Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2017.21435

88 (2017) 60–66
September

The influence of fouling resistance on the nanocomposite microfiltration process

M. Amouamouha, G. Badalians Gholikandi*

Faculty of Civil, Water and Environmental Engineering, Shahid Beheshti University A.C.,Tehran, Iran, email: m_amouha@sbu.ac.ir (M. Amouamouha), Tel. +982173930000, Fax +9816589-53571, email: g.badalians@yahoo.com (G. Badalians Gholikandi)

Received 15 March 2017; Accepted 9 September 2017

ABSTRACT

In order to achieve a better understanding of the fouling phenomenon, the fouling properties of two nanocomposite microfiltration membranes (poly(vinylidene-fluoride) (PVDF) and polyethersulfone (PES)) treating anaerobic baffled reactor effluent were studied. Silver nanoparticles were incorporated into the membrane surface as an anti-bacterial agent. Furthermore, the biogas produced by the anaerobic baffled reactor were applied to clean the membrane surface fulfilling the anti-biofouling approach. Fouling characteristics of both modified and unmodified membranes were investigated through the flux reduction and EPS formation measurements. The morphology of the modified and unmodified membranes surface were studied by SEM. Regarding the difficulties faced in EPS measurement, the authors proposed the resistance-in-series control as a substitute for EPS. Results showed that the gel layer (R_g) resistance progress was limited after each backwashing step while the resistance of the cake layer (R_c) decreased which is in line with extracellular polymeric substances experiment results. The highest reduction belonged to modified PVDF which was more than 49% in R_g and 78% in EPS. These findings were confirmed by the flux reduction improvement result confirming the adequacy of the employed anti-biofouling approach.

Keywords: Nanocomposite membrane bioreactor; Biofouling; Fouling resistance; Extracellular polymeric substance (EPS); Backwash

1. Introduction

Membrane bioreactor (MBR) process has been regarded as a technology capable of efficient organic substances and microbial loads removal with no need to a following disinfection or post filtration step [1]. Widespread application of MBR in wastewater treatment is indebted to its advantages such as small footprint, high quality permeate,and low hydraulic retention time [2]. Moreover anaerobic membrane bioreactors (An-MBR) combining both membrane technology and anaerobic process, is attractive for both industrial sector, and researchers [3].

One of the major drawbacks in MBR application is fouling, which can be distinguished in the form of pore clogging, cake layer or gel layer formation, and cake layer changes, since it could influence the membrane performance and lifespan negatively [4–6]. Gel layer formation as a result of soluble macromolecules, colloids, and inorganic solutes participation has been addressed to be the important fouling form in MBR where the cake layer is due to the retained solids accumulation [7,8]. Biopolymers, either in the form of soluble microbial products (SMP) or extra cellular polymeric substances (EPS) have been reported to be the main factors in the membrane fouling [9–11]. Since SMP is the soluble part of EPS [12], it can be concluded that total EPS is mainly responsible for biofouling in MBR and controlling its concentration would result in fouling control [13]. Hong et al. [14] reported that when SMP content is quite high in the sludge, the gel layer is more easily formed in comparison to the cake layer. EPS calculation could be performed by five physical and chemical methods [15], some of which reported to be sensitive to time or complicated to use [16,17]. On the other hand, separation of the biofilm from the membrane to extract EPS could include some errors. Therefore it is reasonable to seek some solutions with the objective of facilitating these determinations in MBR operation. The

*Corresponding author.

resistance-in-series has been proposed with the aim of better understanding of fouling concept and its mechanism. Using this model makes it possible to determine every individual fouling component separately [18,19].

Polymeric nanocomposite membranes have attracted great attention as a key substance in nanotechnology during last two decades. The reason for emergence of this material as a novel technology could be related to their unique performance, their improved characteristics comparing to their components, design flexibility, reduced life span cost, and enormous application in various industries [20,21]. Polymeric nanocomposites are developed by either distribution of nanoparticles in the polymer matrix or modification of the polymer surface [22]. Since nanosilver has significant antibacterial effect on one hand, and minor influence on humans' health on the other hand, it has been addressed as a promising possibility to develop antifouling membranes [23,24].

