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Irreversible fouling of membrane bioreactors due to formation of a non-biofilm gel-like layer

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ABSTRACT

Extra-cellular polymeric substances (EPS), known to contribute to fouling in membrane bio-reactors (MBR)s, are generally divided into bound and free EPS. The free EPS are able to form a gel-like layer on the membrane active surface. The mechanisms involved in formation of such layer and its effects on performance of the MBR membranes were studied. The free EPS, extracted by centrifugation and microfiltration, contained a significant amount of humic-like substances. Under static contact to the membrane, adsorption of humic-like substances to the membrane occurred and could be explained by conventional adsorption kinetics. Due to static adsorption, surface roughness of the membrane declined significantly indicating that adsorbed matters to the membrane filled the cavities of the membrane surface. Filtration of the free EPS caused 50% water flux decline. The fouling resistance linearly increased with the amount of the humic-like substances retained during filtration as predicted by gel growth theory. A low pressure backwash could re-establish the water flux only up to 70%.

Key words: free EPS, humic-like substances, adsorption, gel formation, fouling resistance,

irreversibility

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INTRODUCTION

A critical operational problem in membrane bio-reactors (MBR)s is fouling which results in decreased permeability and necessitates periodical physical and chemical cleaning. It has been observed that during operation of MBRs a double-layer forms on the membrane active surface e.g. an outer cake and an inner gel layer (Aryal et al. 2009). The outer cake builds up during filtration and falls off during relaxation as observed by T.V. Bugge et al. (2012). In this study, the permeate flux in a lab-scale MBR was modeled as a function of cake build-up and removal for short time operations. It has been observed that the inner gel-like layer, which is located between the loose layer and the membrane and which is not removed by relaxation (Ramesh et al. 2007), is composed of biopolymers (Aryal et al. 2009). Zhang et al. (2006) stated that accumulation of extracellular polymeric substances (EPS) is one of the stages of MBR fouling. Liu et al. (2012) have reported a correlation between the sludge EPS concentration and the

membrane fouling. Thus, it has been hypothesized that the EPS components are important in formation of the gel layer.

EPS components are generally divided into bound and free EPS (Nielsen et. al.1999). A recent study has shown that the free EPS components are in permanent contact with MBR membrane and pass through the membrane during filtration (Poorasgari et. al. 2013). It has been reported that free EPS fraction contains a significant amount of humic-like substances (Meng et al. 2011). The humic-like substances are present in a gel-like layer formed on the MBR membranes (Aryal et. al. 2009). It has been shown that adsorption of humic acid causes irreversible fouling of polymeric ultra filtration (UF) membrane (Jermann et al. 2007).

Based on the mentioned findings, it can be expected that adsorption of EPS molecules and / or gel formation due to passive transport of free EPS towards the membrane surface are the mechanism for irreversible fouling. Experiments have been conducted to determine whether adsorption or gel layer formation or both are important for prediction of fouling in MBR systems by free EPS components.

MATERIALS AND METHODS

Sludge samples

The sludge was sampled from MBR unit of a wastewater treatment plant which was designed for enhanced biological phosphorus removal. The MBR unit was of $6m^3$ volume and operated at 30mbar trans-membrane pressure. Concentration of volatile suspended solid of the MBR sludge was around $6mg \cdot L^{-1}$. Flat sheet membranes were installed in the pilot plant. The active surface of the membrane was polyvinylidene fluoride (PVDF) hydrophilized with polyvinyl pyrrolidone (PVP). The nominal pore diameter was 0.2µm. The membrane was produced by Alfa Laval A/S.

Extraction of free EPS from MBR sludge

Free EPS were extracted from the MBR sludge. Sludge sampling and EPS extractions were done at the same day. Free EPS was extracted by centrifugation and two subsequent filtrations through glass-fiber filters of 1.6µm and mixed cellulose ester of 0.45µm nominal pore diameter. Centrifugation of the sludge was done at 9000g for 1h at 4℃ . Filtration of free EPS was done to remove microorganisms and minimize their interference in the adsorption experiments.

Characterization of free EPS

Measurement of EPS components were done in less than 48h after extraction. During this time the EPS samples were stored in ice-cold water at 4 °C. Concentration of protein and humic-like substances was measured by modified Lowry method (Frølund et. al.1996). Carbohydrate concentration was measured by Anthrone method (Frølund et. al. 1996). The measurements of each sample were at least triplicated.

