turbidity, COD, TOC, Phenolics (PHE), TN and TP, metals presence: Cu, Cr, Fe, Zn.

2. Materials and methods

2.1. Secondary municipal effluent

The Iasi MWWTP consists of two conventional mechanical—biological wastewater treatment lines which were recently fully refurbished and upgraded. The first wastewater line comprises the conventional activated sludge technology, while the second line (the newest) comprises a two-step activated sludge process (first stage with very high organic load, second stage normal organic and sludge load). Sludge disposal is performed by anaerobic mesophilic digestion of the primary and biological excess sludge together with biogas production followed by landfilling. At the present moment, a nutrient removal stage is under construction.

The secondary effluent samples were collected from the MWWTP of Iasi, Romania, over a period of 3 months (October–December 2013). The samples were maintained at a constant temperature of 4˚C until use. The main quality parameters of the secondary effluent are summarized in Table 1.

2.2. UF Equipment and experimental procedure

The ultrafiltration system used during the experiments (Fig. 1) includes the following elements: 5 L effluent storage vessel, demineralized water storage tank, peristaltic pump (Flowmaster FMT 300), tubular membrane module (MIC-RO 240, producer: PCI membranes, UK) with two channels for the membranes to fit in, pulse damper, manometers and pressure valves, and other connectors. The membrane module is very compact (total length = 30 cm) and has a total membrane area of 0.024 m^2. It is made from stainless steel with great resistance to the operating conditions and to more aggressive fluids. The operating conditions for the module are specified in Table 2.

The ultrafiltration system is capable of performing in various operating modes such as *cross-flow* and *dead-end* when referring to the liquid separation and in *direct* or *forward* flushing and backwashing if cleaning

Table 1
Secondary effluent main quality parameters

Quality indicator	Analyzed values*	MAC**
pH	7.44–7.88	6.5–8.5
COD, mg O_2/L	39–57	125
BOD5, mg O_2/L	12–19	25
SS, mg/L	14–17	60
$N–NH_4^+$, mg/L	0.01–0.03	3
NO_2^-, mg/L	0.03–0.6	2
NO_3^-, mg/L	51–52.8	37
TN, mg/L	15.98–19.06	15
TP, mg/L	1.45–2.92	2
PHE, mg/L	0.019	0.3
Cu (Cu^{2+}), mg/L	0.01–0.07	0.1
Cr (Cr^{3+} and Cr^{6+}), mg/L	0.02–0.04	1
Fe (Fe^{2+} and Fe^{3+}), mg/L	0.29–0.44	5
Zn (Zn^{2+}), mg/L	0.07–0.11	0.5

*The analyzed values column shows the range variation of the effluent samples collected during the experiments.
**MAC = maximum acceptable concentration for discharge in water bodies, according to NTPA 001/2005 (Romanian GD 352/2005) [33].

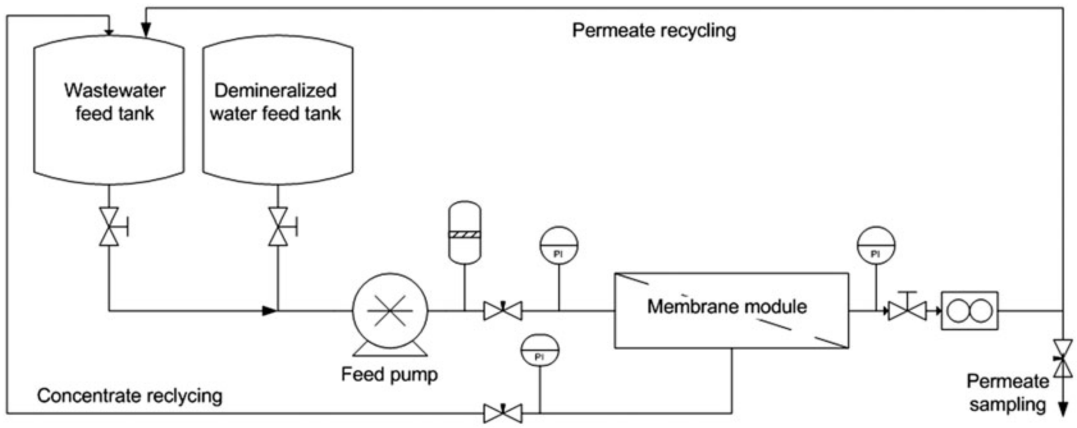

Fig. 1. Ultrafiltration equipment.

