Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.749025

51 (2013) 2575–2583
March

Taylor & Francis
Taylor & Francis Group

Ceramic membrane filtration as seawater RO pre-treatment: influencing factors on the ceramic membrane flux and quality

Zhaoliang Cui[a], Wenbo Peng[b], Yiqun Fan[a,*], Weihong Xing[a], Nanping Xu[a]

[a]*State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China*
Tel./Fax: +86 025 83172277; email: yiqunfan@njut.edu.cn
[b]*Jiangsu Jiuwu High-Tech Co. Ltd, Nanjing 210061, China*

Received 22 August 2011; Accepted 23 September 2012

ABSTRACT

Membrane filtration has been accepted as the preferred pre-treatment method in reverse osmosis (RO) processes in recent years. In this paper, a laboratory-scale ceramic membranes device, which has a potential to be used as pre-treatment for RO desalination, was employed to investigate the performance of ceramic membranes with different pore sizes and under different conditions. Ceramic membranes with pore sizes of 50, 200, 500, and 800 nm were tested, and the effects of pore size, transmembrane pressure (TMP), coagulation method, and NaClO addition on the permeate flux and the permeate quality of ceramic membranes were studied. The results show that the pore size has an insignificant effect on the permeate flux of ceramic membranes but the coagulation method has a significant effect. Pore size and NaClO addition did not have significant effects on the turbidity of the ceramic membrane permeate, but they did affect the SDI_{15} (Silt Density Index) values of the ceramic membrane permeate. A pilot test was executed using a pilot ceramic membrane device with an approximate capacity of $330\,m^3/d$. The TMP was stable with a constant flux of $150\,L/m^2h$ and a cross-flow velocity of 0.015 m/s, and the turbidity and SDI_{15} values were satisfactory for RO, suggesting that ceramic membranes can meet the demands of RO.

Keywords: Ceramic membrane; Seawater desalination; Pre-treatment

1. Introduction

The demand for fresh water to meet domestic and industrial needs is constantly increasing, and nearly 80% of the world's population is exposed to high levels of threat to water security [1]. Desalination technology is an important way to augment the water supply in the arid regions of the world [2–4]. Reverse osmosis (RO) requires far less energy consumption than other desalination methods, which ensures that RO has a good market worldwide [5–7]. However, seawater sources often have particulate and colloidal contaminants as well as hydrocarbons from oil contamination and biological contaminants (algal blooms and other microorganisms), leading to fouling which decreases the permeability of the RO membrane and shortens its life. In practice, a pre-treatment system is required to protect RO membranes from contamination and fouling and thus extend the lifetime of the RO unit [6–8].

Micro-filtration (MF) and ultra-filtration (UF) have been introduced as replacements for conventional pre-

*Corresponding author.

treatment processes such as coagulation, adsorption, sedimentation, sand filtration, and disinfection. With the rapid development of membrane technology in last decade, membrane pre-treatment processes have shown great advantages over conventional pre-treatment processes [9–13]. The combined effect of greater recovery and higher flux rate with MF or UF promises to significantly reduce the RO plant cost [14,15].

Ceramic membranes have been used in the chemical, petrochemical, pharmaceutical, metallurgical, environmental, food, and electronic industries because of their substantial chemical and thermal stability and their high mechanical strength compared to organic membranes. Recently due to a decrease in their price [16,17], these membranes have been adopted for groundwater treatment and have exhibited superior performance compared to conventional treatment [18–22]. Then, they are introduced to the pre-treatment for seawater desalination. Xu et al. [23] investigated the performance of a ceramic membrane with a 50 nm pore size in treating raw seawater and found that zirconium dioxide UF pre-treatment before RO desalination can achieve a consistent ceramic membrane permeate quality and a low fouling potential at high ceramic membrane permeate fluxes. Cui et al. [24] carried out a pilot study using ceramic membranes. The results showed that ceramic membrane is available to pre-treat seawater for RO, even under the condition with very low temperature.

The objectives of this study were the following: (1) to research the influencing factors on permeate flux and quality of the ceramic membranes under different conditions using a laboratory-scale device and (2) to investigate the long-term run performance of the ceramic membranes employing a pilot-scale device with a capacity of 330 m^3/d.

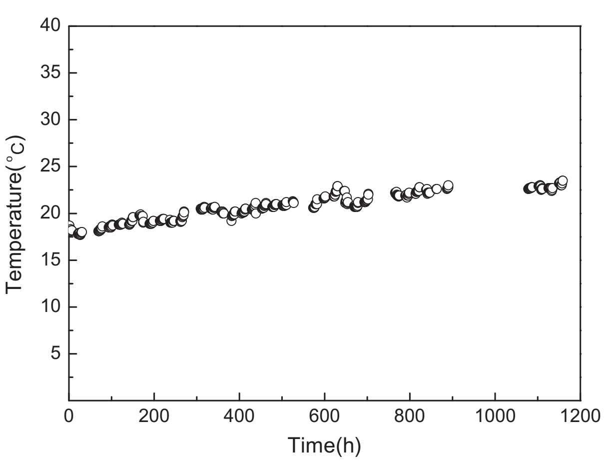


Fig. 1. Temperature of the raw seawater.