Adsorption and filtration experiments

The membrane type was the same as the one used in the pilot plant MBR. The as-received membrane sheets were immersed and shaken in ethanol and subsequently in de-ionized water for 3 to 4 hours to remove the glycerin protective coating from the membrane surface. Then, M-Q water was filtered through the membrane sheets at 2 bar pressure for 24h to compact the membrane and get a fixed permeability. After that, discs of 47mm diameter were cut from the prepared membrane sheets for water flux and adsorption experiments.

Three different setups were used; one for water flux measurement, one for static adsorption and, one for filtration of EPS and backwash after filtration of EPS. The water flux measurement of the prepared membrane discs was done in a dead-end filtration setup where M-Q water was filtered through the prepared membrane discs at 0.5 bar pressure and the permeate flow was measured by gravimetric method. The pressure was supplied from a compressed air source and the compressed air was filtered before reaching the water of the feed tank. The air filter was of the same nominal pore diameter as the PVDF MF. The permeate flow measurements were done before and after adsorption, and after backwashing the membrane discs which were fouled by EPS filtration. The water flux was calculated by dividing permeate flow by the surface area of the membrane disc. The water flux values were corrected for 20°C by applying the below viscosity correction function:

$$J_{20°C} = \frac{\mu_T}{\mu_{20°C}} \times J_T \qquad (1)$$

Where $\mu_{20°C}$ and μ_T are the dynamic viscosity of water as $N \cdot s \cdot m^{-2}$ at 20°C and actual water temperature, respectively. $J_{20°C}$ and J_T are the water flux as $m \cdot s^{-1}$ at 20°C and at actual temperature, respectively. Normalized water flux was obtained by dividing the corrected water flux values measured after adsorption and backwash by those measured for the same prepared membrane discs before adsorption experiments. The fouling resistance was calculated by the Darcy equation:

$$R_f = \frac{\Delta P}{\mu_{20°C} \times J_{20°C,foul}} - R_m \qquad (2)$$

Where R_f is the fouling resistance as m^{-1}, ΔP the trans-membrane pressure as $N \cdot m^{-2}$, μ the dynamic viscosity of water, $J_{20°C,foul}$ is the temperature-corrected water flux after adsorption experiments, with the same unit as mentioned in equation 1. R_m is the membrane resistance as m^{-1}, which was calculated from the water flux of the clean prepared membrane discs.

The adsorption experiments were done in static and dynamic modes. In the current work, the static adsorption means the adsorption due to contact between the membrane and the free EPS at no applied pressure and dynamic adsorption means adsorption due to filtration of free EPS through the membrane.
The static adsorption tests were done in the cells of 20 mL volume made of Teflon. A volume of 10mL free EPS was used for the static adsorption experiments which were conducted at room temperature for different contact times up to 4 hours. No adsorption of humic-like substances to the Teflon cells was detected. The experiments were done with and without shear. The shear was provided by a moving shaker of 1.2Hz frequency and 13cm displacement length.

For each experiment, a fresh prepared membrane disc was used. The static adsorption experiments were triplicated. Adsorption of humic-like substances to the membrane was monitored by measuring UV254 absorbance of the free EPS suspension before and after static contact. The amount of adsorbed humic-like substances was calculated by equation 3:

$$\theta = \left(\frac{UV254_i - UV254_f}{UV254_i}\right) \times \frac{C \times V}{M} \qquad (3)$$

Where θ is concentration of humic-like substances on the membrane as $\mu g \cdot g^{-1}$, $UV254_i$ the UV254 absorbance of the initial free EPS, $UV254_f$ the UV254 absorbance of the free EPS after contact to the PVDF MF membrane, C the concentration of humic-like substances of the initial free EPS as $\mu g \cdot mL^{-1}$. Measuring UV254 absorbance of the dilutions of the free EPS showed that the UV254 absorbance linearly decreases with increasing dilution factor. Besides, measurements showed the UV254 absorbance of the free EPS was linearly correlated to the concentration of the humic-like substances measured by the modified Lowry method. Therefore, a positive linear relationship has been assumed between UV254 absorbance and C. V is the volume of free EPS used for the static contact experiments as mL and M the membrane mass as g. By using MATLAB, equation 4 was applied as a kinetic model for fitting the amount of the adsorbed humic-like substances versus time in the static adsorption experiments:

$$\theta = \theta_{eq}\left(1 - e^{(-K \cdot t)}\right) \qquad (4)$$

Where θ_{eq} is the equilibrium concentration of humic-like substances on the membrane as $\mu g \cdot g^{-1}$, K the mass transfer coefficient as $m \cdot h^{-1}$ and t the contact time as h.

