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Optimization of coagulation step in membrane treatment of municipal secondary effluents

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ABSTRACT

Secondary effluents of municipal wastewater are the major pollutant and the most significant irrigation reservoir at the same time. Although secondary effluents are widely used for irrigation of some crops, the unrestricted irrigation and groundwater recharge require implementation of membrane technologies. A combination of coagulation, ultrafiltration (UF) and nanofiltration (NF) stages has a potential to turn secondary effluents to treasure from waste. The current study focuses on the optimization of the coagulation of secondary effluents from Sede Teiman wastewater treatment plant (Southern Israel). The study was performed with ferric chloride, and the optimal dose was determined in jar tests by parallel measurement of total suspended solids (TSS), UV absorption at 254 nm (UV_{254}) and conductivity. The optimal dose of 130 mg/l $FeCl_3·6H_2O$ (equivalent to 27 mg/l Fe^{3+}) was then applied for pretreatment of secondary effluents prior to UF membrane. The combined coagulation-UF treatment reduced the total organic carbon (TOC) by more than 50%. Moreover, it increased the average flow rate during 30 min filtration cycles by up to 90% when compared without coagulation. The most significant improvement in UF performance due to coagulation was observed in membranes with a molecular weight cut-off (MWCO) greater than 30 kDa.

Keywords: Tertiary treatment; Coagulation; Fouling; Ferric chloride; UF membrane

1. Introduction

Desalination of seawater is becoming a major technology for the production of potable water in Israel. In general, this process is based on a few pretreatment steps, followed by a high pressure reverse osmosis (RO) membrane system. Although not yet implemented, a similar scheme could be applied for the treatment of secondary effluents of municipal wastewater. The benefits of the application are evident. The cost of tertiary treatment of wastewater is estimated at one third of the cost of seawater desalination, due to a lower concentration of dissolved solids (salinity) in the former (18.9 vs. 48 cents/m^3) [1]. The resulting tertiary effluents can be used for unrestricted irrigation including the irrigation of crops that are eaten uncooked [2]. If the quality of tertiary effluents is increased to the quality of drinking water, then tertiary effluents could be used as a secondary source of drinking water under drought conditions.

Secondary effluents are contaminated with high concentrations of nitrates, phosphates and organic matter. In addition, secondary effluents are of relatively high salinity and contain hazardous anthropogenic compounds. The complex tertiary and quaternary treatment

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needed to remove the above impurities is based on a multiple integrated membrane system (MIMS) that includes stages of ultrafiltration (UF) for removal of the residual suspended solids and nanofiltration (NF) for removal of organic trace pollutants and reducing the inorganic salt concentration. Two main obstacles in the direct application of UF for the treatment of secondary effluents are the low retention of organic content, and irreversible fouling, which alters the rejection, decreases the flux, shortens the membrane lifetime, and increases operating pressure and cleaning frequency. The problem of irreversible fouling is often resolved by a chemical cleaning operation that is performed with hypochlorite (HOCl). HOCl's popularity is attributed to its availability, reasonable price and high efficiency for both cleaning and short bio-sanitation actions. However, this chemical is harmful to most commercial polymer-based membranes, and eventually causes impaired performance [3,4].

Membrane foulants (sparingly soluble inorganic compounds, colloidal or particulate matter, dissolved organics, chemical reactants, and microorganisms) can reduce the water flux through a membrane by as much as 90% [5]. Moreover, previous studies have shown that a flux drop of greater than 10% over a 30 min filtration period might lead to irreversible UF fouling [6,7].

