



Rethinking the role of in-line coagulation in tertiary membrane filtration of municipal effluents



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ABSTRACT

In-line coagulation with aluminum or iron salts and ultrafiltration (UF) or microfiltration (MF) membranes is a valuable treatment option. The efficiency of the treatment is often evaluated by the achieved separation degree. That separation-oriented approach implies the coagulation with doses that are prohibitively high for many operations including the tertiary effluent treatment. The main purpose of the advanced wastewater treatment however is the retention of microorganisms and suspended solids, and that goal can be achieved even without coagulants. Thus the in-line coagulation can pursue the prevention or minimization of the irreversible fouling as an ultimate goal not related to the maximal separation of organic and inorganic impurities.

Pilot experiments at conventional activated sludge (CAS) municipal wastewater treatment plant confirmed that the addition of 1 mg/L Fe³⁺ prevents the irreversible fouling as efficiently as the addition of 5 and 10 mg/L Fe³⁺. The economic impact of the suggested alteration is significant. Estimated operational expenses (OPEX) of a filtration at 60 LMH with 45 min cycles and 1 chemical – enhanced backwash per day is around 2 cents (€)/m³, almost a half of an OPEX of the separation-oriented treatment.

Intermittent in-line coagulation down to first 2.5 min of 30 and 45 min filtration cycles is another cost-effective method to successfully depress the fouling. The success is explained by two-stage kinetics of a cake formation. At ripening stage, a layer of flocks restricted by a membrane gradually covers its surface and forms an initial dynamic cake. At operable stage, the cake entraps fresh solutes and prevents their contact with a membrane surface even without a coagulant. A superposition of two approaches reduces the consumption of ferric chloride coagulant by 94%.

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1. Introduction

Treatment of municipal wastewater by a conventional activated sludge (CAS) discharges large amounts of secondary effluents that can potentially be used for irrigation. The irrigation is limited by a constant presence of various impurities including nitrates, phosphates, organic matter, suspended solids and microbial pathogens [1–3]. Ultrafiltration (UF) and microfiltration (MF) advanced membrane treatments can eliminate or diminish the impurities and upgrade the quality of tertiary effluents to the level of unrestricted irrigation or even indirect potable use [4]. The ultimate drawback in UF/MF membrane applications for wastewater reclamation is a considerable organic fouling [5,6]. This fouling increases the membrane resistance, requires more chemicals for an intense membrane cleaning, and results in higher UF/MF operational costs [7].

Both the internal pore blocking and the cake formation are important membrane fouling mechanisms [8–10]. The use of coagulants as a membrane pretreatment has been identified as one of successful strategies to mitigate the fouling and enhance contaminant removal [11–14]. Coagulation with hydrolyzing metallic salts such as aluminum sulfate (alum), ferric chloride and ferric sulfate helps to agglomerate the solutes into flocks large enough to be restricted by typical UF pores [15,16].

Theory and practice of coagulation were developed on the base of a conventional coagulation–flocculation–sedimentation–filtration treatment tray. Here the coagulant is needed to increase the physical retention of an impurity to a level set by health and environmental authorities. Hence the coagulant dose is optimized to achieve a desired retention by a combined treatment, and often determined in lab tests. Coagulation and sedimentation (the jar-test), and coagulation, sedimentation and filtration are two commonly employed tests [17]. In absence of lab tests, the coagulant is added in doses that display stable electro-neutral flocks that

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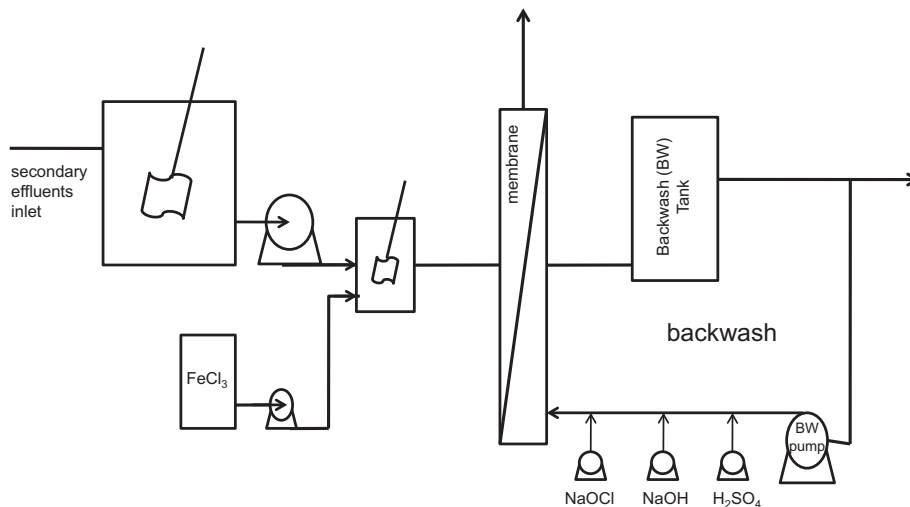


Fig. 1. Basic diagram of the UF pilot at Sede Teiman WWTP.

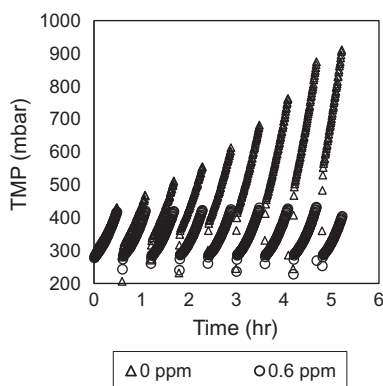


Fig. 2. The TMP as a function of operational time for 0 (upper curve) and 0.6 (lower curve) mg/L Fe^{3+} treating secondary effluents from Sede Teiman WWTP. A sequence of 30 min filtration cycle at 60 LMH was followed by a 56 s hydraulic backwash at 230 LMH. The 50 kDa PES UF membrane was used.

once again help to retain impurities. Visual observations of flock formation and size, zeta potential measurements, and matching between a dose and an impurity based on historical records, are the tests adopted by treatment plants [18]. Common FeCl_3 doses vary between 10 and 30 mg/L [19] and eventually flourish up to 120 mg/L [5,20–22]. Some laboratory experiments are performed even with higher than 1 g/L coagulant doses [23]. The abovementioned range corresponds to 3.5–350 mg/L Fe^{3+} doses.