The dynamic adsorption was done in a dead filtration setup at room temperature where the flow was driven by a vacuum pump of 0.07 bar pressure. No adsorption of humic-like substances to the setup was detected. EPS filtration experiments were done in triplicate by filtering 100mL free EPS suspension divided in five equal volumes of 20mL at room temperature. The retention of humic-like substances was calculated by equation 5:

$$R = \frac{UV254_{feed} - UV254_{filtrate}}{UV254_{feed}} \qquad (5)$$

Where R is the retention of the humic-like substances, $UV254_{feed}$ the UV254 absorbance of the free EPS before filtration and $UV254_{filtrate}$ the UV254 absorbance of the free EPS after filtration through the PVDF MF membrane. The amount of the humic-like substances retained by the membrane was calculated by equation 6:

$$\theta = \sum_{n=1}^{n=5}\left(\frac{R \times C \times V}{M}\right) \qquad (6)$$

Where V is the volume of free EPS filtered through the PVDF MF membrane in each step and n is the number of the steps. The θ was calculated as $mg \cdot g^{-1}$.

Membrane surface analyses

A NTEGRA NT-MDT atomic force microscope was used in tapping mode for roughness analysis which was conducted on the active surface of the clean membrane and the active

surface of the membrane after static contact with the free EPS. The static contact was done for 12h at 4°C. A surface area of 15µm×15µm was scanned on each sample.

RESULTS AND DISCUSSION

Free EPS components of MBR sludge

The free EPS extracted from the MBR sludge was analysed. The measurements showed that it contains $20\pm2\,mg\cdot L^{-1}$ humic like substances and no protein. The carbohydrate concentration was measured $4\pm1\,mg\cdot L^{-1}$. The mentioned concentration of humic-like substances of the free EPS is comparable to the one reported by Liu et. al. (2012) but they had also observed presence of protein and a much higher concentration of carbohydrate.

Static adsorption and its effects

Static adsorption experiments were conducted by exposing the membrane active surface to the micro-filtered free EPS extracted from MBR sludge. Figure 1.a shows adsorption rate of the humic-like substances is higher at the beginning of the static contact and it decreases over the contact time. The higher initial adsorption rate is more pronounced for the experiments with shear than for the experiments without shear. For the experiments without shear, the adsorption seemed to be continuing after 4 hours contact time; while, the adsorption almost levelled off at 4h contact time for the with shear experiments. All of the mentioned observations can be explained by film theory. At the beginning, the adsorption sites are free and the concentration difference between the adsorptive suspension and the membrane is at a maximum but it decreases over the contact time resulting in a decrease of adsorption rate. The shear reduced the thickness of the film, increased the mass transfer coefficient and shortened equilibration time to 4h. The equilibration time and the adsorbate mass observed in the present study are comparable to those observed in the static adsorption of poly phenols of flavan-3-ol family to a poly ether sulfon (PES) -PVP MF membranes (Cratlade, Vernhet 2006).
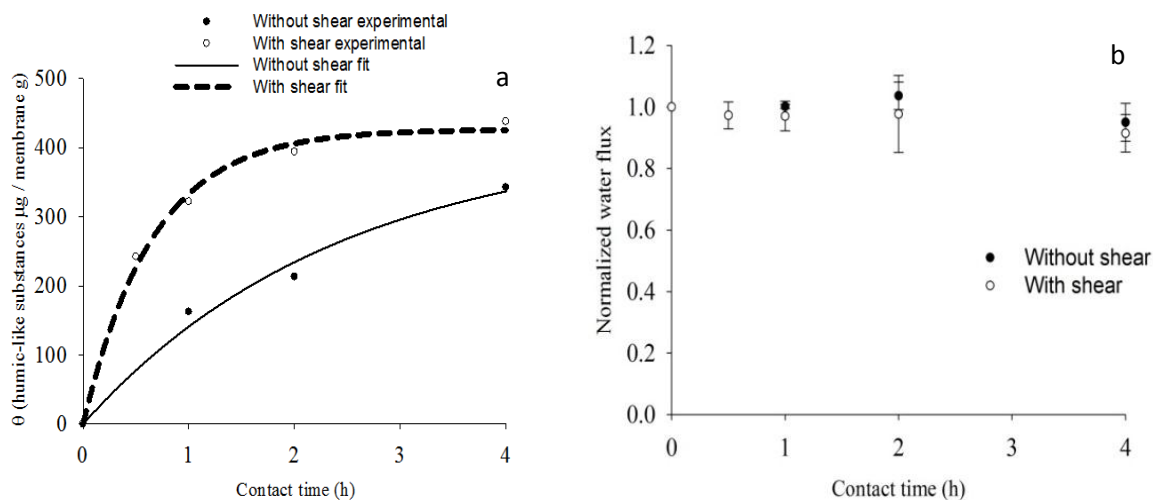