Table 2
Operating conditions for the membrane module, [34]

Operating conditions	Values
Typical permeate flow	5–50 mL/min
Typical recommended pressure	40 bar for RO; 4 bar for UF
Typical recommended recycle flow rate	18 L/min for RO, equivalent to 2.5 m/s
Pressure drop (water) at 2 m/s	15 kPa (2 psi)
Pressure drop (water) at 4 m/s	50 kPa (7 psi)

operations are considered. For this study, the system was operated in *cross-flow* mode, at a constant tangential velocity of 9.51 cm/s with both concentrate and permeate recycling to the feed tank, to minimize feed concentration variations during tests. Membrane cleaning was performed by forward flushing to preserve membrane integrity. For each test, a 40 mL permeate sample was collected and preserved for water quality indicators assessment. The experiments were performed at the pH of the secondary effluent (see Table 1). In all tests, the reference temperature considered for the calculations of demineralized water flux and permeate flux is 20℃.

The experimental protocol included the following tests: first the determination of the clean water flux, performed with demineralized water for each new set of membranes, followed by series of tests under increased pressure values (1, 1.5, 2, and 2.5 bar) and ending with the study of the membranes' behavior over longer periods of time (in this case 4 h of continuous operation, at 2 bar). The washing test (5 min each) performed with demineralized water was conducted after each ultrafiltration test. In order to obtain reproducible results, three series of ultrafiltration tests were conducted for each membrane set. Each series of tests encompasses four tests at each of the pressures mentioned previously followed by a long test (4 h duration). In this operating mode, the volume reduction factor (VRF) can be calculated, as defined in Eq. (1) [17]:

$$\mathrm{VRF} = \frac{V_0}{V_R} \tag{1}$$

where V_0 = initial feed volume, mL; V_R = retention volume calculated as the difference between initial feed volume and permeate volume, mL.

Another equation used to explain the fouling phenomena was proposed by Mousa et al. [35]:

$$I_t = 1 - \frac{V_p}{V_{DW}} \tag{2}$$

where I_t = fouling index, V_p = volume of permeate collected in a certain period of time, mL; V_DW = volume of demineralized water collected in the same period of time, mL.

The quality of the permeate and removal efficiencies are assessed using Eq. (3):

Table 3
Tested membranes

Nr	Membrane	Material	MWCO, Da	Nominal pore size, nm	Properties
1	ESP04	Modified polyethersulfone (mPES)	4,000	3.46	Hydrophilicity: 2* pH: 1–14 Pressure: max 30 bar Temperature: 80˚C Solvents resistance: medium
2	EM006	Modified polyethersulfone (mPES)	6,000	4.13	Hydrophilicity: 4* pH: 1.5–12 Pressure: max 30 bar Temperature: 65˚C Solvents resistance: medium

Note: *values within range 1–5.

$$RE = \frac{c_i - c_f}{c_i} \times 100\% \tag{3}$$

where RE = removal efficiency of each pollutant, %; c_i = initial pollutant concentration, mg/L; c_f = final pollutant concentration, mg/L.

The commercial membranes tested were purchased from PCI membranes, UK and have the following properties, as indicated by the producer (Table 3). The nominal pore size was calculated using Eq. (4) determined by Lentsch et al. [36]:

$$d = 0.09(MWCO)^{0.44} \tag{4}$$

where d = nominal pore diameter, nm; and MWCO = molecular weight cut-off, Da.

2.3. Analytical methods and apparatus

The COD was determined according to the Standard Method SR EN ISO 6,060:1996 using a C9800 Reactor Hanna Instruments as a block digester and a Jasco UV–vis 530 spectrophotometer to analyze the samples for COD determination of samples from the processes.

A Shimadzu TOC-V_{CPN} analyzer coupled with a TNM-1 unit was used to monitor the permeate quality, in terms of TOC (using the method that calculates non-volatile organic carbon and volatile organic carbon) and TN indicators. The method employed for phenolics analysis is EPA 420.1 for the spectrophotometrical Phenolics determination.

The BOD indicator was determined by OxiTop® method (WTW, Germany) which consists of pressure measurement in a closed system. The micro-organisms present in the sample consume the oxygen and form CO_2, which is absorbed by NaOH, creating a vacuum that can be measured as a mg/l BOD value. The BOD values are directly displayed by the pressure sensor.

Turbidity determinations of wastewaters containing SSs and permeate were performed using ISO 7027:2001 method with a Hanna HI 93703-11 logging microprocessor turbidity meter.

The phosphorus and metals concentrations were determined according to the Standard Methods SR EN ISO 6878:2005 for TP indicator and corresponding SR EN ISO 8288:2001 for each of the metal concentrations (Cu, Cr, Fe, Zn).