In this study, the efficiency of nanocomposite membrane bioreactor (NMBR) was studied with the objective of finding a technique which can overcome biofouling issue. The combination of the applying process and the membrane material was assessed in this study in order to discover a straightforward way to interpret the fouling behaviour according to the operational parameters, which are often available in wastewater treatment plants, not complicated microbial terms. The membranes hydrophobicity and morphology was measured as an influential parameter on the subject. The hydraulic operational parameters of the NMBR was monitored carefully to determine resistanece-in-series. So the gel layer resistance and EPS formation was calculated and observed as the representative of the two sides of the study.

2. Materials and methods

A laboratory scale MBR was used to study the flux reduction differences between the nanocomposite (silver nanoparticles at thicknesses of 30 nm were applied to modify the commercial surface of PVDF and PES; hereinafter called PVDF30 and PES30, respectively) and the pure membrane. Nanocomposite membranes were prepared by a physical deposition method called physical vapor deposition (PVD). First, the membranes were immersed in the deionized water. Then the samples were put in an ultrasonic shaker for 10 min to remove any probable contamination. After preparation, the membrane were installed precisely in the vacuum chamber and the pressure was reduced to 6–8 $\times 10^{-5}$ m bar with the coating rate of 0.9–1 Å/s to control the process speed. When the mentioned pressure was achieved, silver nanoparticles were deposited on the surface at thicknesses of 30 nm.

The hydrophobicity of the membrane surface was observed by a contact angle meter (DSA100, Krüss, Germany). Distilled water was dropped onto the active layer of the surface using a micro liter syringe with a flat needle, and then the contact angle was calculated. In order of minimizing the experimental error, the data were collected at least 3 times from 2 different places. The mean values were reported as the contact angle measurements. The morphology of the membranes surface was investigated by performing Scanning Electron Microscope (SEM) test to study the silver presence, and its impact on fouling before and after backwash. Prior to SEM performance for anti-biofouling study, the samples were fixed as described by Li et al. [23].

Since the synthetic wastewater can guarantee the consistency of the influent flow properties, it was used to feed the reactor. A cross-flow microfiltration set-up was used as illustrated in Fig. 1. The pilot fitted with flat sheet (PVDF) and (PES) microfiltration membranes with a mean pore size of 0.22 μm (Millipore, Durapore©) with the dimension of 15 cm× 15 cm was operated for 7 d. The wastewater was pumped from the anaerobic baffled reactor (ABR) effluent via a booster pump (KJ-2500, Deng yuan, Taiwan).The initial feed flux was 104 L/m^2·h for the both modified and unmodified PVDF and PES membranes. A further step to improve the performance of the combined system of ABR and the membrane bioreactor is using the gas produced in ABR to backwash the membranes with the aim of reaching a better mixing on one hand and preventing the solids deposition on the membrane surface on the other hand. To achieve the goal of complete backwash the feed flow crossed the feed side synchronically with the biogas blowing underneath the membranes with the ratio of 0.7:0.3, and the concentrate valve was fully opened during backwash. This method seems to be hopeful to optimize the anti-fouling efficiency as much as possible. The biogas was scoured onto the membrane surface in the combination with a recirculation flow in order to backwash the membrane (Fig. 1).

The experiment has two stages, the first one was operation and the other was the backwashing with mixed flow of the biogas (produced by anaerobic baffled reactor) and the feed flow. The backwash process was conducted for 15 min, once every 24 h. The trans-membrane pressure (TMP) was measured by pressure sensors (Pakkens, Turkey) and TMP was constant during operation stage and it was equal to 1.2 bar, approximately. The feed quality during microfiltration test was summarized in Table 1. The reduction in permeation flux was considered as an index for the membrane fouling behaviour.

In order to reach a better understanding of the significance of this study, the resistance result was accommodated by the EPS measurements. EPS was extracted via centrifuging method as illustrated by Liu and Fang [15].