A definition of in-line coagulation prescribes no removal of coagulated flocks prior to UF [24]. A formation of settleable flocks is no longer necessary and in fact even undesirable. Still publications report optimal, under and over coagulant doses linking the in-line coagulation with the retention efficiency and lab tests. These doses trigger a formation of insoluble metal hydroxides such as $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$, and an increase in membrane fouling due to pore blocking and capillary clogging [25]. Large sludge volumes with high Al/Fe content require a separate expensive treatment before a discharge. At the same time, an expected gain in the retention of organic matter is not high. Lab studies show that a typical coagulation-UF treatment retains up to 45% of organic matter, and the membrane alone can retain up to 20% [5]. Attained permeate concentrations of 7–10 mg/L dissolved organic carbon (DOC) are arbitrary. A control over irreversible fouling sounds more important. Here and thereafter the irreversible fouling in

constant-flux UF membrane operations is defined as a compulsory increase in initial transmembrane pressure (TMP) after a hydraulic backwash [26] performed between two consecutive filtration cycles. The irreversible fouling adversely affects water production and membrane permeability [27].

The in-line coagulation, in fact, can target the control over the irreversible fouling as an ultimate task. The fouling is mainly caused by macromolecular compounds such as polysaccharides and proteins [28], and the assumption is that the neutralization of these compounds can be achieved at low coagulant doses. Lowered retention of impurities can partially be compensated by a depressed concentration-polarization effect. The new/old purpose of in-line coagulation has to be tested in long-run pilot studies. A first positive indication that in-line coagulation can distinctly target the irreversible fouling was found in lab studies that reported no flux difference in experiments with 2 and 5 mg/L Fe^{3+} [29]. Those are arbitrary concentrations used in lab studies. Previous pilot studies investigated different coagulants [30] or various pre-treatments [31] but never the connection between minimum coagulant dose and membrane permeability data. The prevention of irreversible fouling under pilot conditions with minimal coagulant doses has never been reported before.

2. Materials and methods

2.1. Sede Teiman WWTP

Pilot experiments were performed at Sede Teiman municipal wastewater treatment plant (WWTP) located 12 km north-west of the city of Beer-Sheva (Southern Israel). The plant treats approximately 45,000 m^3 of wastewater per day using CAS biological treatment. The secondary effluents are characterized by DOC of 13.5 ± 1.5 mg/L, BOD of 5.1 ± 1.9 mg/L, COD of 44.8 ± 9.0 mg/L, $\text{UV}_{254\text{nm}}$ of 0.276 ± 0.027 1/cm, dissolved orthophosphate as PO_4 of 7.0 ± 4.3 mg/L, Total Kjeldahl Nitrogen (TKN) of 20.3 ± 12.1 mg/L, ammonia NH_4 of 11.7 ± 8.7 mg/L, total iron of 0.04 ± 0.03 mg/L, turbidity of 2.3 ± 0.5 NTU, hardness computed as CaCO_3 of 200.0 ± 24.2 mg/L, specific conductance of 1278.1 ± 132.3 $\mu\text{mho}/\text{cm}$ at 25 °C, pH of 7.5 ± 0.2 , and a temperature of 23.4 ± 3.6 °C. Above parameters are averages and standard deviations of routine data collected during the study and comprehended by measurements performed by Mekorot Ltd. in 2009. Secondary effluents are used by local farmers for the restricted irrigation of technical crops such as cotton, and for a landscape development.

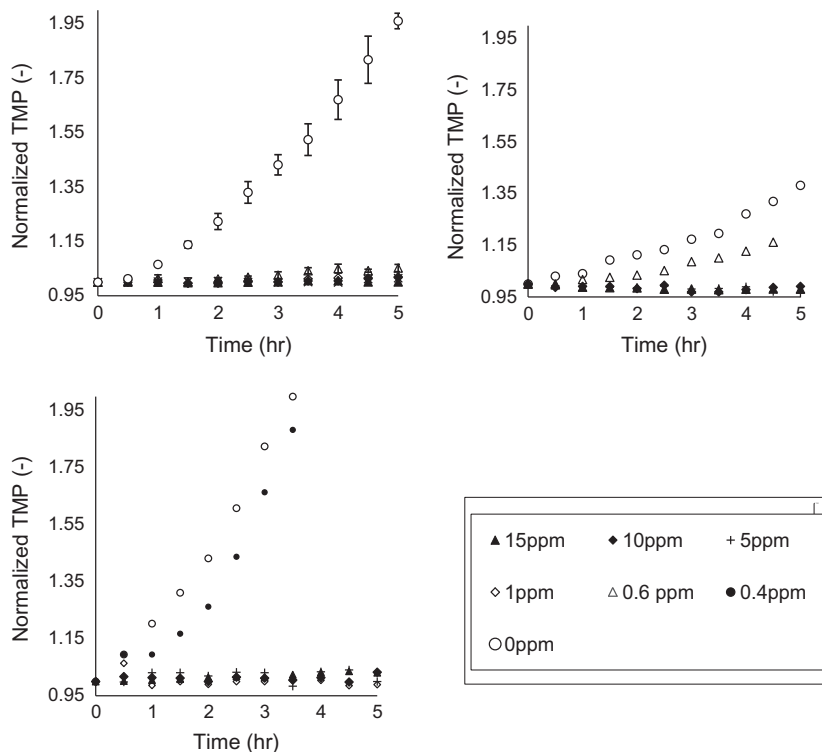


Fig. 3. Changes in TMP during a filtration cycle with 50 kDa (top left, average initial TMP 271 ± 28 mbar), 100 kDa (top right, average initial TMP 248 ± 93 mbar) and 0.2 μm (bottom left, average initial TMP 58 ± 8 mbar) modules. A sequence of 30 min filtration cycle at 60 LMH was followed by a 56 s hydraulic backwash at 230 LMH. Feed pH is 7.5 ± 0.2 . The coagulant doses were 0 (empty circles), 0.4 (black circles), 0.6 (empty triangles), 1 (empty diamonds), 5 (crosses), 10 (black diamonds), and 15 (black triangles) mg/L Fe^{3+} . The error bars at 50kDa graph are the standard deviations calculated for duplicate experiments.