3. Results and discussion

3.1. Permeate fluxes and influence of operating conditions

Before any experiments, the new membranes were soaked in demineralized water for 24 h in order to eliminate the conditioning products. Afterward, clean

Table 4
ESP04 and EM006 membranes permeability for demineralized water

Series no	Value	Determination coefficient
ESP04 membrane-DWP		
Series 1	11.29 L/m^{2}hbar	$R^2 = 0.99$
Series 2*	17.44 L/m^{2}hbar	$R^2 = 0.99$
Series 3	17.57 L/m^{2}hbar	$R^2 = 0.99$
EM006 membrane- DWP		
Series 1	10.67 L/m^{2}hbar	$R^2 = 0.99$
Series 2*	10.54 L/m^{2}hbar	$R^2 = 0.98$
Series 3	10.74 L/m^{2}hbar	$R^2 = 0.99$

*Series 2 DWP values are obtained on the same set of membranes as Series 1. For Series 3, a new set of membranes has been used.

Table 5
Fouling indexes registered as a function of pressure, after 1 h tests (Series 2 and 3), EM006 membrane. Mousa et al. [35]

Pressure, bar	Fouling index, Series 2	Fouling index, Series 3
1.0	0.48	0.51
1.5	0.51	0.52
2.0	0.41	0.53
2.5	0.56	0.54

water flux was determined for each set of membranes. This parameter allows the calculation of membranes permeability for demineralized water (DWP). The results in terms of membrane permeability obtained for the two membranes ESP04 and EM006 are presented in Table 4.

The main UF operating conditions investigated in this study are: pressure (p) and operating time (t). These parameters influence the membrane productivity, expressed as flux of collected permeate. The permeate flux variations as a function of time and as a function of pressure are presented in Fig. 2. Throughout all series of tests, the permeate flux displays a constant pattern in time for both membranes, as it can be observed from Figs. 2(a) and 1(d). Considering the applied pressures, ranging between 1 and 2.5 bar, there is a linear increase of permeate flux with the increase of pressure (Fig. 2(b) and (c)). The permeate flux values are much higher in the case of ESP04 membrane, correlated also with the membrane permeability for demineralized water, presented in Table 4.

Since the filtration through EM006 membrane is slower than the ESP04 membrane, it is expected that molecules or small particles smaller than the pore diameter of the 6 kDa yet larger than the diameter of the 4 kDa will tend to deposit on the inner surface of the first membrane. Mousa et al. [35] has encountered the same phenomena with a membrane of 50 kDa as

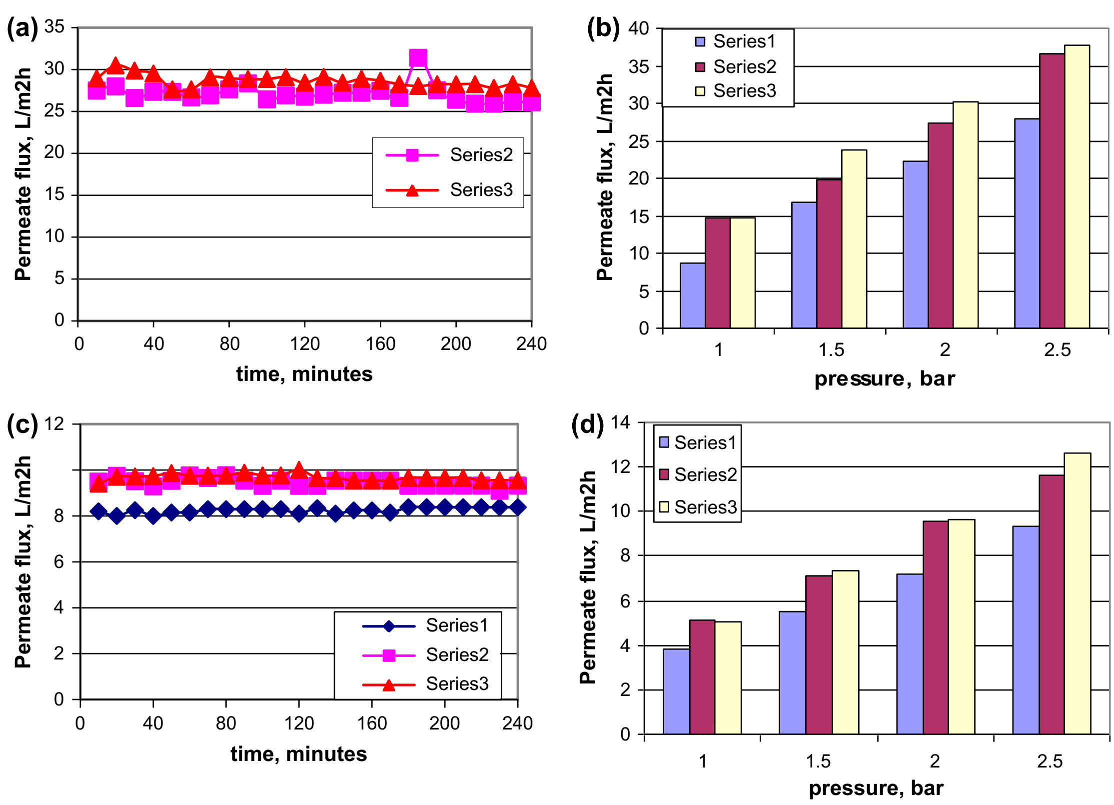

Fig. 2. Flux permeate variation as a function of time, at 2 bar, (a) ESP04 membrane and (c) EM006 membrane and as a function applied pressures, at $t = 1$ h (b) ESP04 membrane and (d) EM006 membrane.

