TREATMENT OF PRODUCED WATER USING MICROFILTRATION MEMBRANE MODIFIED BY NANO PARTICLES

Chen, Xiujuan[1,2] Huang, Gordon[1,4] An, Chunjiang[1,3] Wu, Yinghui[1,2]

[1] Institute for Energy, Environment and Sustainable Communities, University of Regina, Canada

[2] Faculty of Engineering and Applied Science, University of Regina, Canada

[3] Department of Building, Civil and Environmental Engineering, Concordia University, Canada

[4] gordonhuang0818@gmail.com

Abstract: Membrane filtration technology has been considered as a promising alternative for produced water treatment. However, membrane fouling is a critical problem that affects wastewater treatment efficiency. Membrane surface modification has been regarded as an effective method to improve membrane antifouling ability. In this study, a novel membrane surface modification method was proposed to obtain a super-hydrophilic membrane with high water permeability and great oil rejection through cold plasma-induced poly acrylic acid (PAA) graft-polymerization followed by nano-ZnO self-assembly. The results indicated that a PAA layer was uniformly formed on the membrane surface, and ZnO nanoparticles (NPs) were strongly immobilized by the PAA layer. The firm PAA-ZnO coating on membrane surface brought about dramatically improvements of membrane performances both in permeation flux and pollutant rejection rate.

Keywords: Microfiltration membrane; Surface modification; Nano particles

1   BACKGROUND

Increasing produced water generation caused by petrochemical activities such as onshore/offshore oil recovery have caused serious health risks and the destruction of ecosystems, becoming an urgent global environmental problem (Chu et al., 2014). The development of effective methods for produced water treatment is desired and full of challenges, particularly for the separation of oil/water emulsions (Zhao et al., 2014). Most of the traditional techniques, such as gravity separation, flocculation and flotation, suffer from low efficiency, high cost, and secondary pollution (Chen et al., 2018, Wang et al., 2018). In comparison, polymer filtration membranes have been frequently applied in practical applications of produced water treatment owing to their lower cost and ready availability (Mukherjee and De, 2018). Among them, polyvinylidene fluoride (PVDF) membranes are extensively used due to its outstanding mechanical properties, thermal stability, and chemical resistance. Nevertheless, PVDF membranes still suffer from membrane fouling because of its hydrophobic nature, which will eventually result in decrease of permeate flux and treatment efficiency.

To address this issue, a number of advanced PVDF membranes have been developed by various modification techniques with the incorporation of nanoparticles (NPs) to improve the membrane hydrophilicity and antifouling ability (Bet-Moushoul et al., 2016). Among them, ZnO NPs have attracted interests in membrane modification due to its special properties (Zinadini et al., 2017). However, most of previous research on ZnO NPs for PVDF membrane modification was limited to blending ZnO NPs into the casting solution. The improvements of membrane properties such as hydrophilicity and fouling resistance were restricted by doing so. The modification efficiency was affected because the ZnO NPs agglomerated in the casting solution, causing them to be entirely enfolded by the polymer matrix. In comparison, immobilizing ZnO NPs on the membrane surfaces using techniques of coating or chemical grafting to form

a stable functional layer could be a more effective modification approach. Most of the ZnO NPs can disperse on PVDF membrane surfaces to maximally improve their performances. The challenge of this approach is how to stably immobilize ZnO NPs on the membrane surface, since ZnO NPs cannot self-assemble onto PVDF membrane surface without bonding with suitable functional groups.

Therefore, in this research, a novel membrane surface modification method was proposed to obtain a super-hydrophilic membrane which was modified from PVDF membrane through cold plasma-induced poly acrylic acid (PAA) graft-polymerization followed by simple nano-ZnO self-assembly. The functional groups of PAA layer on membrane surface could strongly bind with ZnO NPs. The improvement of membrane performance was studied for the application of produced water treatment.