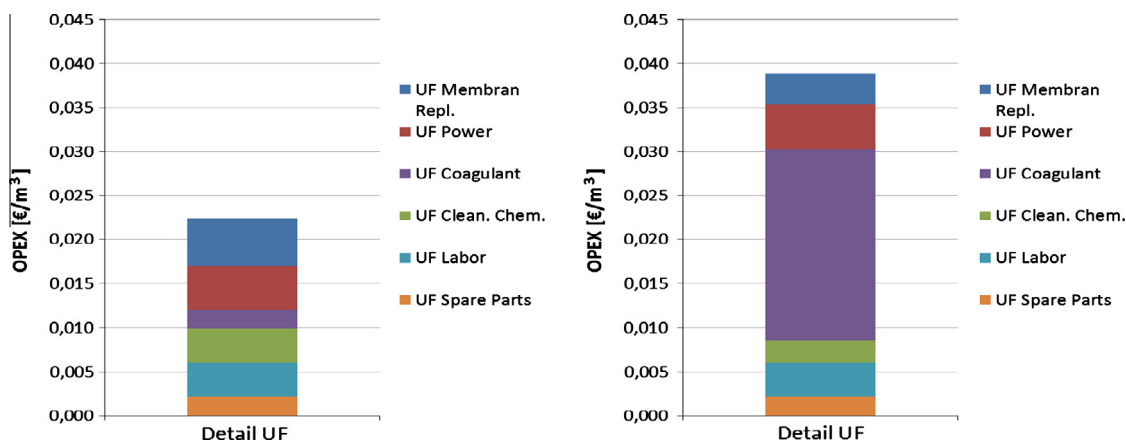


Fig. 4. Operational expense (OPEX) in Euros [€] per a cubic meter of effluents treated with 1 mg/L Fe^{3+} at 60 LMH (left) and 10 mg/L Fe^{3+} at 90 LMH (right).

2.2. The UF pilot

In our experiments secondary effluents were used as a feed for a filtration pilot. The pilot was provided by inge AG (Greifenberg, Germany). The WWTP effluents were pumped from the feed tank through a screen filter into a coagulation chamber. The hydraulic residence time in the chamber varied between 10 and 21 s depending on the flow rate. The 10% w/v Fe^{3+} stock solution was received by mixing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (CARLO ERBA, Arese, Italy) and deionized water (DIW). Altering the speed of a peristaltic dosing pump MS/CA-12/DC (ISMATEC, Germany) changed the applied coagulant doses between 0 and 15 mg/L Fe^{3+} .

The entire study was performed with three polyethersulfone (PES) hollow fiber modules having different molecular weight

cut-offs (MWCOS). The 50 and 100 kDa modules were in UF and 0.2 μm was in MF ranges. The module length was 1.5 m and the total membrane surface area in each module was 1 m^2 . Modules incorporated multibore hollow fibers that contain 7 capillaries each. An internal diameter of a single capillary was 0.9 mm. The modules were washed hydraulically between runs and chemically once every 24 h. After a cleaning the experiments were performed with the same module. Fig. 1 presents a schematic draw of the pilot.

The pilot was operated in “inside-out” semi dead-end mode (cross-flow was applied between filtration cycles by a forward flush cleaning). Typically, the pilot was operated in filtration pressure range between 0.2 and 0.8 bars translated into flow rates between 50 and 130 $\text{L}/\text{m}^2\text{-h}$ (LMH). Hydraulic backwashes were

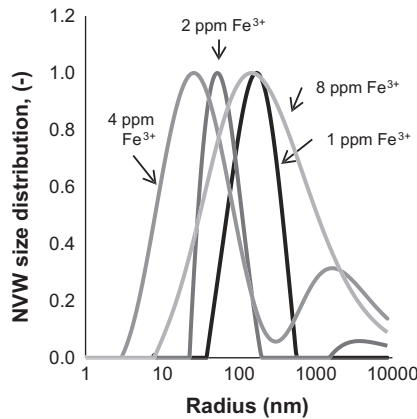


Fig. 5. The results of DLS experiments on a model solution that contained DDW at pH 7.4 and 10 mg/L $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$. The normalized volume-weighted (NVW) size distribution is a method to present the relative intensity of the light scattering in each size class by normalizing the volume-weighted light scattering incidents up to 100%.

performed with the permeate using a separate backwash pump that supplied a pressure up to 2.8 bars equal to a flow up to 230 LMH. The recovery calculated as the ratio of net to gross permeates production (the latter includes the volume of filtrate spent during the backwash) varied between 0.86 for 50 LMH and 0.95 for 130 LMH. Chemically enhanced backwash (CEB) was performed with stock solutions (w/w) of 37% NaOH, 50% H_2SO_4 , and 12% NaOCl that were injected into the backwash pipe with a separate pump. A general CEB protocol included backwash with NaOH for 60 s followed by a soaking for 20–30 min at pH 12–12.5. That step was followed by an acid cleaning when the module was backwashed for 60 s at 120 LMH, and left to soak at pH 2 for 15 min in a solution of H_2SO_4 . Before, between and after soakings the module was drained and hydraulically rinsed for 56 s with the filtrate at 230 LMH.

2.3. The operational setup

A typical operational cycle was 30 min filtration with 60 LMH followed by a hydraulic backwash for 56 s with 230 LMH. Experiments with 45 min filtration cycle and 130 LMH 30 s hydraulic

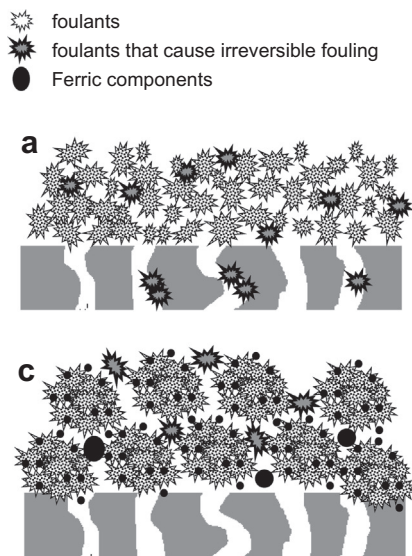


Fig. 6. The pictorial view of filtration of secondary effluents performed with no (a) and with coagulant (b–d). The prevention of irreversible fouling by the coagulation in solution (b) and by the cake (c) results in the idea of short-time coagulation at the beginning of each cycle (d).