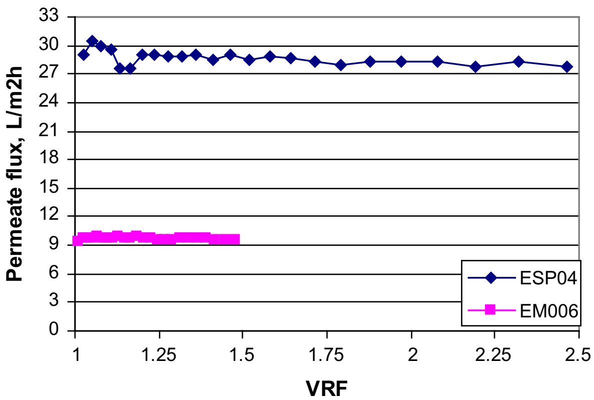

Fig. 3. Permeate flux variation with VRF, $p = 2$ bar.

compared to a membrane of 10 kDa. To check the fouling phenomena that may affect the membranes productivity, a few indicators are discussed.

The VRF increases with the decrease of the retention volume in time. The calculated VRF in this study varies within 1–2.5 for the ESP04 membrane, and between 1 and 1.5 for the EM006 membrane. As the retention volume decreases with the processing time, the VRF parameter increases through the course of the each experiments [36]. The variation of VRF being higher in the case of ESP04 membrane, it is more likely that fouling phenomena will occur for this membrane, rather than for the EM006 membrane. Fig. 3 presents the permeate fluxes versus VRF, for the 4 h tests, performed under a pressure of 2 bar, series 3 of tests for both membranes.

The I_t fouling index proposed by Mousa et al. [35] is another method to assess the membrane status faster and without tedious calculation and it can be applied on any type of membrane. I_t describes the fouling phenomena related also to adsorption of particles into membranes pores. The fouling index was calculated for both membranes. For the EM006 membrane, the fouling index ranges between 0.4 and 0.55, in all cases (Table 5). The same index was calculated for the ESP04 membrane and the results are indicated in Fig. 4. In general, for the 4 kDa membrane, the registered fouling indexes are situated between 0.1 and 0.25. The differences between series 2 of results and series 3 are that in the last case, the membranes were new; therefore, lower values for the fouling index were obtained.

The fouling index displays a constant profile in time, as shown in Fig. 5, in the case of long tests. Also during these tests, the fouling index of the new membranes (Series 3) is lower. This means that during the series 2, the 4 kDa membrane registers the presence of fouling phenomena, probably associated to the adsorption of particles into the membranes pores.

Based on the fouling index values, under the same operating conditions, the main conclusion is that EM006 membrane is more likely to foul when compared to the ESP04 membrane.

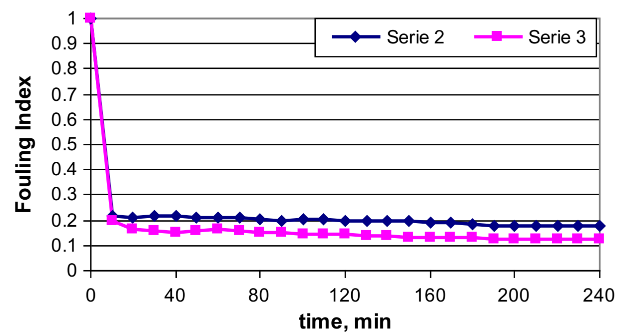

Fig. 5. Comparison between fouling indexes, Series 2 and Series 3 (new set of membranes), at $t = 4$ h and $p = 2$ bar, ESP04 membrane.