Coagulation and adsorption onto powered activated carbon (PAC) are two different pre-treatment methods that can significantly reduce fouling. Although the complexity and cost of these pre-treatments currently limit full scale implementation of such a scheme, wide pilot testing has been performed and extensively reported. In general, the retention of organic content assessed through aggregate parameters such as biological oxygen demand (BOD), chemical oxygen demand (COD) or dissolved organic carbon (DOC), is encouraging. Using turbidity to measure concentration of organic content, Abdessemed and Nezzal reported that flocculation with $CaCl_2$ and adsorption on powdered activated carbon (PAC) reduces COD in secondary effluents of domestic wastewater by 80% [8]. Shon et al. reported 86% COD removal with 40 mg/l $FeCl_3$ (equivalent to 14 mg/l Fe^{3+}) and 20 mg/l PAC [9]. In general, ferric chloride was compared favorably to aluminum sulfate (alum) and therefore was used in the majority of studies [10]. Higher ranges of 120 mg/l $FeCl_3$ (equivalent to 41 mg/l Fe^{3+}) and 1 g/l PAC have been reported [11–15] and were sufficient to remove 91% DOC from biologically treated secondary effluents of municipal wastewater. Removal of 88% of organic matter from synthetic wastewater with 50 mg/l $FeCl_3$ (equivalent to 17 mg/l Fe^{3+}) and 0.5 g/l PAC was reported by Kim et al. [16]. A combination of 130 mg/l $FeCl_3{\cdot}6H_2O$ (equivalent to 27 mg/l Fe^{3+}), 0.6 g/l PAC and UF at a dead end cell were sufficient to keep the DOC level below 3 mg/l [2]. Adsorption on 0.6 g/l octadecyltrimethylammonium bromide (ODTMA) - bentonite and flocculation with 130 mg/l $FeCl_3$ reduced the dissolved organic carbon (DOC) level by 46% [17]. The role of membrane pore size was determined by parallel examination of DOC retention and fouling through membranes with a molecular weight cut off between 2 and 100 kDa. The membrane played a minor role in the retention of DOC after pretreatment, ranging from a negligible 2.9% for a 100-kDa-MWCO membrane to 17% for 10- and 2-kDa membranes. The latter membranes, however, developed significant fouling, with a 35% flux drop during the first 30 min of the filtration cycle. The drop in flux for the 50- and 100-kDa membranes was low and approximated 3% on average. The optimal MWCO interval of 20- to 50-kDa in combination with flocculation/PAC pretreatment produced a significant reduction in organic content with minimal membrane fouling [2].

A majority of previous experiments were performed under well-defined lab conditions. It was therefore decided to conduct the pilot studies in a wastewater treatment plant (WWTP) in order to test the secondary effluent, to be used later on as the raw influent of a NF desalination membranes system. The study also inspected the role of membrane pore size and coagulant addition in minimizing membrane fouling. The minimized cost of the MIMS through optimization of the pretreatment stages was targeted.

2. Materials and methods

2.1. Jar test

The optimal coagulant concentration was determined with jar tests. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) in wide (0–500 mg/l) and narrow (90–180 mg/l) concentration ranges was poured into 6 well stirred 800 ml glass jars in a conventional multiple stirrer (PHIPPS & BIRD STIRRER, 7790-402). The slurry was (i) mixed rapidly at 100 rpm for 1 min; (ii) mixed slowly at 30 rpm for 20 min; and (iii) allowed to settle quiescently for 30 min. Samples collected by slow decantation from the upper part of the test jars were analyzed for conductivity (Cyberscan con 10, Eutech Instruments, Singapore), pH (PHM210, Radiometer Analytical SAS, France), total suspended solids (WTB Binder, Class 2ED 115/E2 #00-17337, Binder Inc., USA) and DOC (Apollo 9000 TOC analyzer, Tekmar Company, Cincinnati, OH).

2.2. MIMS

The experiments were performed in WWTP of Beer Sheva (southern Israel) in Sede Teiman. The secondary effluents were pumped through tailor-made UF

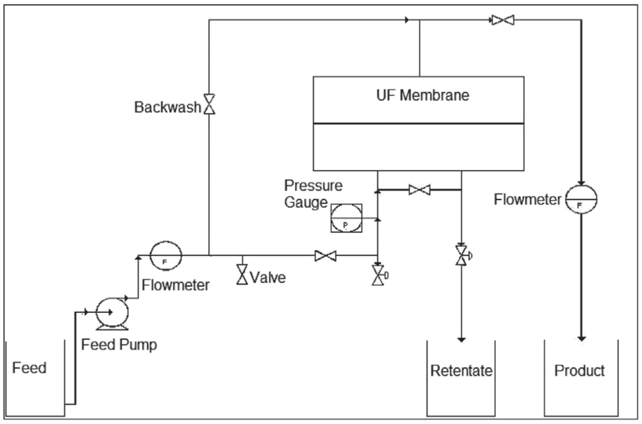

Fig. 1. The UF Flowchart.