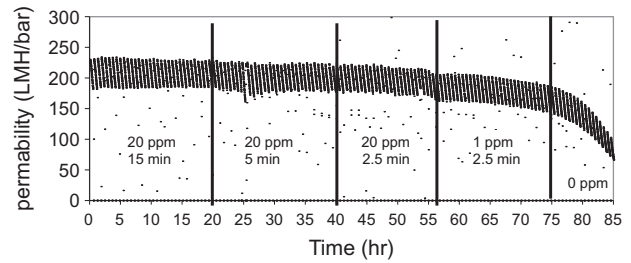


Fig. 7. Membrane permeability vs. filtration of WWTP secondary effluents with different coagulant dosing times and doses. The 50 kDa membrane, 30 min filtration cycles, backwash 56 s at 230 LMH, no CEB.

backwash were also conducted. The experiments with 50 kDa module were performed at constant 20 ± 2 °C temperature. Other experiments were performed at different seasons when the feed temperature changed between 19 and 29 °C. The permeability as a function of the temperature was corrected with the following formulae

$$P_{20^\circ\text{C}} = \frac{P(T)}{\eta(20^\circ\text{C})/\eta(T)} \quad (1)$$

where $P_{20^\circ\text{C}}$ (LMH/bar) is the normalized permeability at 20 °C, P (LMH/bar) is the permeability at temperature T and the temperature correction factor is given as a ratio of shear viscosities η at 20 °C and at temperature T . The latter was calculated automatically as

$$\eta(T) = 17.91 - 0.6T + 0.013T^2 - 1.3 \cdot 10^{-8}T^3 \quad (2)$$

by a software supplied by Inge AG [32]. TMP was normalized to the initial TMP_0 value measured at the beginning of the first cycle. The error bars at 50 kDa figures within the paper represent the results of duplicate experiments and measurements.

2.4. Chemicals and analysis

Concentrations of total iron and phosphorus in the feed/permeate were monitored with DR/890 Colorimeter (Hach, CO, USA) using 8008 and 8114 protocols respectively [33]. The standard error in the measurements is ± 0.2 mg/L as provided by the

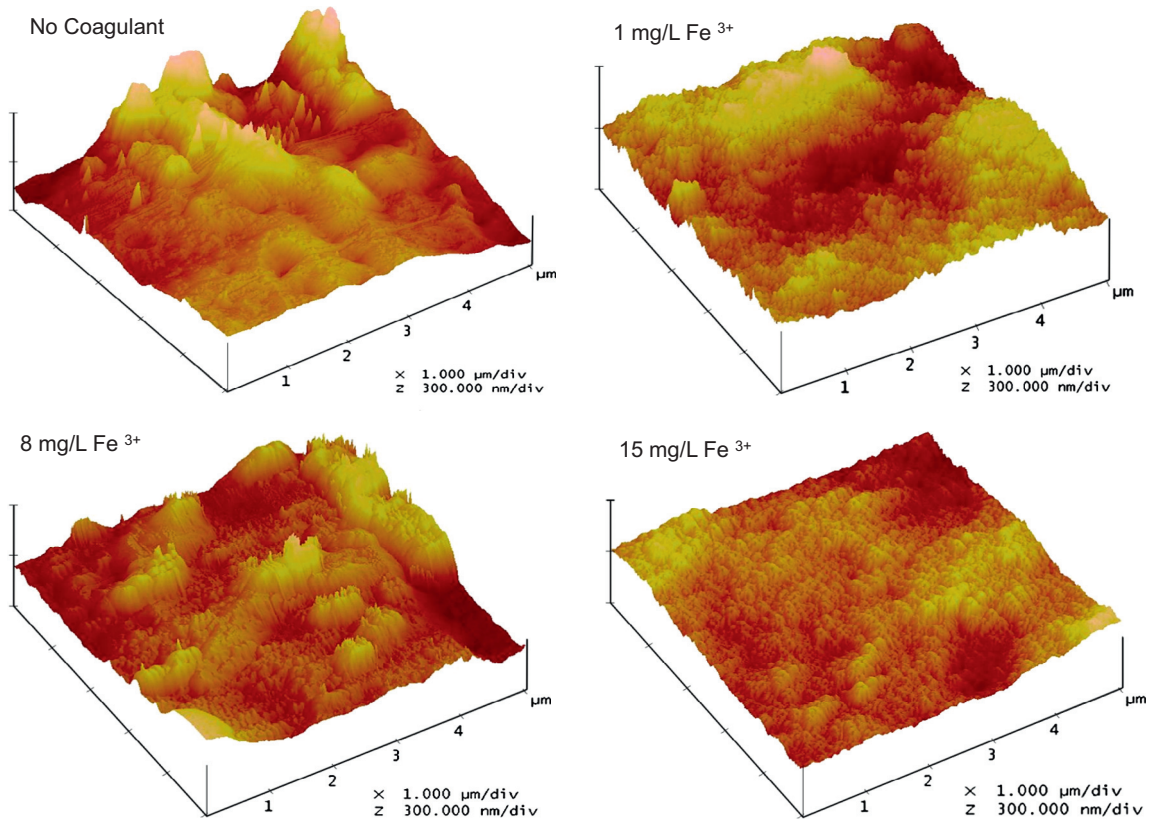


Fig. 8. AFM of PES-50 (MICRODYN-NADIR GmbH) that treated WWTP secondary effluents coagulated with 0 (top left), 1 (top right), 8 (bottom left) and 15 (bottom right) mg/L Fe^{3+} . Fouling experiments were performed in lab conditions.

manufacturer. DOC concentration was measured with DOC analyzer Apollo 9000 (Teledyne Tekmar, OH, USA). The removal efficiency R.E. was calculated as

$$\text{R.E.} = 1 - \frac{X_p}{X_s} \quad (3)$$

where X_s and X_p are the values of a parameter X in secondary effluents and permeate respectively.

X-Ray Photoelectron Spectroscopy (XPS) surface analysis was performed at Ilse Katz Institute for Nanoscale Science and Technology with Thermo Fisher ESCALAB 250 spectrometer at vacuum pressure of $2 \cdot 10^{-12}$ bar. Fouled membrane samples were irradiated with monochromatic Al $K\alpha$ (1486.6 eV) X-rays. Survey spectra were recorded with pass energy of 150 eV and high energy resolution measurements were performed with pass energy of 20 eV. The core level binding energies of the different peaks were normalized by setting the binding energy for C1s at 284.8 eV.