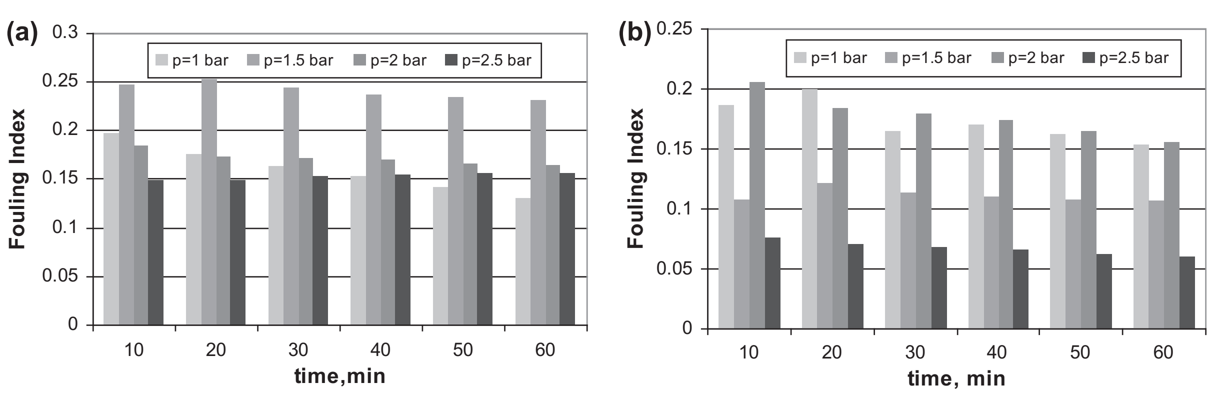

Fig. 4. Comparison between fouling indexes, (a) Series 2 and (b) Series 3 (new set of membranes), ESP04 membrane, at $t = 1$ h.

3.2. Technical performance of UF process

The technical performances of UF process are assessed by the removal efficiencies of solids, organic pollutants, nutrients, and metals, all reported for the permeate. The SSs presence is assessed on the basis of turbidity. The retention of non-biodegradable organic compounds is determined by three indicators: COD, TOC, PHE, and the nutrients presence is given by the total content of nitrogen and phosphorous (TN and TP). The metals and heavy metals presence: Fe, Cu, Cr, Ni, Zn is also monitored.

For both membranes types, under all experimental conditions investigated, the following permeate quality indicators: SS and PHE were 0, thus, the removal efficiency is 100%.

One of the most important aspects related to the reclamation of municipal effluents are the organic loads, reflected in the values of COD and TOC indicators. Under these circumstances, the operating parameters of the ultrafiltration process play an important role. In the case of the ESP04 membrane, the results displayed in Fig. 6(a), indicate that the removal efficiency expressed as COD content varies with pressure between 25 and 40% and the removal efficiency expressed as TOC register a constant profile as a function of pressure, approx. 20%. The variation of removal efficiency expressed as COD may be caused by the method of determination which is less accurate in the low values range of non-biodegradable compounds concentrations. In 4 h (long tests), for the same membrane (Fig. 6(b)), the removal efficiencies display a strong decrease. The best results are obtained for 2 h of continuous operation.

Considering the case of the EM006 membrane, the results are similar in terms of variations as a function of pressure (Fig. 6(c)) and time (Fig. 6(d)), but there are a few observations in the behavior of the 6 kDa membranes, compared to the ESP04 membrane. Firstly, the EM006 membrane is able to retain better the non-biodegradable compounds, in 1 h tests, no matter the applied pressure, when compared to the ESP04. In this case, the removal efficiencies are between 40 and 50% in terms of COD and 50 and 60% in terms of TOC. Secondly, the drop of removal