In addition to monitor qualitative performance, indicating by pollution removal efficiency, and the quantitative determination, calculated by permeation flux, the filtration hydraulic function should be analysed as well [25]. As Darcy's law illustrated, the resistance-in series was calculated according to the following equation:

$$J(t) = \frac{1}{A_m}\frac{dV}{dt} = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu\left(R_m + R_f\right)} \tag{1}$$

where J is the permeation flux of the membrane (m^3/m^2·s), V is the permeate total volume (m^3), A_m is the area of the membrane (m^2), ΔP is the membrane pressure (Pa), μ is the viscosity of the permeate (N·s/m^2), R_t is the total resistance of the membranes (m^{-1}), R_m is the intrinsic resistance of the membrane (m^{-1}), R_f is the resistance of the fouling (m^{-1}). Since the TMP is constant in this research, the reduction of the permeate flux would be associated with fouling occurrence. As it can be interpreted from the Eq. (1), at constant

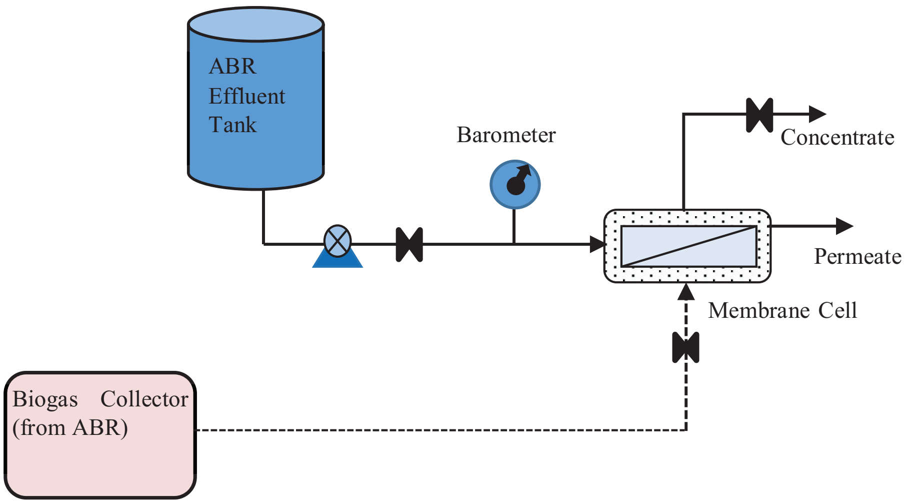

Fig. 1. Schematic of the microfiltration setup.

Table 1
Characteristics of ABR effluent used as feed to MF process

Water quality index	Average amount
pH	6.9
Turbidity (FTU)	37
TS (mg/L)	48
COD (mg/L)	500
CFU	2.3*10^6

TMP, by increasing the resistance, the flow filtration will decrease [26].

The fouling resistance is consisting of the cake layer resistance (R_c) and the resistance of the gel layer (R_g). The first one is reversible made by MLSS particles and the latter is associated with the blocking of the pores and irreversible deposition. Hence the fouling resistance would be stated as:

$$R_f = R_c + R_g \tag{2}$$

In order to calculate the mentioned equation, R_m was measured using pure water according to the second part of the Eq. 1 $\left(R_m = \frac{\Delta P}{\mu J}\right)$. R_t could be calculated at the end of the filtration process as R_m. Subsequently, R_f gains by subtracting R_m from R_t. The produced biogas by the anaerobic reactor was used to rinse the cake layer, and then R_c was determined from the permeation flux and ΔP values. By calculation of all the resistances, R_g could be calculated from Eq. (2).

For EPS extraction, the membranes were immersed in 90% NaCl and shaked 5 times, then they were dipped in tween®20 with the concentration of 5% and stirred 20 times. After suspending in the mentioned solution, 10 µL of the samples were taken, diluted in 10 cc of 90% NaCl and completely stirred. This solution was used for the EPS extraction by a physical method; centrifugation. After the high-speed (20000G, 4°C, 20 min) centrifugation, the microbial cells were eliminated through the filtration by a 0.2 µm membrane and then the supernatant were used as EPS samples [15].

3. Results and discussion

30 nm silver deposition resulted in greater hydrophobic effect on PES surface compared to PVDF. The measurements revealed that the contact angle of the membranes was 75°, 120°, 61°, 128° for pristine PVDF, PVDF30, pure PES, PES30, respectively. SEM was applied to inspect the membranes surface after modification (Fig. 2) and before and after conducting backwash (Fig. 3) as well. From Fig. 2 it can be observed that silver deposited properly on the surface of both membranes but the deposition was more uniform on the PVDF.