(Fig. 1) followed by NF membrane cells. The experiments were performed with commercially available polyethersulphone PES-10 (Koch UF HFK-131), PES-50 (Microdyn-Nadir UH050p, Wiesbaden, Germany) and polysulphone PS-30 (GE Osmonics UF ER) membranes. The active membrane area was 139 cm^2 (13 cm × 13 cm). The coagulation was performed in a batch mode inside the raw effluent tank. The fast and slow mixing were performed with impeller (Fried electric, DS-2E). The initial flux rates of 53, 177 and 452 l/m^2-h for PES-10, PS-30 and PES-50, respectively, were measured. The filtration was performed at 9:1 filtrate to retentate ratio. Flux and transmembrane pressure (TMP) were measured every 2 min. Backwash was performed every 30 min for 5 min using tap water at a pressure that exceeds the operational TMP by 1 bar. The experiments were performed in triplicates for each membrane.

2.3. Pore size determination

The membrane pore size was determined in the lab with a previously described stirred cell [6]. Parallel determination was performed by the water permeability and solute tests. The former test, based on Hagen–Poiseuille equation, allows determination of the mean pore size:

$$d_p = 2\sqrt{\frac{8\mu\Delta x M}{A_k}} \tag{1}$$

where μ is the viscosity of water, Δx is the membrane thickness, A_k is the membrane surface porosity (0.16 for PS-30 and 0.08 for PES-10, determined by weighing of dry and wet samples), and M is the membrane permeability.

In the present work solute transport tests were performed with polyethylene glycol/polyethylene oxide PEG/PEO polymers, and with dextrans (Fluka GmbH, Germany). Seven PEG of 0.3, 0.6, 3.35, 6, 10, 20, 35 kDa and three PEO of 100, 200 and 600 kDa molecular weights (MW) were used. The wide MW range of PEG/PEO polymers was selected to obtain the 0 to 100% polymer rejection. The Dextrans of MW of 6, 40, 70 and 100 kDa were used. Each solution was prepared in deionized water (MilliQ quality) at 1 g/l initial concentration. The concentrations of origin and permeate solutions were measured as DOC. The rejection percentage was calculated as:

$$R = \left(1 - \frac{C_{i,p}}{C_{i,0}}\right) \times 100\% \tag{2}$$

where $C_{i,p}$ is the concentration of polymer fraction i in the permeate (mg/l), and $C_{i,0}$ is the concentration of polymer fraction i in the feed (mg/l).

The obtained rejection values were plotted against the hydrodynamic radii of the polymers. Molecular weights were converted into hydrodynamic radii by comparing the diffusivities of the spheres obtained from the Stokes–Einstein equation (Eq. (3)) with the diffusivities of organic molecules with molecular masses above 1000 Da, as suggested by Polson (Eq. (4)):

$$D_{AB} = \frac{kT}{6\pi r\mu} \tag{3}$$

where D_{AB} is the diffusivity of a perfect sphere in water (m^2/s), k is the Boltzmann constant (J/K), T is the absolute temperature (K), r is the radius of the sphere (m), and μ is the water viscosity (Pa s):

$$D_{AB} = \frac{9.4 \times 10^{-15} T}{\mu (M_A)^{\frac{1}{3}}} \tag{4}$$

where M_A is the molecular weight of the large molecule in Da.