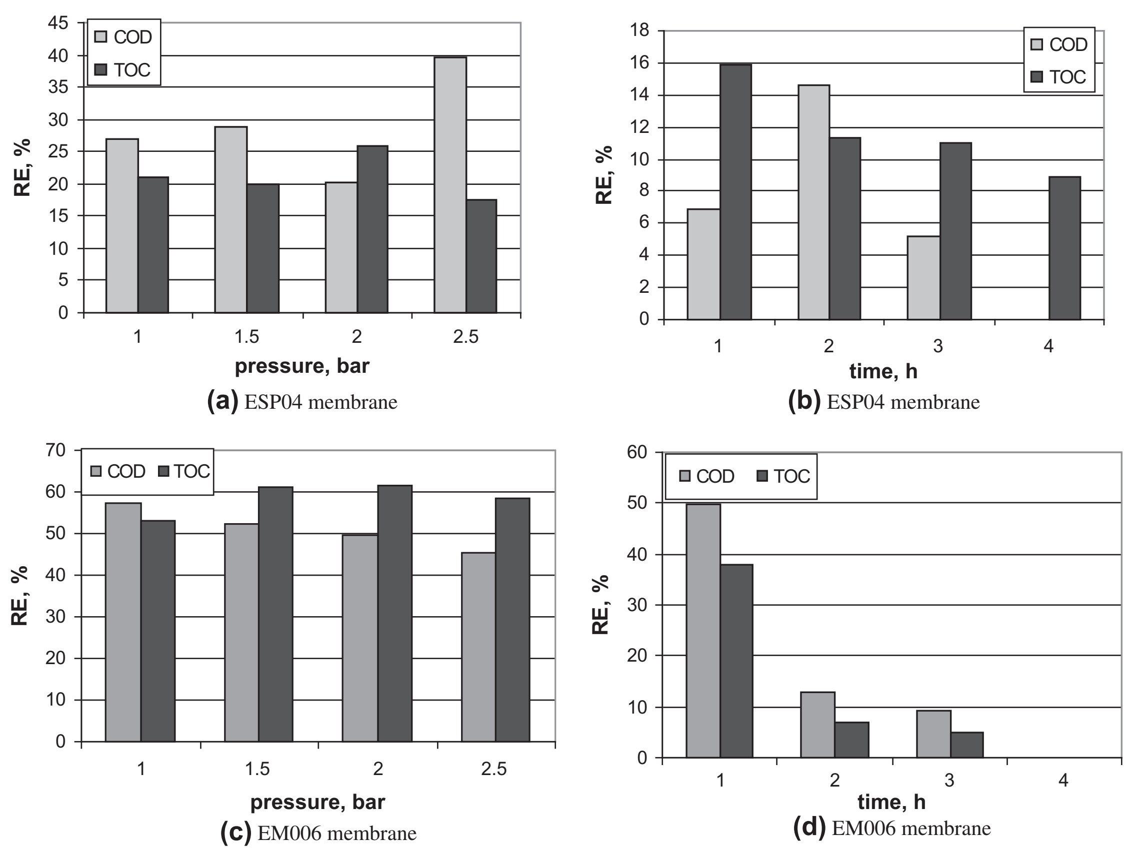

Fig. 6. Removal efficiency (expressed as COD and TOC) variation as a function of pressure and operating time, (a) and (c) during 1 h (b) and (d) at $p = 2$ bar.

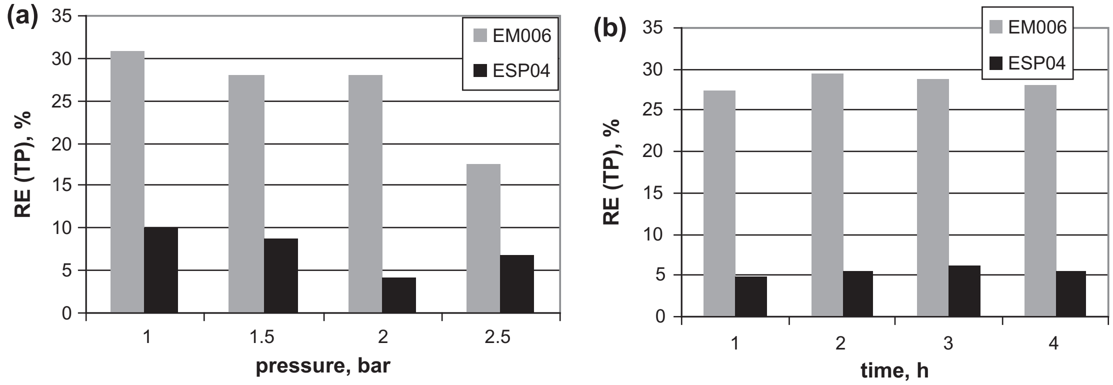

Fig. 7. Removal efficiency (expressed as TP) variation as a function of (a) pressure, during 1 h tests and (b) operating time, for both membranes, at $p = 2$ bar.

efficiency in time is significant, the 6 kDa membrane displaying good results in the first hour of operating conditions, afterward, the removal efficiencies decreasing significantly.

The analysis, corresponding to the nutrients presence, revealed the fact that the compounds containing nitrogen are not retained significantly by both membranes. In this case, it can be considered that the removal efficiency expressed as TN is 0, irrespective of the UF operating conditions. When referring to the phosphorous compounds presence in the permeate, the results presented in Fig. 7, indicate the fact that both membranes are capable of retaining this type of pollutants. The removal efficiency expressed as TP varies between 15 and 30% for the EM006 membrane and decreases with the increase of applied pressure and 4 and 10% for the ESP04. In time, the EM006 is retaining constantly approx 30% of the P-containing compounds. To come to a conclusion, the EM006 membrane displays superior performances in retaining the pollutants with P. The results in terms of phosphorous compounds removal are in agreement with other studies reported in literature, performed on UF membranes [24,37].