Atomic Force Microscopy (AFM) measurements were performed at ambient conditions using a Bruker Dimension 3100 (Santa-Barbara, CA) mounted on an active anti-vibration table. A 100 μm scanner was used. The 512×512 pixel images were collected in tapping mode, with a scan size of up to 5 μm at a scan rate of 1 Hz. Roughness parameters were extracted from AFM topography using the instrument software. The root mean square (rms) roughness was calculated as

$$\text{rms} = \sqrt{\frac{\sum (Z_i - Z_{av})^2}{N}} \quad (4)$$

where Z_i is the height value for a particular point on the image, Z_{av} is the mean height of all the pixels in the image and N is the total number of pixels within the image.

AFM and XPS analysis were performed with flat 50 kDa PES membranes supplied by MICRODYN-NADIR GmbH (Germany) to avoid technical limits in the characterization of hollow fibers. Membrane fouling experiments were performed in the lab of microbial ecology at the main BGU campus under dead-end mode in stainless steel cell with 169 cm^2 (13×13 cm) membrane area. The cell was continuously fed with secondary effluents from Sede Teiman WWTP. The coagulant at 0, 5 and 15 mg/L Fe^{3+} doses was supplied by IWAKI EW-BO8VC metering pump. Filtration cycles of 25 min long with the 64 LMH were regulated automatically by a programmable logic controller Vision570™ (Unitronics).

Dynamic light scattering (DLS) spectra were collected with CGS-3 (ALV, Langen, Germany) particle sizer. Measured samples were illuminated by a 22 mW He-Ne laser beam at 632.8 nm followed by a collection of more than 50% of scattered light at angles between 12.5° and 150° . The CGS-3 measures all particles in a range between 2 nm and 2 μm . Correlograms were calculated by ALV/LSE 5003 correlator and Laplace inverted with CONTIN software [34]. A model solution that contained double distilled water (DDW) at pH 7.4 and 10 mg/L disodium hydrogen phosphate $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich) was used. The pH was corrected with 1 M NaOH.

3. Results

Pilot experiments were performed at Sede Teiman WWTP. Fig. 2 shows the results of typical UF experiments performed with and without the coagulant. The experiment with no coagulant resulted in an exponential increase of the initial TMP. Already after 5 h filtration time the TMP exceeded the preset upper operable limit of 0.8 bars and a chemical cleaning was launched. An addition of 0.6 mg/L Fe^{3+} kept the TMP during the same 5 h within a low range

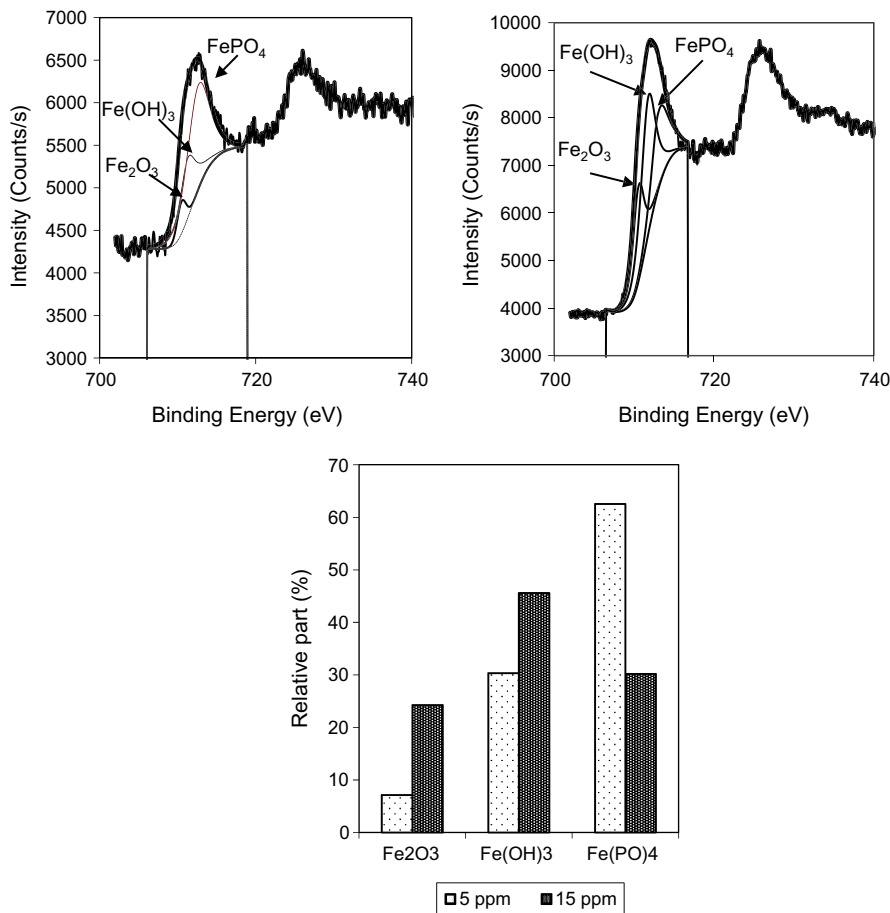


Fig. 9. XPS spectra of C_{1s} peaks at the surface of PES-50 (MICRODYN-NADIR GmbH) fouled by the secondary effluents treated with 0 (top left), 5 (top right) and 15 (bottom left) mg/L Fe³⁺. The relative peak intensities for low, medium and high binding energies at the three coagulant doses are on bottom right.

between 0.25 and 0.45 bars. A 0.5 mg/L dose of Fe₂(SO₄)₃ was reported in MF experiments [26].

Fig. 3 supports tendencies presented on Fig. 2 with normalized TMP data collected during experiments with other coagulant doses and with 100 kDa and 0.2 μm membrane modules. Significant irreversible fouling was observed in all experiments performed with no coagulants. The irreversible fouling in 50 kDa module was successfully depressed with 0.6 mg/L Fe³⁺. One mg/L was needed to depress the fouling in 100 kDa and 0.2 μm modules. Surprisingly, same irreversible fouling development trends were observed in experiments with 5, 10 and 15 mg/L Fe³⁺. In order to rule out the possibility of over backwashing, the backwash flux was reduced from 230 to 130 LMH (0.93 recovery), and a clear shift towards a faster development of irreversible fouling at 130 LMH was noticed. Another experiment with 30 and 45 min filtration cycles shows no significant difference in normalized TMP values ($n = 3$, data not shown).