Fig. 1: Static adsorption of free EPS (a) and its effect on water flux (b)

There is a good agreement between the experimental results and the values predicted by equation 4 which is based on the film theory. The equilibrium concentration has been calculated 426 $\mu g \cdot g^{-1}$ and the mass transfer coefficient has been calculated 1.15×10^{-4} $m \cdot s^{-1}$ for the experiments without shear and 4.2×10^{-4} $m \cdot s^{-1}$ for the experiments with shear. Figure 1.b shows that the static adsorption did not cause a significant change in water flux.
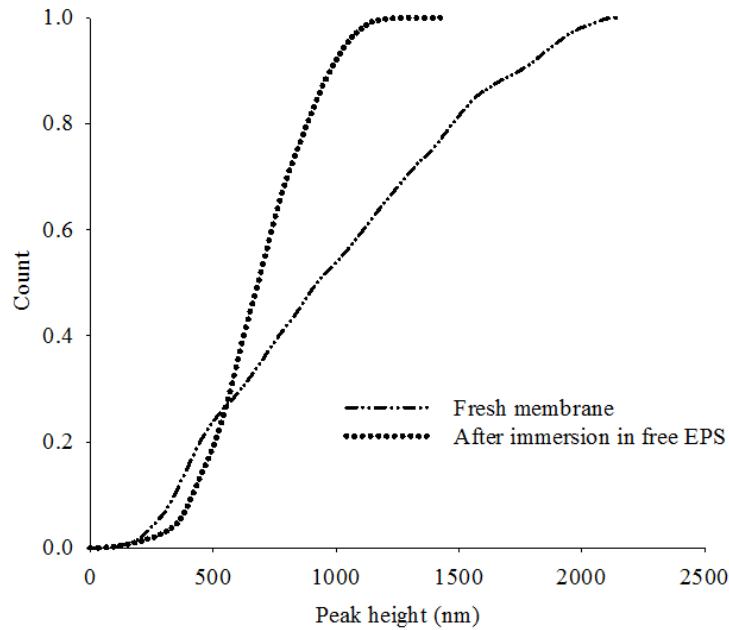

Fig. 2: Effect of static adsorption of free EPS suspension on membrane surface roughness

The surface roughness of the membrane surface was analysed before and after contact to free EPS. Figure 2 shows that the peak height and its distribution become less after contact to free EPS suspension. The free EPS components attach to the membrane surface and they fill the cavities and reduce the height of the peaks. This observation confirms adsorption of free EPS components to the membrane surface under static contact condition.

Dynamic adsorption and its effects

The microfiltered free EPS was filtered through PVDF MF membrane to study the effects of the dynamic adsorption on the PVDF MF membrane. Figure 3.a shows that retention of humic-like substances is higher at the beginning of filtration of the free EPS and it decreases as filtration continues. The retention almost levelled off when the ratio between filtered EPS suspension and membrane surface area reached $50 \, L \cdot m^{-2}$. This indicates that the retention is initially controlled by the adsorption capacity of the membrane. At the beginning, the absorption sites on the membrane surface and within its pore channels are free so a higher amount of the humic-like substances is supposed to be retained by the membrane. As more EPS suspension is filtered, as less adsorption sites remain free and the retention becomes less. An interesting point is that the retention does not become zero i.e.