As depicted in Fig. 3, the bacteria adhesion on nanocomposite membranes surface reduced even in the absence of backwash procedure. Another significant result is the impact of biogas on the biofilm adhesion on the membranes surface which is augmented on nanocomposites surface. This means that the combined applying process and the material modification is capable of efficient fouling reduction as assumed. A further point which should be noted is intensified hydrophobic property of the membranes after modification according to the result of the contact angles. Comparing the result of hydrophobicity with SEM images before and after backwash, it can be declared that the modified surface had a less tendency of bacteria captivating which is applicable to both PVDF and PES. As shown in Fig. 3, for both PVDF and PES, the bacteria adhered on nanocomposite membranes less than pure membranes. This situation improved even more after biogas backwashing for all membranes. In other words, the combination of applying backwash system and surface modification is capable of biofilm reduction, significantly. As it is evident from Fig. 3, the combination is more effective in PVDF membranes (both nanocomposite and pure). This result was confirmed by EPS measurements as well. Additionally since the fouling resistance and EPS formation appeared to be less on

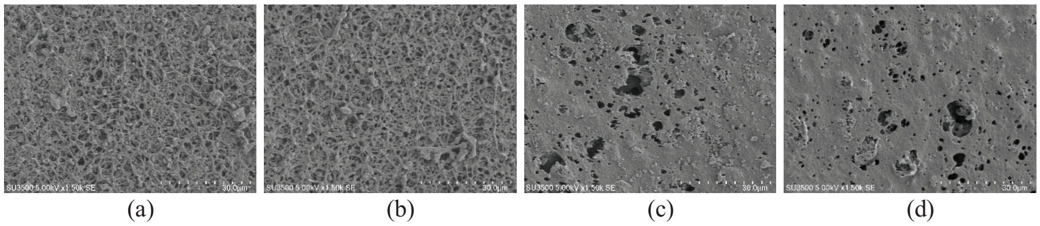

Fig. 2. SEM images of modified membrane surface before antibacterial test; (a) PVDF 30, (b) pure PVDF, (c) PES30, (d) pure PES.