The metals content expressed as four main cations (Fe, Cr, Cu, Zn) was also investigated in this study. It has to be mentioned that the secondary effluent has low concentrations of metals, in general, varying between 10 and 110 μg/L for heavy metals and 290 and 440 μg/L for Fe (Table 1) which can be explained by the fact that the inlet flow entering the Iasi MWTP is mainly domestic in nature. The UF permeate registers lower values e.g. for 26–32 μg Cr /L; 34.5–51.4 μg Cu /L; 10–60 μg Zn /L and 100–200 μg Fe /L, depending on the process parameters variations. The removal efficiencies expressed as metal ions retention as a function of UF operating conditions is presented in Fig. 8. This is similar to the case reported by Dialynas and Diamadoupoulos [23], where the secondary effluent was ultrafiltered on membranes with nominal pore

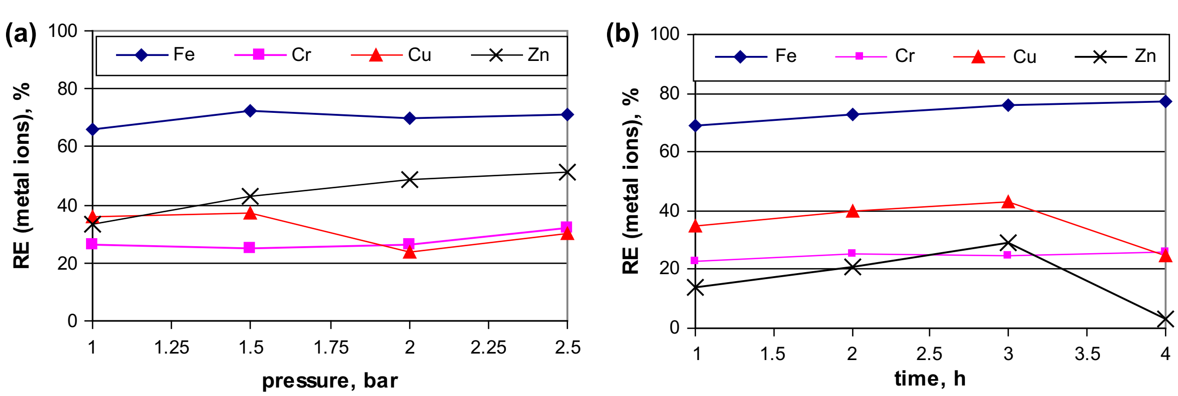

Fig. 8. Removal efficiency (expressed as metal ions) variation as a function of (a) pressure, ESP04 membrane, during 1 h tests and (b) time, EM006 membrane, at $p = 2$ bar.

Table 6
Fouling indexes variation as a function of time, $t = 4$ h, $p = 2$ bar, (Series 2 and 3), EM006 membrane

Time, h	Fouling index, Series 2	Fouling index, Series 3
1	0.43	0.55
2	0.42	0.54
3	0.42	0.53
4	0.41	0.52

size of 40 nm, under maximum 0.5 bar. These authors also obtained removal efficiencies for metal ions. The explanation for the metals removal during UF process is that the metals are in particulate form and can be retained by both membranes.

In 1 h tests, the EM006 membrane displays better results than the ESP04 membrane. This fact combined with the smaller volumes of permeate collected in time in the case of the EM006 membrane can be attributed to the deposition or adsorption of particles smaller than 6 kDa, but larger than 4 kDa. More investigations are required in this direction to confirm the phenomena occurring at the membrane surface. In the case of long tests (4 h), the 4 kDa has a more constant trend in terms of permeate quality, even though the

Table 7
Comparison between permeate quality and international requirements for water reuse

Water quality indicator		Permeate quality	US regulations**	Spain regulations***
pH	Agricultural reuse	7.44–7.88	6.5–8.4	5.5–9
	Restricted urban reuse		6.0–9.0	5.5–9
	Industrial application		8.3–10	5.5–9
BOD, mg O_2/L	Agricultural reuse	12–19	≤ 30	n.a.
	Restricted urban reuse		≤ 30	n.a.
	Industrial application		≤ 30	n.a.
COD, mg O_2/L	Agricultural reuse	10–30	n.a.	≤ 30
	Restricted urban reuse		n.a.	≤ 30
	Industrial application		n.a.	≤ 30
SS, mg/L	Agricultural reuse	0	≤ 30	≤ 35
	Restricted urban reuse		≤ 30	≤ 20
	Industrial application		≤ 30	≤ 5
NO_3^-, mg/L	Agricultural reuse	50–52	5–30	≤ 50
	Restricted urban reuse		n.a.	≤ 50
	Industrial application		n.a.	≤ 50
TN, mg/L	Agricultural reuse	15.98–19.06	n.a.	≤ 3
	Restricted urban reuse		n.a.	≤ 3
	Industrial application		n.a.	≤ 3
TP, mg/L	Agricultural reuse	0.5–0.87	n.a.	≤ 0.4
	Restricted urban reuse		n.a.	≤ 0.4
	Industrial application		n.a.	≤ 0.4
Fe, mg/L	Agricultural reuse	0.1–0.2	≤ 5	n.a.
	Restricted urban reuse		n.a.	≤ 2
	Industrial application		≤0.02–0.05	≤ 2
Cu, mg/L	Agricultural reuse	0.035–0.052	≤ 0.2	≤ 0.2
	Restricted urban reuse		n.a.	n.a.
	Industrial application		≤0.01	n.a.
Cr, mg/L	Agricultural reuse	0.026–0.032	≤ 0.1	≤ 0.1
	Restricted urban reuse		n.a.	n.a.
	Industrial application		n.a.	n.a.
Zn, mg/L	Agricultural reuse	0.01–0.06	≤ 2	≤ 2
	Restricted urban reuse		n.a.	n.a.
	Industrial application		n.a.	n.a.