The hydraulic diameter of the polymers (d) was calculated by combining Eqs. 3 and 4:

$$d = 0.156 M_A^{0.33} \tag{5}$$

3. Results and discussion

The membrane pore size was determined by passive solute tests. The results for PS-30 and PES-10 are depicted in Figs. (2 and 3), respectively. The determined

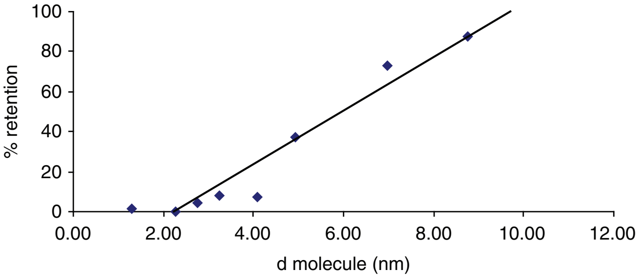

Fig. 2. PEG/PEO retention curves at PS-30 membrane (solute diameter vs. retention %).

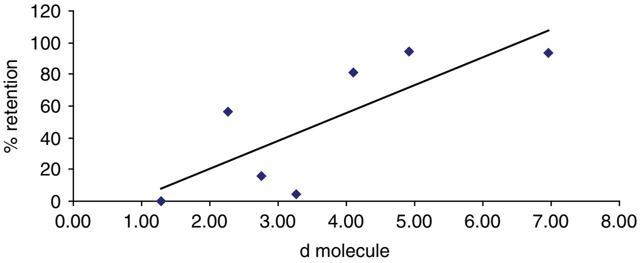

Fig. 3. PEG/PEO retention curves at PES-10 membrane (solute diameter vs. retention %).

MWCO of PS-30 and PES-10 were 215 and 57.3 kDa, and were transferred into membrane pore sizes of 8.9 and 5.9 nm, respectively.

The optimal coagulant dose was determined in parallel by total suspended solids (TSS), DOC and conductivity. The results of TSS measurements are depicted in Fig. 4. The minimum concentration of 4 mg/l suspended solids was achieved with 300 mg/l $FeCl_3 \cdot 6H_2O$ (equivalent to 62 mg/l Fe^{3+}). Based on previous data, and considering further processing of the permeate by NF/RO treatment, the range of coagulant concentration was lowered to 100–200 mg/l and an additional experiment was performed [2–8]. Fig. 5 depicts the influence of lowered coagulant concentration on TOC and conductivity. The 10 mg/l DOC level was measured at 130 mg/l $FeCl_3 \cdot 6H_2O$ (equivalent to 27 mg/l Fe^{3+}). The obtained concentration is similar to the value reported previously [2]. The relatively low conductivity of 1100 µS/cm at that coagulant dose is explained by a balance between the dose needed for coagulation and a higher dose with larger residual $Fe_{(s)}$ concentration in the solution. In addition, the higher dose of the coagulant lowers the pH and introduces more charged $Fe^{3+}_{(aq)}$ and chloride ions that increase the conductivity. That is in contrast to net ferrohydroxide flocks that form at neutral pH levels of 6–7.

The obtained optimal dosing of coagulant was used for a pretreatment of Sede Teiman secondary effluents prior to the UF membrane filtration. The flux through PES-10, PS-30 and PES-50 during 30 min filtration and 5 min backwash in experiments with and without coagulation step are depicted in Figs. (6–8). The initial flux after backwash of PES-10 was low and it was therefore decided not to continue with additional cycles. Without coagulant, the flux dropped by 39%, 47% and 64% for PES-10, PS-30 and PES-50 respectively. The higher degree of fouling with PS-30 and PES-50 is explained by the internal blocking of the membrane pores by molecules with hydrodynamic radii comparable to the pore size. Higher mass transfer rates with higher initial fluxes contribute to the observed order of blocking. Similar observations were described previously [18].