2 METHODS

Poly acrylic acid (PAA), PVDF microfiltration membrane (0.1 μm pore size), and ZnO NPs (< 100 nm) were used. The technique of cold plasma surface treatment was applied to induce PAA polymerization by introducing chemical initiators on PVDF membrane surface. The PAA-grafted membrane was then dipped in the aqueous nano-ZnO suspension to attach ZnO NPs. The modified membrane was comprehensively characterized by contact angle measurement, scanning electron microscope (SEM) images, elemental analysis, attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), and synchrotron-based X-ray analyses. The synchrotron-based X-ray analyses were carried out at the beamline 07B2-1 (VESPERS) at the Canadian Light Source (Saskatoon, Canada). The membrane performances including water flux and oil rejection rate were measured using a CF016 cross-flow membrane test skid with 20.6 cm^2 of effective membrane area (Sterlitech Corporation, Kent, USA). The feed oily water was obtained by mixing commercial diesel and DI water, and the chemical oxygen demand (COD) concentration was determined by a Hach 2800 COD analyzer. All experiments were carried out in 20 ± 1 °C. The permeation flux (J, L/m^2·min) and COD removal rate (R, %) of the membrane can be calculated as:

$$J = \frac{V}{A \times \Delta t}$$

$$R(\%) = \frac{C_f - C_p}{C_f} \times 100$$

where, V is the permeate water volume (L), A is the membrane area (m^2), Δt is the permeation time (min), C_p is the COD concentration in the permeate solution (mg/L), and C_f is the COD concentration in the feed solution (mg/L).

3 RESULTS

The present research studied the surface modification of PVDF microfiltration membrane to obtain a super-hydrophilic membrane for produced water treatment. An extreme thin PAA layer without compromising the bulk structure was formed on the membrane surface through cold plasma induced graft copolymerization. The ZnO NPs were self-assembled and distributed in the PAA layer. According to Figure 1, SEM images show a thin PAA polymer layer formed on the membrane surface with uniform structure after plasma-grafted polymerization. Compared to the surface of pristine PVDF membrane, the formed PAA layer does not block the original pores. After nano-ZnO self-assembly, the membrane surface was coated with ZnO NPs via the PAA layer.

The PAA-ZnO coating on membrane surface converted its hydrophobic nature to hydrophilic, the water contact angle dramatically decreased from 101.1° to less than 18° (Figure 2(a)). This resulted in significant improvements of membrane performances both in water permeation flux and pollutant rejection rate. The separation performance of the modified membrane was evaluated using a cross-flow filtration system. As shown in Figure 2(b), the modified membrane showed extremely high permeation flux (more than 1200 L/m^2 min), which was much larger than that of the pristine membrane (less than 100 L/m^2 min). The overall COD rejection rate of the optimized membrane was also higher than that of the pristine membrane (Figure 2(c)). These results was due to that the fixed ZnO NPs through the grafted PAA layer remarkably improved

the membrane hydrophilicity and did not block the membrane pores. It was concluded that a substantially higher permeability could be achieved and a higher oil rejection could also be obtained after membrane modification.
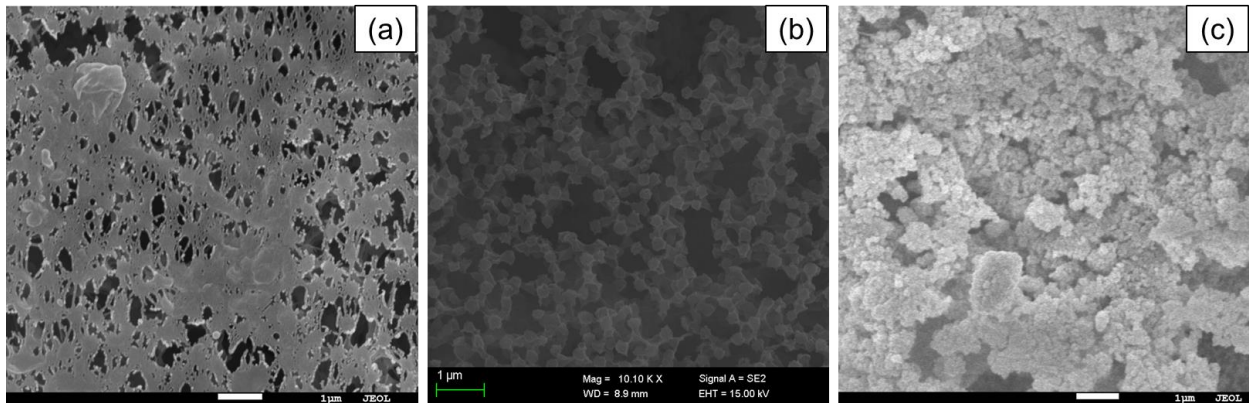