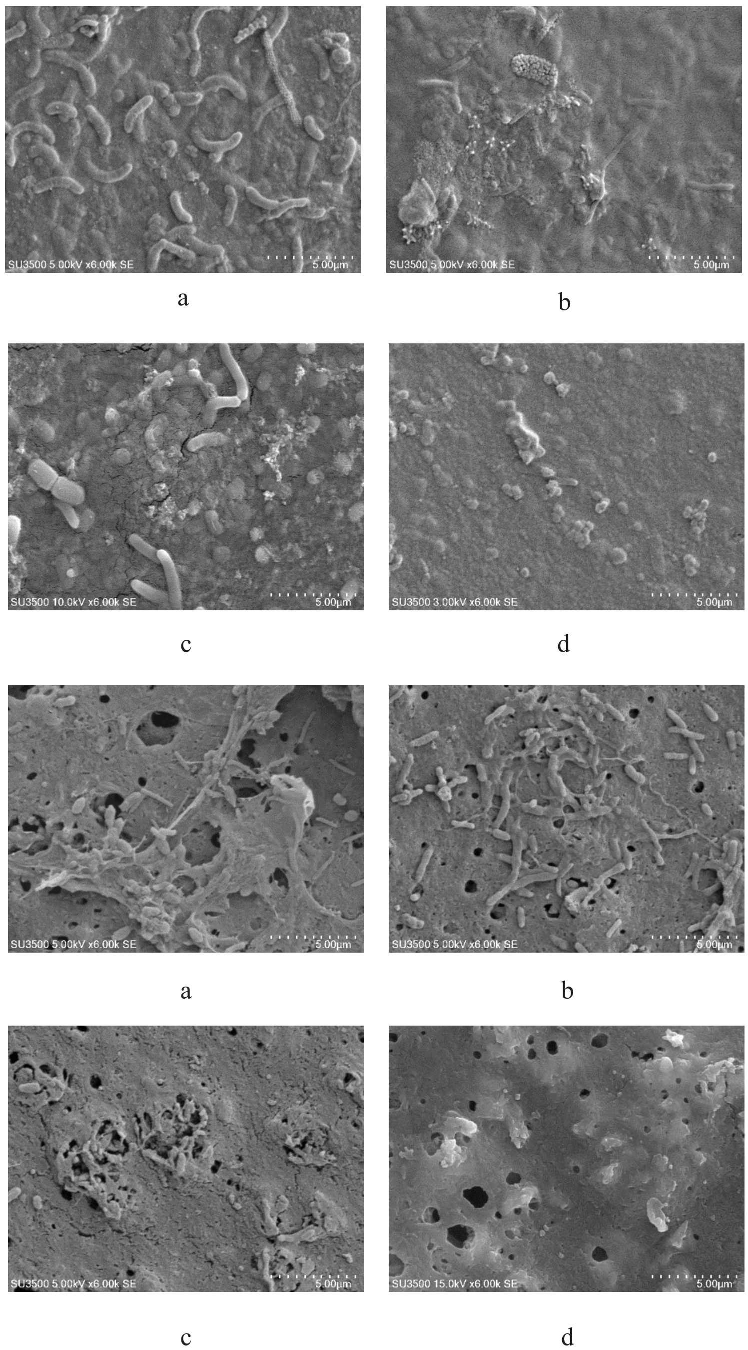

Fig. 3. Morphology of the membranes surface (a) pure membranes without backwashing, (b) pure membranes backwashed by biogas, (c) nanocomposite membranes without backwashing, and (d) nanocomposite membranes backwashed by biogas.

PVDF nanocomposite membrane, it is compatible to common sense to consider the physical coating more proper for PVDF.

The gel layer resistance was determined according to the previous section calculation. 7 d of filtration by nanocomposite and pure membranes showed that gel layer resistance is the increasing part of the fouling with time processing. This means that the irreversible part of the fouling is augmenting over the time leading to permanent flux reduction and decline in the membrane life span subsequently.

As depicted in Fig. 4a–d, the cake layer resistance decreased after backwashing step and reaching steady state after rinsing for both PES and PVDF membranes. A more precise comparison between PES and PVDF revealed that even though PES had a higher initial flux due to its more hydrophilic inherent, PVDF gel layer amount was less (Fig. 4a and 4c). The situation was even more comparable in their nanocomposites as PVDF30 gel layer was much smaller (Fig. 4b and 4d). This means the flux reduction is more in PES membranes regardless of its primary higher water permeability (as it was equal to 31.7 and 37% for pristine PVDF and PES whereas this reduction was 9 and 17.8% for modified PVDF and PES respectively). Comparing pure and modified PVDF (Fig. 4a and 4b), it could be concluded that not only the gel layer resistance is smaller, but also the resistance of the cake layer is lower which can be related to the surface modification. This effect existed for PES as well (Fig. 4c and 4d) but it was less impressive. The reduction of gel layer resistance (R_g) was 42.4% for PES and 49.9% for PVDF in their nanocomposites. This could be described by the difference of the hydrophobicity of PES and PVDF. Hence the more the hydrophobic the membrane is, the less resistance would be encountered.

Accommodating the gel layer resistance data with EPS amount formed on the membranes surface after backwashing illustrated that the gel layer resistance can be addressed as the hydraulic substitute for EPS. In other words, instead of measuring EPS and SMP as the foulants, the gel layer resistance can be measured based on the controlling operation parameters which are monitored daily. Membrane fouling is divided into either reversible, which can be removed by backwash or surface rinsing, or irreversible fouling, which can be restored through chemical cleaning. As the results showed, the biogas scouring was able to recapture a part of TMP even in irreversible mode of fouling and improve the pore plugging or chemisorption mechanisms. A further outcome from the resistance (Fig. 4a–d) could be the relation between the backwashing time and the resistance. As it shown, more the backwashing was performed, more the resistance would be. This means, although backwashing could mitigate the resistance in each step, the amount of the irreversible fouling increased over time which is in a good agreement with EPS determination.

The reason for the above discussion can be the relationship between the fouling resistance components and the logical correlation between EPS and the gel layer. As depicted in Fig. 5a–d, The EPS decreased by surface modification and biogas scouring yet it increased over time. This findings confirmed that biofouling occurrence and progress could be postponed