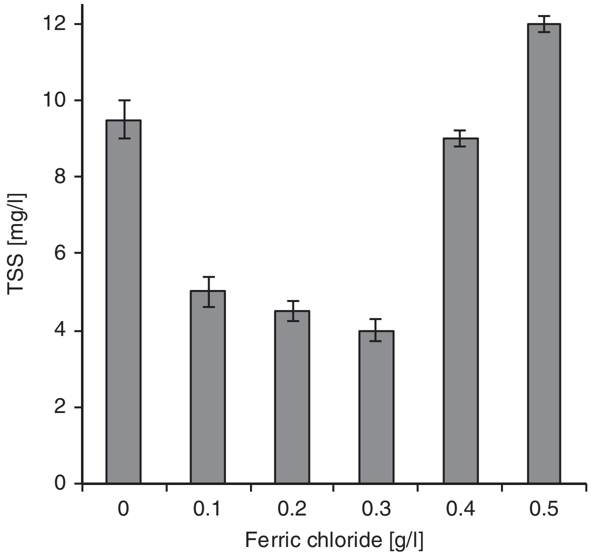

Fig. 4. TSS test.

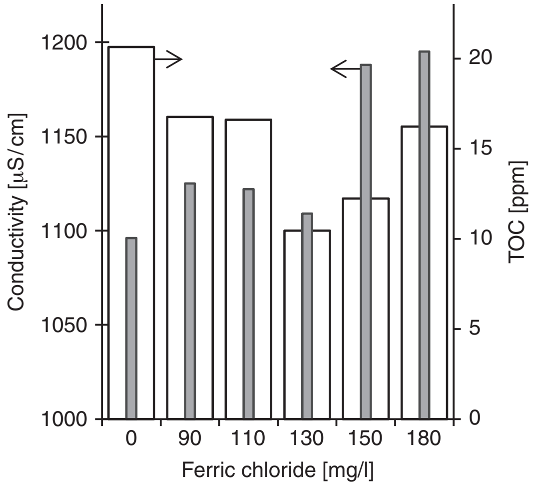

Fig. 5. TOC and conductivity test.

Addition of the coagulant lowered the fouling. At the same time, the average flow rate through PS-30 was

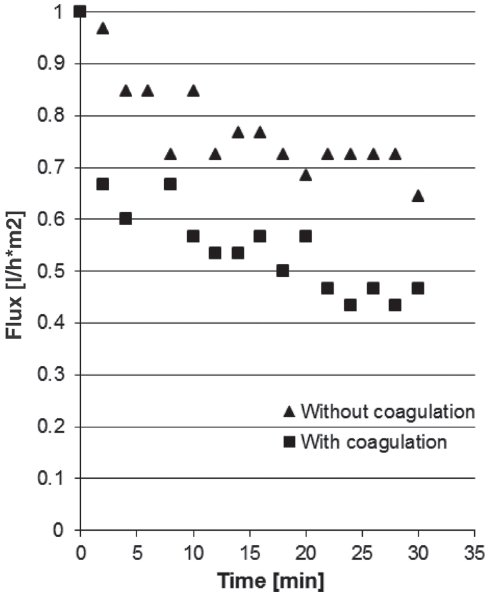

Fig. 6. Flux drop in PES-10.

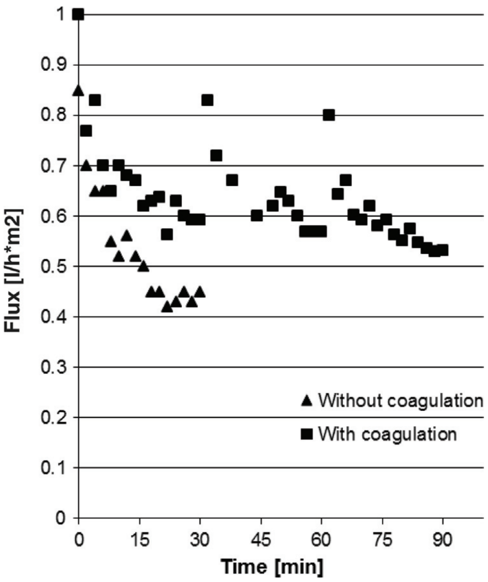

Fig. 7. Flux drop in PS-30.

increased by 28% and through PES-50 by 90% during a 30 min filtration cycle. The flux reduction was minimized from 64% to 40% reduction for PES-50 and from 47% to 41% for PS-30. Opposite results for PES-10 (increase in flux drop from 39% to 53%) were related to the coagulation mechanism. During initial flock nucleation there is a certain concentration of nanoparticles added to the solution. The coagulation flocked organic matter larger than 10 kDa but also added nanoparticles during initial nucleation [19]. Thus the nanoparticles freely penetrated