Figure 1: SEM images: (a) original PVDF membrane, (b) PAA grafted membrane, and (c) modified membrane
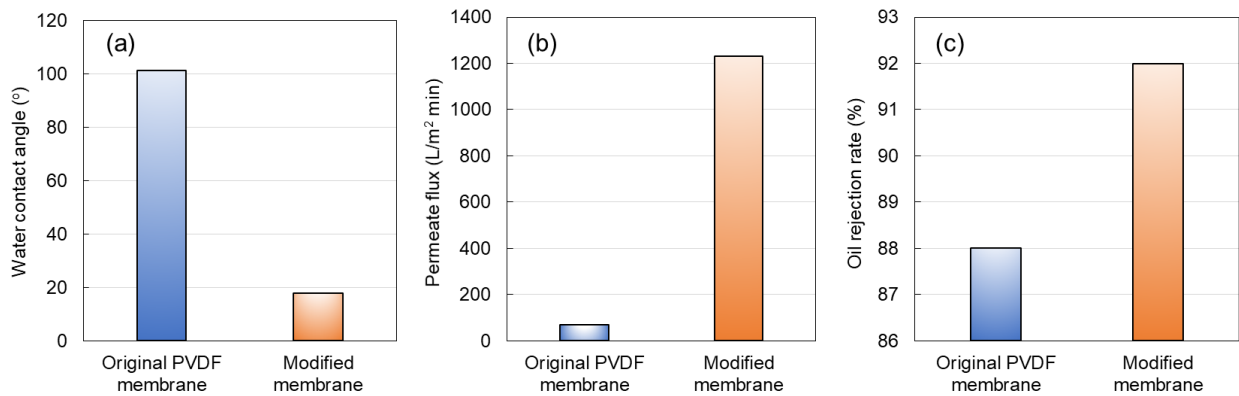

Figure 2: Comparisons between the original PVDF membrane and modified membrane: (a) water contact angle, (b) permeate flux, and (c) oil rejection rate

4   CONCLUSION

This research presented an approach of membrane modification for produced water treatment. The results are useful to demonstrate the effects of surface modification on PVDF membrane performance, and thus help to improve treatment efficiency and reduce treatment cost. Further studies will be needed to obtain more theoretical support for the mechanisms of membrane antifouling. Different modification approaches for different membrane types should also be investigated for produced water treatment.

References

Chu, Z., Y. Feng and S. Seeger (2014). "Oil/Water Separation with Selective Superantiwetting/Superwetting Surface Materials." Angewandte Chemie International Edition 54(8): 2328-2338.

Zhao, S., G. Huang, G. Cheng, Y. Wang and H. Fu (2014). "Hardness, COD and turbidity removals from produced water by electrocoagulation pretreatment prior to reverse osmosis membranes." Desalination 344: 454-462.

Bet-Moushoul, E., Y. Mansourpanah, K. Farhadi and M. Tabatabaei (2016). "TiO2 nanocomposite based polymeric membranes: a review on performance improvement for various applications in chemical engineering processes." Chemical Engineering Journal 283: 29-46.

Chen, X., G. Huang, C. An, Y. Yao and S. Zhao (2018). "Emerging N- nitrosamines and N- nitramines from amine-based post-combustion CO 2 capture – A review." Chemical Engineering Journal 335: 921-935.

Mukherjee, M. and S. De (2018). "Antibacterial polymeric membranes: a short review." Environmental Science: Water Research & Technology.

Wang, W., G. Huang, C. An, S. Zhao, X. Chen and P. Zhang (2018). "Adsorption of anionic azo dyes from aqueous solution on cationic gemini surfactant-modified flax shives: Synchrotron infrared, optimization and modeling studies." Journal of Cleaner Production 172: 1986-1997.

Zinadini, S., S. Rostami, V. Vatanpour and E. Jalilian (2017). "Preparation of antibiofouling polyethersulfone mixed matrix NF membrane using photocatalytic activity of ZnO/MWCNTs nanocomposite." Journal of Membrane Science 529: 133-141.