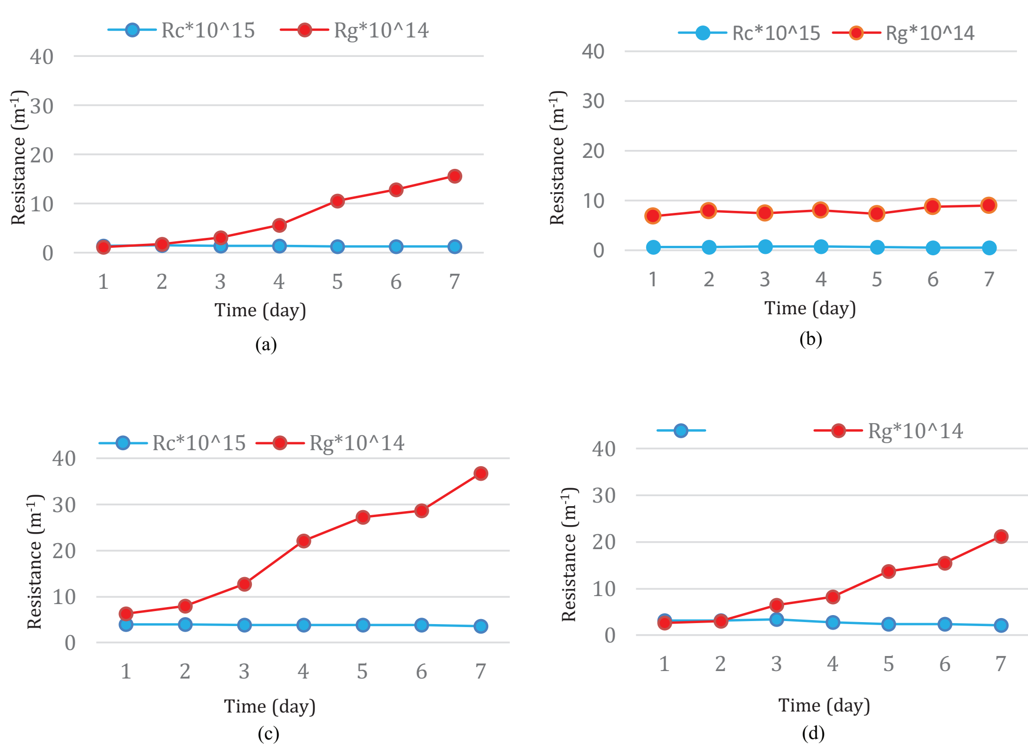

Fig. 4. (a). The cake layer and the gel layer resistance changes in 7 d for pure PVDF, (b). The cake layer and the gel layer resistance changes in 7 d for PVDF30, (c). The cake layer and the gel layer resistance changes in 7 d for pure PES, (d). The cake layer and the gel layer resistance changes in 7 d for PES30.