the humic-like substances continue to accumulate on the membrane surface. This might result in build-up of a gel-like layer by the retained humic-like substances since polymers are able to produce a gel network above a certain concentration (Stevens 1999).
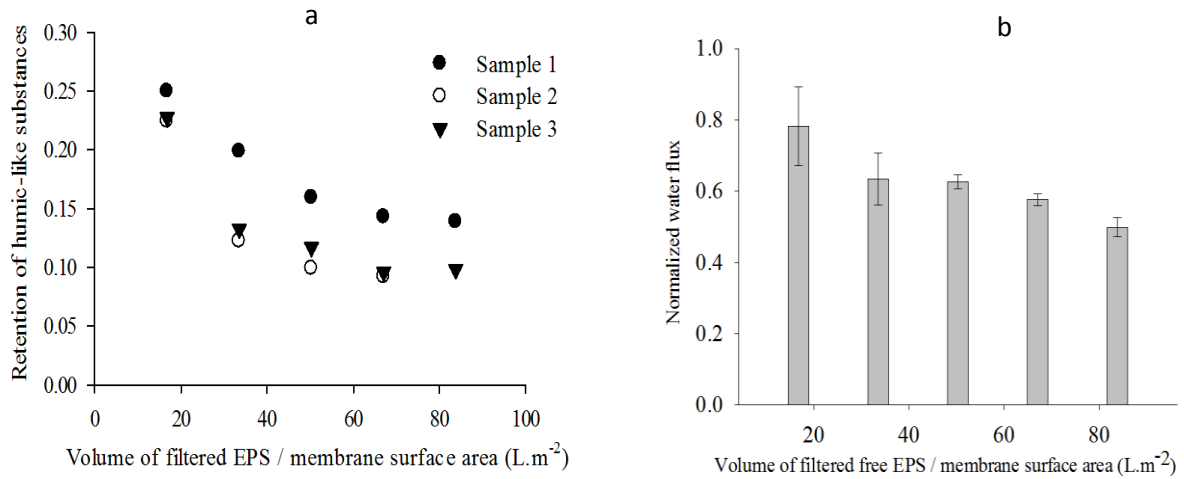

Fig. 3: Retention of humic-like substances (a) and flux decline due to filtration of free EPS (b)

Figure 3.b shows that water flux decreases after filtration of free EPS. The normalized water flux decreased with increase of filtered EPS and it declined to 50% when the ratio between filtered EPS suspension and membrane surface area reached $84 \, L \cdot m^{-2}$.

There is a similarity between the trend of normalized water flux and retention versus the volume of filtered free EPS. Therefore, a correlation was expected between the fouling resistance which is calculated from the flux data and the amount of the retained humic-like substances which is calculated from the retention data. Figure 4 shows the fouling resistance is in an acceptable positive linear correlation with the amount of humic-like substances retained during filtration of free EPS. This linearity indicates the applicability of the gel growth theories for prediction of flux decline (Christensen et al. 2006) during filtration of free EPS. The amount of the humic-like substances retained during filtration of free EPS is almost 8 times higher than that adsorbed during static adsorption. This may explain the significant effect of dynamic adsorption on water flux compared to the static adsorption which did not affect water flux significantly. The high amount of adsorbed humic-like substances can be explained by the fact that during filtration of free EPS the humic-like substances are transported to deeper adsorption sites of the membrane which might not be accessible by static adsorption. Further, some of the humic-like substances might be larger than the membrane pores or some of the pores and therefore rejected by the membrane.
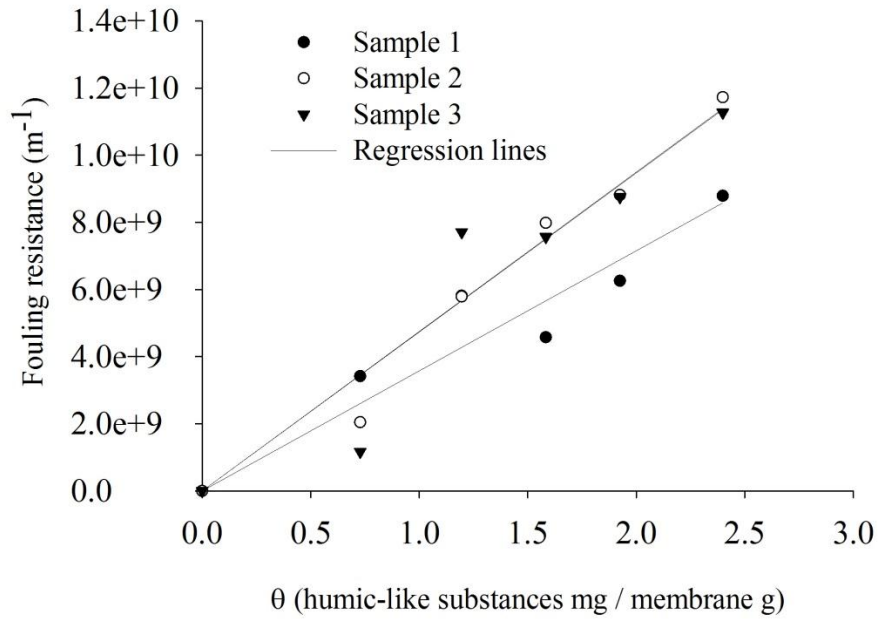
Fig. 4: Correlation between fouling resistance and the amount of retained humic-like substances