The absence of a link between the depression of the irreversible fouling and a coagulant dose runs counter our intuitive expectations. It was therefore postulated that in-line coagulation coupled with UF/MF can be performed with an effective coagulant dose (ECD). We define ECD as the lowest concentration of a coagulant (in mg/L of a cation) that under specific site conditions prevents the development of the irreversible fouling in UF/MF membranes as efficiently as any dose above it. In the conditions of Sede Teiman WWTP the ECD was 1 mg/L Fe³⁺. Fig. 4 compares estimated operational expenses (OPEX) of in-line coagulation of secondary effluents with ECD and 10 mg/L Fe³⁺. The latter dose almost doubles operational costs from 2.2 to 3.9 cents (€) per a cubic meter of

treated secondary effluents. The ECD is significantly lower than optimal coagulant doses reported in previous studies. For example, Zheng et al. [30] coagulated secondary effluents from WWTP Ruhleben (Berlin, Germany) with 6, 12 and 24 mg/L Fe³⁺ prior to UF with 100 kDa PES membranes. Doses between 2.2 and 81 mg/L were reported by Lee et al. [35]. Doses of 10 and 13 mg/L Polyaluminium chloride (PACl) were used by Diaz et al. [36]. Doses of 1.5 and 10 mg Al³⁺/L were used in lab studies of fouling behavior of transparent exopolymer particles [37].

The significant difference in the degree of irreversible fouling in experiments below and above ECD was examined with DLS measurements performed on module phosphate solutions. Fig. 5 shows the results of DLS at various Fe³⁺ doses. No particles were found at coagulant doses below ECD. A relatively narrow peak with 150 nm mean average diameter was found with the ECD addition. The peak shifts towards lower 60 and 25 nm mean averages with the addition of 2 and 4 mg/L Fe³⁺ respectively. The addition of 8 mg/L Fe³⁺ produces the widest peak when particles with mean average diameters between 10 nm and above 1 μm were reported. Large particles were also seen in secondary peaks when 2 and 4 mg/L Fe³⁺ were added. The DLS results coupled with XPS analysis (*vide infra*) suggest that the ECD separates between the presence of large flocks above ECD and the absence of flocks below it.

Fig. 6 details a possible coagulation – UF scenario. The UF not coupled with in-line coagulation results in a direct contact between foulants and the membrane surface (Fig. 6a). Foulants adsorb on the membrane surface and/or clog membrane pores thus significantly reducing the transmembrane flux. The flux cannot be restored by a hydraulic backwash and requires a CEB. The

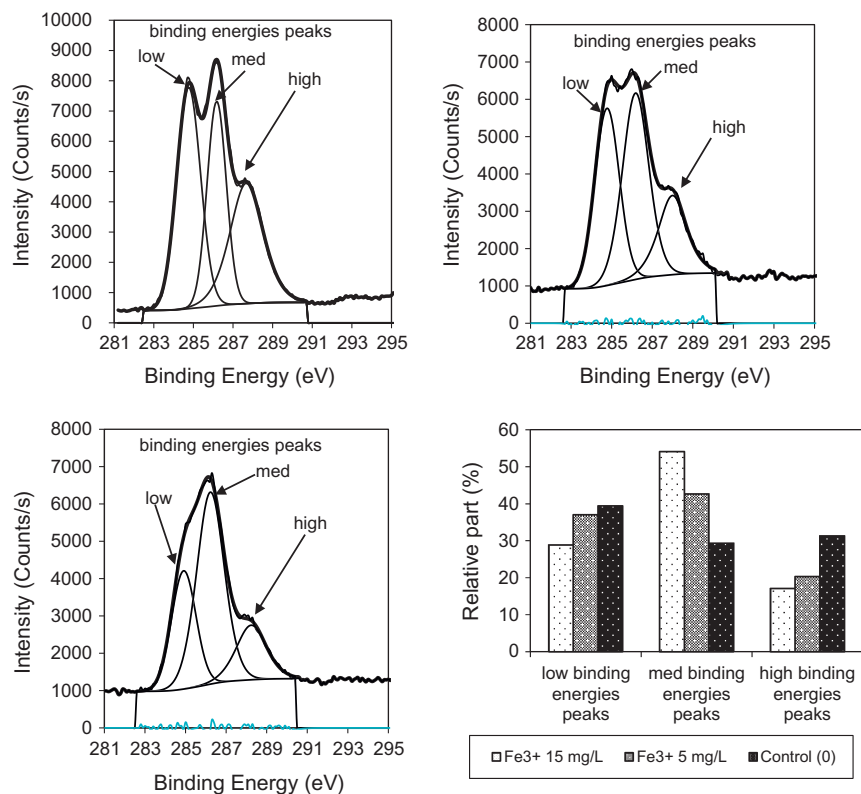


Fig. 10. XPS spectra of Fe_{2p} peaks at the surface of PES-50 (MICRODYN-NADIR GmbH) fouled by the secondary effluents treated with 0 (bottom left), 5 (top left) and 15 (top right) mg/L Fe³⁺. Relative parts of Fe₂O₃, Fe(OH)₃ and Fe(PO)₄ in the effluent cake are in the bottom right.