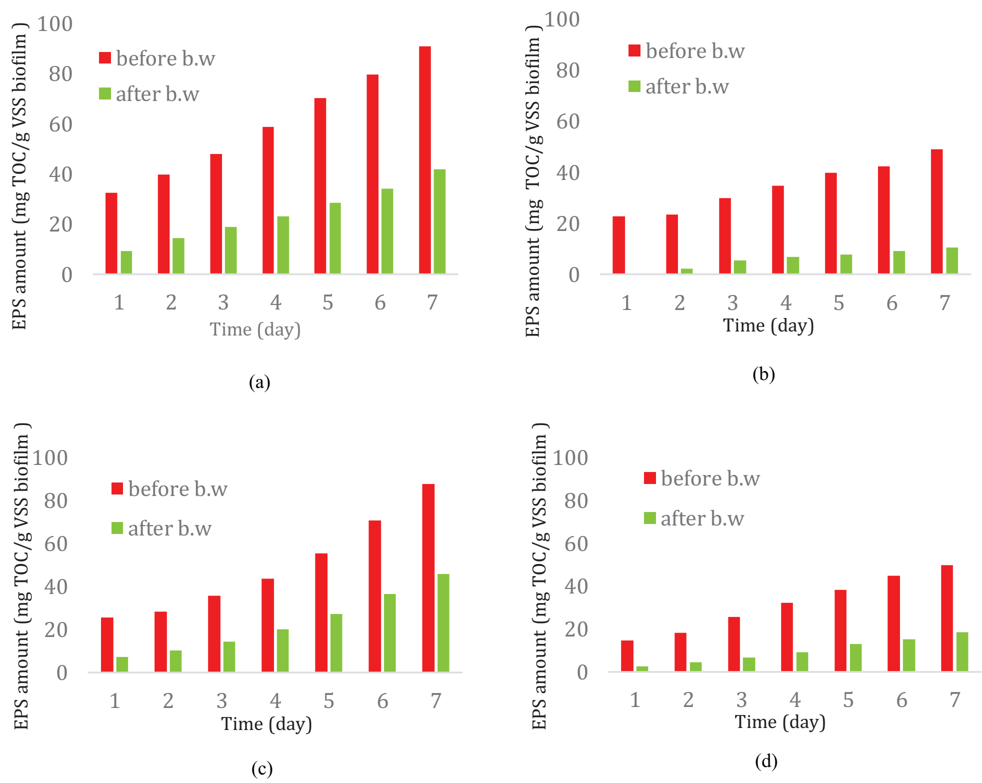

Fig. 5. (a). EPS determination in 7 d for pure PVDF, (b). EPS determination in 7 d for PVDF30, (c). EPS determination in 7 d for pure PES, (d). EPS determination in 7 d for PES30.

by the synchronous combination of the nanosilver coating and the biogas sparging on the membrane surface. After 7 d of operation and daily backwash, EPS decreased 53.9%, 78.3%, 47.7%, and 62.8% in PVDF, PVDF30, PES, and PES30 respectively. This confirms the anti-bacterial effect of silver and the reduction of EPS by biogas as described by [14]. The EPS reduction result is in line with the gel layer resistance amounts. In other words EPS decrease with decreasing R_g. As the following figure reveals, biogas backwashing has a significant impact on EPS and the resistance mitigation. This effect could be justified as cleaning by biogas reduced the fouling related to the cake layer formation at first. The second notion could be the effect on the proper growth condition for biofilm provided by the biofilm attachment over time. It should be noticed that a part of the deduction is associated with the modification according to Fig. 5a–d.

As it shown in Fig. 5, passing the time increased EPS amount formed on the surface of both unmodified and modified membranes. The difference between EPS amount in nanocomposites and pure membranes is an evident to approve the positive antibacterial influence of nanosilver in both anti-growth and anti-adhesion aspects.

4. Conclusion

The results of this investigation confirmed that the hydraulic resistance-in-series could apply as a fouling determinant instead of EPS formation control in MBR operation. Backwashing by biogas would affect these resistance especially for the cake layer as the gel layer has been addressed as the irreversible part. The SEM images verified the assumption of this article which was the study of backwash effect on the reversible part of the fouling (demonstrated by R_c). Additionally, the study results illustrated that PVDF, which has a lower initial flux and a more hydrophobic inherent, exhibited more improvement in anti-bacterial adhesion, flux reduction control and EPS formation. This is a significant finding since it would pave the way of using hydrophobic membrane in filtration industry. These results would defend the application of the applied system, combination of backwash biogas and surface modification, even though for hydrophobic membranes.

References

[1] S. Judd, The MBR Book: Principles and Applications of Membrane Bioreactors for Water and Wastewater Treatment, 2nd ed., Butterworth-Heinemann, Oxford, 2011.

[2] M.M. Rahman, M.H. Al-Malack, Biochemical kinetics of cross flow membrane bioreactor processes in the treatment of refinery wastewater, Int. J. Environ. Res., 6(1) (2012) 285–296.

[3] M. Aslan, Y. Saatçi, Ö. Hanay, H. Hasar, Membrane fouling control in anaerobic submerged membrane bioreactor, Desal. Water Treat., 52(40–42) (2014) 7520–7530.

[4] I.S. Chang, P. Le-Clech, B. Jefferson, S. Judd, Membrane fouling in membrane bioreactors for wastewater treatment, J. Environ. Eng., 128(11) (2002) 1018–1029.

[5] O.T. Iorhemen, R.A. Hamza, J.H. Tay, Membrane bioreactor (MBR) technology for wastewater treatment and reclamation: membrane fouling, Membranes, 6(2) (2016) 33.