Irreversibility of fouling

Irreversibility of fouling was studied by backwash. Figure 5 shows that the flux decline caused by filtration of free EPS is only up to 70% recovered by backwash. This observation is in line with the study done by Ramesh et al. (2007) where they found humic substances as one of the components of irreversible fouling layer formed on the membrane active surface.
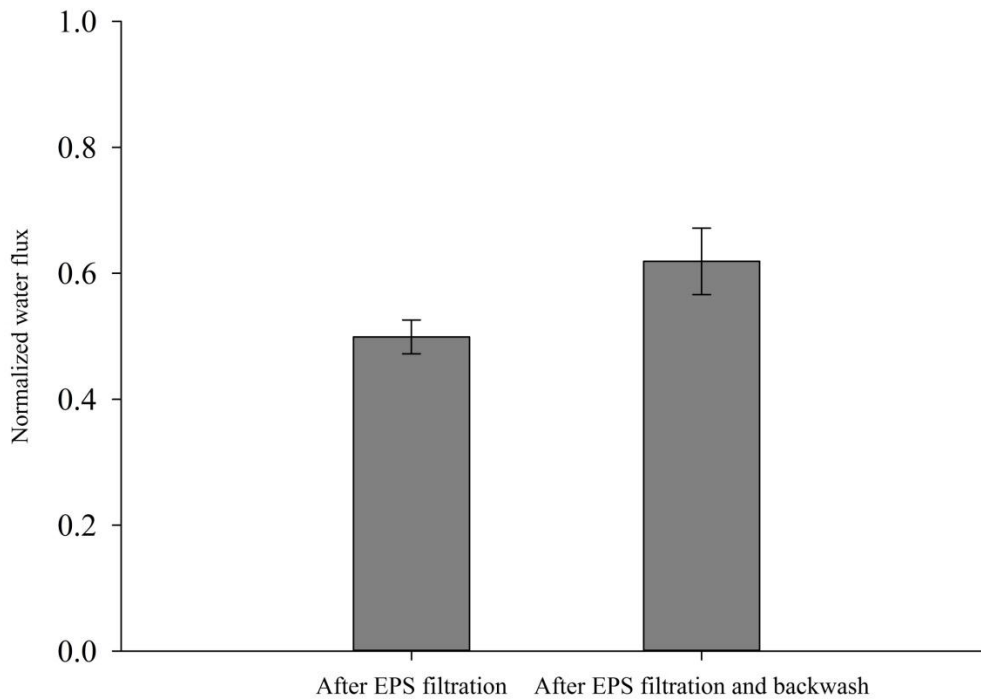
Fig. 5: Effect of backwash on water flux of the fouled membranes

CONCLUSION

Multi-layer fouling is observed in membrane bioreactors where an inner gel-like layer forms between the loose cake and the membrane surface. It has been shown that formation of the inner layer may be due to adsorption and accumulation of the EPS components which are present in the supernatant of the MBR sludge and extracted as free EPS. The free EPS contained a significant amount of humic-like substances. It was shown that the humic-like substances adsorbed to the membrane surface during static contact but this adsorption caused no significant change in water flux; whereas, filtration of the free EPS caused formation of a gel-like layer resulting in a significant decline in water flux. Backwash could re-establish the water flux only up to 70% of the initial. There was a linear correlation between the amount of humic-like substances retained by the membrane and the resistance produced during free EPS filtration. This correlation may enable us to predict irreversible flux decline from the amount of retained humic-like substances.

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