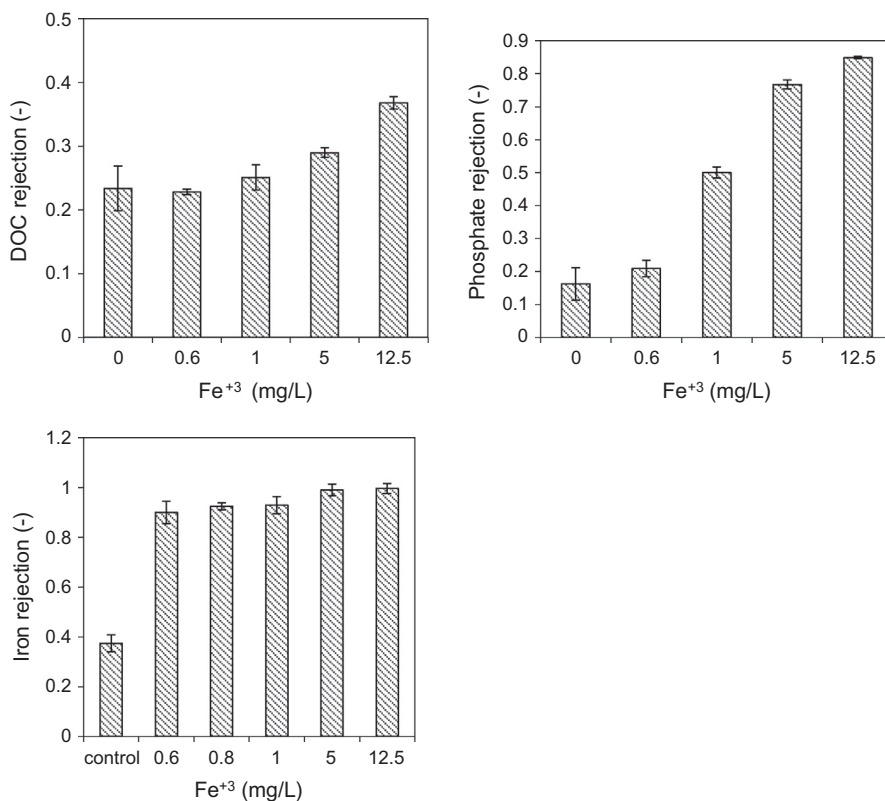


Fig. 11. Retention of dissolved organic carbon (DOC, top left), total Fe (bottom left) and PO₄ (top right) by PES-50 and Fe³⁺. A sequence of 30 min filtration cycle at 60 LMH was followed by a 56 s hydraulic backwash at 230 LMH. The initial TMP was 300 mbar. Experiments were performed at 23.4 ± 3.6 °C. Feed pH is 7.5 ± 0.2. DOC in the feed 13.5 ± 1.5 mg/L, PO₄ in the feed 7.0 ± 4.3 mg/L, Fe in the feed 0.04 ± 0.03 mg/L.

Table 1

Atomic composition [%] and atomic ratios on membrane surface by XPS after the treatment of the secondary effluents with 0, 5 and 15 mg/L Fe³⁺.

| | C | N | O | P | Fe | N/C |
|--------|------|-----|------|-----|-----|-------|
| 0 ppm | 64.2 | 7.3 | 27.8 | 0.4 | 0.1 | 0.114 |
| 5 ppm | 51.9 | 5.3 | 37.6 | 1.9 | 1.9 | 0.102 |
| 15 ppm | 44.8 | 3.6 | 44.6 | 1.4 | 4.7 | 0.81 |

development of irreversible fouling is clearly viewed in experiments performed below ECD on Figs. 2 and 3. The prevention of irreversible fouling at ECD can be due to two mechanisms – a neutralization of main foulants such as proteins and polysaccharides [9,38] in the feed (Fig. 6b), or a formation of an initial Fe(OH)₃ surface cake immediately at the beginning of a cycle (Fig. 6c). Two mechanisms are not mutually exclusive, and their relative contribution depends on feed conditions and the coagulant dose. Fig. 6d depicts an initial cake formed on the membrane surface and a continuous effective prevention of the irreversible fouling at ECD and above.

Following our hypothesis we decided to apply a short coagulation at the beginning of each cycle. The idea was to create the initial cake that prevents the irreversible fouling as efficiently as the full coagulation during the entire run. Considerable savings in coagulant doses and in sludge disposal were two expected benefits of a successful implementation of a short coagulation. Fig. 7 depicts permeability values as a function of Fe³⁺ dose and dosing time. The 20 mg/L dose during first 15, 5 and even 2.5 min of each cycle resulted in stable permeability. Each experiment lasted between 15 and 20 h., after the experiment a CEB was applied. A cleaned module was operated again with no signs of a cumulative irreversible fouling. We further decreased the dose to the ECD applied during first 2.5 min. In our conditions that was the minimum coagulation time. The ECD at 2.5 min results in a reasonable decline in the permeability. At the end a control experiment performed with no coagulant resulted in a rapid permeability drop. The filtration was stopped already after 10 h and a CEB was lunched.

Fig. 8 presents three-dimensional AFM micrographs of flat membranes fouled with in-line coagulated secondary effluents. In these images, bright areas present top cake points and dark regions indicate valleys or bottom points in membrane cake [39]. Although the micrographs look alike, they differ in the degree of roughness. The rms roughness (Eq. (4)) decreases from 40 ± 1 nm at 0 and 1 mg/L Fe³⁺, to 32 nm at 8 mg/L Fe³⁺ and 19 nm at 15 mg/L Fe³⁺. The decreased roughness suggests that a more uniform and probably thicker cake is formed on the membrane surface at higher coagulant doses.

We further investigated the difference in adsorption layers formed on the membrane surface using X-ray photoelectron spectroscopy (XPS). Table 1 shows the XPS elemental analysis of a flat membrane fouled with in-line coagulated secondary effluents. An increase in the coagulant dose resulted in a lower peak intensity of total carbon and total nitrogen and a higher intensity of oxygen and ferric peaks. The increase in the intensity of the latter peaks is explained by the formation of ferric hydroxide flocks typical for sweep coagulation [40]. The peak intensity of nitrogen is related to a steric rejection of biopolymers such as proteins and polysaccharides. An insignificant improvement in the retention of biopolymers with the addition of a ferric coagulant was also observed previously [36]. The relative intensity of the N peak in the cake is oppositely related to the coagulant dose – the highest with no coagulant particles and lows when more ferric particles land on the cake. The decrease in N/C ratio and in the relative part of nitrogen-rich compounds indicates an additional retention of organic matter with a low nitrogen and high carbon and oxygen content such as humic compounds. The enhanced retention of humic

compounds at higher coagulant doses was also reported previously [29,30]. The intensity of the phosphorus peak increased with the addition of 5 mg/L Fe³⁺ but dropped when a higher 15 mg/L Fe³⁺ dose was added. Somewhat different from the retention of N-compounds, most of the P-containing compounds were retained at low dose and the decrease in the phosphorus intensity peak at 15 mg/L Fe³⁺ is due to further retention of additional compounds.