Notes: Agricultural reuse non-food crops.

Industrial application e.g. feed water in boilers.

*Values are calculated based on the best average removal efficiency obtained for each specific quality indicator, in 1 h tests.

**Data available from USEPA Report 2012 [38].

***Data available from Spanish Regulations RD 1620/2007 and RD 849/1986 with modifications [39,40].

removal efficiencies are lower compared to the 6 kDa membrane.

To be able to compare the quality of the obtained permeate with legal requirements for reused water, it has to be mentioned that at international level, the situation in 2012 is the following: in USA, 48 out of 55 States have guidance or regulations targeted on reclaimed water or reports on case studies, while in EU, there are only two countries with implemented legislation on water reuse, namely, Cyprus and Spain, and case studies in other countries (like Italy and Greece). In Table 7, a comparison of water quality resulting from the UF stage and the US and Spanish legal requirements for water reuse is presented. The comparison is made considering the potential applications of reclaimed water, as mentioned before, agricultural reuse: irrigation for non-food crops (in Dancu greenhouses) and restricted urban reuse: cleaning operations for the Iasi MWWTP facility platforms. Also, the most restrictive water quality parameters are included for the case of industrial reuse as feed water in boilers.

The data obtained in this study show that UF performed using 4 and 6 kDa membranes can achieve good quality effluents, with most of the investigated quality indicators in compliance with international standards on water reuse. However, it has to be considered that the data presented in Table 6 for permeate quality are obtained in the case of short tests (1 h of operation) and do not give an indication about the permeate quality in continuous operating conditions, like for example, when implementing the technology in the MWWTP. Furthermore, it was observed from the long tests (4 h) results, that the removal efficiencies have a clear tendency of decreasing for all the pollutants studied, this being a good starting point for pilot-scale studies.

4. Conclusions

In this study, ultrafiltration was considered as an advanced treatment stage for the secondary effluent coming from Iasi MWWTP. The objective was to assess the performances of UF process in the view of effluent reuse, either in agricultural purposes (water for irrigation of non-food crops) or in urban reuse (within the MWWTP, or in other purposes).

Considering the membrane performances in terms of permeate quality, the results indicate that the ESP04 has a permeate flux 1.6 times higher than the EM006 membrane. In this case, it is more likely that for the EM006 membrane, the molecules or small particles smaller than the pore diameter of the 6 kDa yet larger than the diameter of the 4 kDa will tend to deposit on the inner surface of the membrane. The phenomena occurring at the membrane surface were analyzed by VRF index, which in this case shows variations of 1–2.5 for the ESP04 membrane, and between 1 and 1.5 for the EM006 membrane, meaning that ESP04 is more susceptible to fouling. In contrast, the I_t index shows the degree of fouling caused not only by the cake layer presence, but also associated with the adsorption phenomena. In our case, the fouling index calculated indicates that EM006 is more likely to foul during UF ($I_t = 0.4–0.55$) in comparison with ESP04 membrane ($I_t = 0.1–0.25$).

Referring to the permeate quality, the results indicated that membrane EM006 is capable of retaining better the pollutants investigated, especially in the case of short tests (1 h). However, for 4 h tests, the ESP04 give a more constant permeate quality. The best removal efficiencies were obtained for pressures in the case of 1.5 and 2 bar. The solids present in the secondary effluent were retained completely by both membranes. The removal efficiencies vary significantly depending on pressure, time, and MWCO, but the best removal efficiencies registered for the non-biodegradable compounds are up to 50% for COD, 60% for TOC, and 100% for PHE. The compounds containing N did not show any significant removal, while the ones containing P were removed up to 30%. Furthermore, the metal ions concentrations investigated, after UF, indicate different proportions of retentions: Fe up to 80%, Cr up to 25%, Cu up to 30%, and Zn up to 40%, which can be attributed to the particulate form of the compounds containing these cations.

The data obtained in this preliminary study show that UF performed using 4 and 6 kDa membranes can achieve good quality effluents, with most of the investigated indicators in compliance with international standards on water reuse. In conclusion, the ultrafiltration of the secondary municipal effluent from Iasi MWWTP, applied as an advanced treatment step, is a feasible option for water reclamation, but special attention is required to the nitrogen-containing compounds and especially, nitrates concentration which is slightly exceeding the maximum admissible concentration.

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