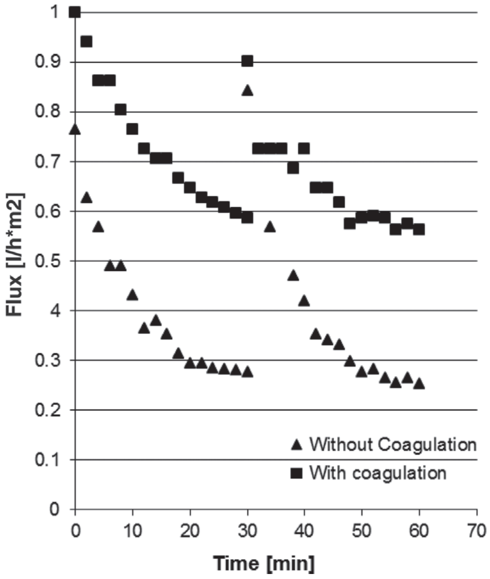

Fig. 8. Flux drop in PES-50.

through membranes with larger pore size but increased the internal blocking of the PES-10 pores. The formed flocks contributed to the lowered fouling in PES-50 membranes but not in the smaller ones. The coagulation made the fouling reversible, as evident from backwash studies. A similar conclusion was achieved by measuring the weight-averaged MW of compounds in the filtrate of the UF membrane with or without a pretreatment. In this type of analysis, a significant reduction in the weight-averaged MW was detected, ranging from mean values of 675 Da (in the absence of a pretreatment stage) to 314 Da (in the condition that included a pretreatment stage) [5].

The initial flux was linearly dependent on the membrane pore size. The initial absolute flux was measured at three times greater for each 20 kDa enlargement of the membrane pore size, starting from 53.2 l/m^2-h in 10 kDa membrane. Table 1 summarizes the turbidity test results for the three membranes. UF alone can reduce the turbidity levels by more than 75%. Further reduction can be achieved by coagulation.

Table 1
Turbidity levels of different water sources in NTU

Effluent stage/ Membrane type	PES 10 kDa	PS 30 kDa	PES 50 kDa
Wastewater(untreated)	*3.8*	*4.7*	*2.8*
After UF	0.4	1.2	0.4
After Coagulation	2.0	3.3	1.9
Coagulation+UF	0.4	0.4	0.3

4. Conclusions

The coagulation is an essential pretreatment step needed for proper UF membrane operation. The filtration performed without coagulant resulted in significant fouling observed by severe flux drop, and in lower reduction of organic matter. However the found optimal coagulation concentration is rather high and is based on jar-test experiment. The high ferric chloride concentration can be reduced if the combined treatment includes the UF membrane step. The reduction can contribute to the economics of the treatment.

The careful choice of the membrane will minimize the fouling and allow a higher degree of DOC retention. Opposite to the intuitively expected the membrane with low MWCO does not improve much the retention of organic matter but certainly causes severe fouling. It is therefore desirable to carefully design the treatment setup and to choose the membranes that combine low fouling with reasonable organic matter removal. In our study those were the membranes with MWCO higher than 30 kDa. The combination of a proper membrane and optimal coagulation regime resulted in more than 50% DOC removal. The overall goal of the project is to receive the secondary effluents in the quality of drinking water, and higher degree of organic retention is a serious encouraging sign along the road. The average TOC levels below 3 mg/l and absence of dangerous organic compounds may soon allow unlimited use of the secondary effluents for irrigation and for groundwater recharge.

References

[1] P. Glueckstern, M. Priel, E. Gelman and N. Perlov, Wastewater desalination in Israel, Desalination, 222 (2008) 151–164.

[2] U. Goren, A. Aharoni, M. Kummel, R. Messalem, I. Mukmenev, A. Brenner and V. Gitis, Role of Membrane Pore Size in Effective Tertiary Flocculation/Adsorption/Ultrafiltration Treatment of Municipal Wastewater, Sep. Purif. Technol., 61 (2008) 193–203.