The Fe_{2p} XPS spectra of a cake of secondary effluents coagulated with 0, 5 and 15 mg/L Fe³⁺ are depicted on Fig. 9. Previous works assigned the binding energies of 711.3–711.8 eV to Fe(OH)_x, 710.8–710.9 eV to Fe₂O₃, 708.2–710.4 eV to Fe₃O₄ and 712.5 eV to FePO₄ compounds ([41,42] and references therein). The results display changes in percentage of iron compounds as a function of the coagulant dose. Most significant changes occur with ferric phosphate. The 0% retention with no coagulant (data not shown) changes into 63% at 5 mg/L Fe³⁺ and drops to 30% as the dose increases to 15 mg/L Fe³⁺. Thus the relative retention of phosphorus compounds mostly as ferric phosphate indeed happens at low coagulant dose up to 5 mg/L Fe³⁺, as suggested in discussion of Table 1. The Fe(OH)₃ percentage increases from 0% to 30% to 45% with 0, 5 and 15 mg/L Fe³⁺ respectively.

Fig. 10 shows typical XPS spectra for C_{1s} photoemission peaks at the membrane surface after a treatment of secondary effluents with 0, 5 and 15 mg/L Fe³⁺. We figure that a discrete analysis of carbon peaks cannot be performed due to a large polidiversity of carbon compounds in secondary effluents. Instead we divided the peaks into the regions of low, medium and high binding energies. The C_{1s} peak of 284.8 eV corresponds to carbon-carbon bonds, the peak of 286.3 eV is associated with phenolic, alcohol, carbonyl, and hydroxyl groups, and the 288.2 eV peak is linked to carboxyl and ester groups ([43] and references therein). Relative peak intensity depends on the addition of Fe³⁺ – the intensity of low and high binding energy peaks decrease while the intensity of medium binding energy peak increases. The increase in the relative intensity of the latter peak is probably due to a higher retention of humic compounds with the addition of a coagulant [44]. An initial drop in the intensity of the high binding energy peak at no coagulant is related to the steric retention of biopolymers as explained above.

Fig. 11 details retentions of phosphate, DOC, and iron as a function of added Fe³⁺. The addition of coagulant significantly improved phosphate retention. The 10% retention with no coagulant was upgraded to 86% retention (0.6 mg/L P) at 12.5 mg/L Fe³⁺. The retention of phosphorus is vital in prevention of the eutrophication of receiving surface water bodies [45,46] and often PO₄ removal is an ultimate coagulation target. In a combined UF-reverse osmosis (RO) wastewater treatment the sufficient PO₄ retention will minimize the RO scaling potential [30]. The initial 22% DOC retention at 0 mg/L Fe³⁺ is linked to biopolymers and high molecular weight compounds retained by the membrane itself as speculated above. Further increase towards 35% was observed at 5 and 12.5 mg/L Fe³⁺ and reflects the retention of humic compounds. The retention of more than 90% iron at any Fe³⁺ dose proves that all the coagulant is consumed during the treatment. The enhanced formation of Fe(OH)₃ between 5 and 12.5 mg/L Fe³⁺ is well correlated with a jump between 22% and 35% in the DOC retention.

4. Discussion

Many lab and several pilot studies on membrane tertiary treatment of municipal wastewater had been performed. Several studies examined the link between the irreversible fouling and the coagulant dose however the vast majority dealt with an optimized retention of various impurities. The optimization is based on rela-

tively or even prohibitively high concentrations of coagulants. These concentrations can be significantly reduced by in-line coagulation, although the purpose of the coagulation should be diversified. Under the new definition the coagulation can be either viewed as a part of the conventional tray described above, or be simply used to prevent the irreversible fouling. The latter goal permits a significant cut in coagulant doses, likely due to a change in a coagulation mechanism. High retention efficiency can be achieved by a combination of charge neutralization and sweep coagulation with the addition of meaningful coagulant doses. A successful prevention of an irreversible fouling is realized by the neutralization of charged compounds, usually at low coagulant doses.

There are several advantages to the coagulation with an optimal dose. The coagulation with optimal or slight “overdose” is known to scientists and water practitioners, it maximizes the retention, it protects the membrane, and the dose itself can be detected in lab tests or retrieved from historical records. The single significant drawback is a high coagulant dose that increases operational costs. The in-line coagulation with ECD has seldom been tested before, its effect on the lifetime of a membrane is not known, it requires membrane pilot testing, and the expected organic retentions are not high. Under current pilot conditions the main difference was in the retention of phosphorus. However the optimal phosphorus retention depends on the future effluent use and it is not a pre-requisite for every advanced treatment. Among positive effects of in-line coagulation with ECD are (i) a reduction in the footprint of the treatment plant as compared to a conventional one (by absence of flocculation and sedimentation basins); (ii) a reduction in operational costs with shorter coagulation times and lower coagulant dosages (at current, the coagulant cost can reach up to 40% of the total operational cost); and (iii) increased treatment sustainability with smaller sludge volumes.

The in-line coagulation with ECD or slightly above ECD showed no adverse irreversible fouling effect in pilot studies. Flocks formed at that coagulant dose generate an initial cake and prevent a direct contact between the irreversible foulants and the membrane surface. The formation of an initial cake is sufficient for the entire run, even if the coagulation is stopped after few first minutes. The cake thickness and composition vary with the coagulant dose. The XPS results support the claim that proteins are retained without or at low coagulant doses. The phosphate is removed at the average coagulant doses as the ferric phosphate prior to the massive formation of ferric hydroxide at high coagulant doses. The carbon peak analysis implies that the gain in the retention of DOC is in a form of humic substances. The AFM analysis shows a decreased roughness as the coagulant dose increases, most likely due to a formation of a massive cake.

5. Conclusions

The in-line coagulation of secondary effluents can seek an optimal retention of impurities or a depression of irreversible fouling. The optimal retention is achieved with meaningful concentrations of coagulants and can efficiently depress the fouling. Applied coagulant doses are however prohibitively high for many operations including advanced membrane wastewater treatment. A depression of the fouling can be achieved with ECD determined as the lowest coagulant dose needed to successfully depress the irreversible fouling under given site conditions. The flux mitigation with ECD does not necessarily maximize the retention yet it significantly reduces the coagulant consumption. The coagulation can also be performed intermittently, in our conditions for the initial 2.5 min of each run. Coagulation with ECD and/or short times at the beginning of a cycle are two cost-efficient environment-

friendly practices that path a way for a full-scale advanced membrane treatment of municipal wastewater.

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