[6] J. Chen, M. Zhang, F. Li, L. Qian, H. Lin, L. Yang, X. Wu, X. Zhou, Y. He, Y.B.Q. Liao, Membrane fouling in a membrane bioreactor: high filtration resistance of gel layer and its underlying mechanism, Water Res., 102 (2016) 82–89.
[7] X.M. Wang, T.D. Waite, Role of gelling soluble and colloidal microbial products in membrane fouling, Environ. Sci. Technol., 43 (2009) 9341–9347.
[8] Z. Wang, J. Ma, C. Tang, K. Kimura, Q. Wang, X. Han, Membrane cleaning in membrane bioreactors: A review, J. Membr. Sci., 468 (2014) 276–307.
[9] N.O. Yigit, I. Harman, G. Civelekoglu, H. Koseoglu, N. Cicek, M. Kitis, Membrane fouling in a pilot-scale submerged membrane bioreactor operated under various conditions, Desalination, 231 (2008) 124–132.
[10] G.B. Gholikandi, M. Khosravi, Upgrading of submerged membrane bioreactor operation with regard to soluble microbial products and mathematical modeling for optimisation of critical flux, Desal. Water Treat., 39 (2012) 199–208.
[11] M.E. Ersahin, H. Ozgun, Y. Tao, J.B. Van Lier, Applicability of dynamic membrane technology in anaerobic membrane bioreactors, Water Res., 48 (2014) 420–429.
[12] C.S. Laspidou, B.E. Rittmann, A unified theory for extracellular polymeric substances, soluble microbial products, and active and inert biomass, Water Res., 36(11) (2002) 2711–2720.
[13] Water Environment Federation (WEF), Membrane Bioreactors: Manual of Practice, No. 36, McGraw-Hill New York, 2011.
[14] H. Hong, M. Zhang, Y. He, J. Chen, H. Lin, Fouling mechanisms of gel layer in a submerged membrane bioreactor, Bioresour. Technol., 166 (2014) 295–302.
[15] H. Liu, H.H. Fang, Extraction of extracellular polymeric substances (EPS) of sludges. J. Biotechnol., 95(3) (2002) 249–256.
[16] B. Frølund, T. Griebe, P.H. Nielsen, Enzymatic activity in the activated-sludge floc matrix, Appl. Microbiol. Biotechnol., 43(4) (1995) 755–761.
[17] S. Liang, C. Liu, L. Song, Soluble microbial products in membrane bioreactor operation: behaviors, characteristics, and fouling potential, Water Res., 41(1) (2007) 95–101.
[18] M. Li, Y. Zhao, S. Zhou, W. Xing, F.S. Wong, Resistance analysis for ceramic membrane microfiltration of raw soy sauce, J. Membr. Sci., 299 (2007) 122–129.
[19] I.S. Chang, R. Field, Z. Cui, Limitations of resistance-in-series model for fouling analysis in membrane bioreactors: A cautionary note, Desal. Water Treat., 8 (2009) 31–36.
[20] J. Jain, S. Arora, J.M. Rajwade, P. Omray, S. Khandelwal, K.M. Paknikar, Silver nanoparticles in therapeutics: development of an antimicrobial gel formulation for topical use, Mol. Pharmacol., 6(5) (2009) 1388–1401.
[21] P. Dallas, V.K. Sharma, R. Zboril, Silver polymeric nanocomposites as advanced antimicrobial agents: classification, synthetic paths, applications, and perspectives, Adv. Colloid Interface Sci., 166(1) (2011) 119–135.
[22] K. Faghihi, M. Hajibeygi, Synthesis and properties of polyimide/silver nanocomposite containing dibenzalacetone moiety in the main chain, J. Saudi Chem. Soc., 17(4) (2013) 419–423.
[23] J.H. Li, X.S. Shao, Q. Zhou, M.Z. Li, Q.Q. Zhang, The double effects of silver nanoparticles on the PVDF membrane: surface hydrophilicity and antifouling performance, Appl. Surf. Sci., 265 (2013) 663–670.
[24] M.E. Samberg, P.E. Orndorff, N.A. Monteiro-Riviere, Antibacterial efficacy of silver nanoparticles of different sizes, surface conditions and synthesis methods, Nanotoxicology, 5(2) (2011) 244–253.
[25] K. Bani-Melhem, Z. Al-Qodah, M. Al-Shannag, A. Qasaimeh, M.R. Qtaishat, M. Alkasrawi, On the performance of real grey water treatment using a submerged membrane bioreactor system, J. Membr. Sci., 476 (2015) 40–49.
[26] W. Guo, H.H. Ngo, J. Li, A mini-review on membrane fouling, Bioresour. Technol., 122 (2012) 27–34.