[3] V. Gitis, R.C. Haught, R.M. Clark, J. Gun and O. Lev, Application of nanoscale probes for the evaluation of the integrity of ultrafiltration membranes, J. Membr. Sci., 276 (2006) 185–192.

[4] Y.-N. Kwon and J.O. Leckie, Hypochlorite degradation of crosslinked polyamide membranes I. Changes in chemical/morphological properties, J. Membr. Sci., 283 (2006) 21–26.

[5] H.K. Shon, S. Vigneswaran, R. Ben Aim, H.H. Ngo, I.S. Kim and J. Cho, Influence of flocculation and adsorption as pretreatment on the fouling of ultrafiltration and nanofiltration membranes: Application with biologically treated sewage effluent, Environ. Sci. Technol., 39 (2005) 3864–3871.

[6] D. Kuzmenko, E. Arkhangelsky, S. Belfer, V. Freger and V. Gitis, Chemical cleaning of UF membranes fouled by BSA, Desalination, 179 (2005) 323–333.

[7] E. Arkhangelsky, D. Kuzmenko and V. Gitis, Impact of chemical treatment on properties and functioning of polyethersulfone membranes, J. Membr. Sci., 305 (2007) 176–184.

[8] D. Abdessemed, G. Nezzal and R. Ben Aim, Coagulation-adsorption-ultrafiltration for wastewater treatment and reuse, Desalination, 131 (2000) 307–314.

[9] H.K. Shon, S. Vigneswaran and H.H. Ngo, Effect of partial flocculation and adsorption as pretreatment to ultrafiltration, AICHE J., 52 (2006) 207–216.

[10] J. Haberkamp, A.S. Ruhl, M. Ernst and M. Jekel, Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behavior in ultrafiltration, Water Res., 41 (2007) 3794–3802.

[11] V. Gitis, A. Lerch and R. Gimbel, Retention of humic acid by ultrafiltration with polyaluminium coagulant, J. Water Supply Res. T., 54 (2005) 213–223.

[12] J.W. Lee, J.I. Chun, H.J. Jung, D.H. Kwak, T. Ramesh, W.G. Shim and H. Moon, Comparative studies on coagulation and adsorption as a pretreatment method for the performance improvement of submerged MF membrane for secondary domestic wastewater treatment, Sep. Sci. Technol., 40 (2005) 2613–2632.

[13] H. Liu and L. Song, Titanium-based photocatalysis as the pretreatment for ultrafiltration of secondary municipal effluent with low concentration of organic matters, Water Resources Management IV, WIT Transactions on Ecology and the Environment (Eds. Brebbia C.A.; Kungolos A), 103 (2007) 411–420.

[14] X.D. Wang, L. Wang, Y. Liu and W.S. Duan, Ozonation pre-treatment for ultrafiltration of the secondary effluent, J. Membr. Sci., 287 (2007) 187–191.

[15] S.H. Chuang, W.C. Chang, T.C. Chang and S.J. You, Improving the removal of anions by coagulation and dissolved air flotation in wastewater reclamation, Environ. Technol., 27 (2006) 493–500.

[16] S.L. Kim, J.P. Chen and Y.P. Ting, Study on feed pre-treatment for membrane filtration of secondary effluent, Sep. Purif. Technol., 29 (2002) 171–179.

[17] N. Siebdrath, G. Ziskind and V. Gitis, Cleaning secondary effluents with organoclays and activated carbon, J. Chem. Technol. Biotechnol., (2011), DOI 10.1002/jctb.2681.

[18] S. Abdolhamid, G. Ali, M. Toraj and S.M. Sayed, Experimental performance evaluation of polymeric membranes for treatment of an industrial oily wastewater, Desalination, 262 (2010) 235–242.

[19] L. Yang, B. Sun and W. Huang, Study on Removal of Organics of Different Molecular Weight by Coagulation-Membrane Filtration Process, J. Sustain. Develop., 3 (2010) 191–196.