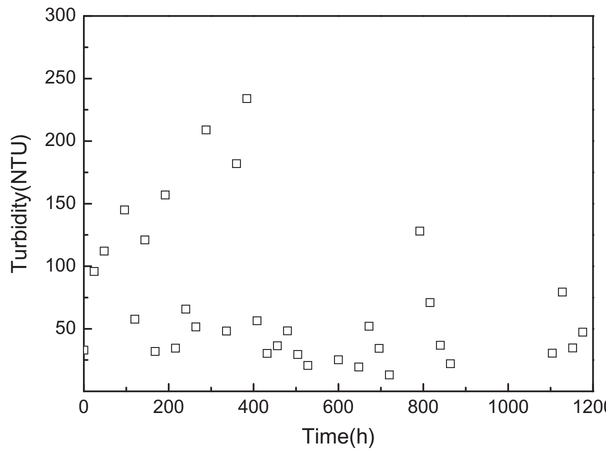


Fig. 2. Turbidity of the raw seawater.

2. Experimental

2.1. Seawater

Seawater used for this study was collected from a seawater desalination reverse osmosis (SWRO) plant located on an island near the East China Sea. The temperature and turbidity of raw seawater during the experimental period from May 13th to June 30th, 2010 are presented in Figs. 1 and 2, respectively. The temperature fluctuated from 17.5 to 23.5 °C and the turbidity varied over a wide range from 13.2 to 234 NTU.

2.2. Membrane and system

2.2.1. Laboratory device

A laboratory-scale experiment was performed to investigate the performance of the ceramic membrane under different conditions. Four ceramic membrane units with the configuration of multi-channel were employed in the experiment. The ceramic membranes were manufactured by Jiangsu Jiuwu High-Tech Co., Ltd. of China. Details about the ceramic membranes used in the filtration test are given in Table 1, while the experimental setup is shown in Fig. 3. Each ceramic membrane unit was mounted within a polypropylene (PP) module that was held vertically. The schematic diagram of this device is shown in Fig. 4. The feed seawater was pumped into the ceramic membrane modules from the feed tank by the feed pump. The transmembrane pressure (TMP) was monitored using two pressure gauges located at both ends of the ceramic membrane modules and controlled by valves at both ends of the ceramic membrane module. The retentate and permeate were recycled back to the feed tank.

Table 1
Characteristics of the membranes used in the experiment

Module	Module A	Module B	Module C	Module D
Separation layer material	ZrO_2	Al_2O_3	Al_2O_3	Al_2O_3
Support material	α-Al_2O_3	α-Al_2O_3	α-Al_2O_3	α-Al_2O_3
Pore size (nm)	50	200	500	800
Surface area (m^2)	0.22	0.22	0.22	0.22
Length (mm)	1,016	1,016	1,016	1,016
Number of channels	19	19	19	19
Inner diameter (mm)	3.8	3.8	3.8	3.8
Outer diameter (mm)	31	31	31	31

Fig. 3. Experimental setup of the ceramic membrane filtration system.

Four ceramic membrane modules with pore sizes of 50, 200, 500, and 800 nm were used. A dead-end operation mode was adopted under different TMPs of 0.5, 1.0, and 1.5 bar. The retentate was pushed through the valve opening at the end of the modules for 10 s every 15 min.

2.2.2. Device employed by the pilot test

A pilot-scale experiment was carried out to investigate the long-term run performance of the ceramic membrane system. The ceramic membrane units were the same as the one employed by the laboratory-scale experiment (with a pore size of 50 nm). The membrane units were mounted within unplasticized polyvinyl chloride (UPVC) modules that were fixed in parallel and vertically on a train. The train had 30 modules, and each module had 14 ceramic membrane units. The capacity was approximately 330 m^3/d with a permeate flux of 150 L/m^2h.

A constant flux and a low cross-flow velocity (CFV, 0.015 m/s) were used in the pilot test; the flow diagram of the ceramic membrane filtration system is shown in Fig. 5. Raw seawater flowed into the blend tank, while $FeCl_3$ was injected into the tank at 10 mg/L. Next a pipe transported the seawater to a feed tank from the middle of the blend tank. NaClO was pumped into the pipe at a concentration of 1.5 mg/L. The seawater was pumped into the ceramic membrane system, which was controlled by a programmable logic controller (PLC) and operated in the constant flux mode. During the operation, backwashing with permeate was performed for 60 s every 30 min. A chemical enhanced backwash (CEB) procedure that utilized NaClO at a concentration of 400 mg/L or HCl at a concentration of 200 mg/L was alternatively performed for 60 s every 24 h.

The main operational parameters of the ceramic membrane system are presented in Table 2.

3. Results and discussion

3.1. Permeate flux under various conditions

The permeate fluxes of ceramic membranes under TMP of 1.0 bar with different pore sizes are shown in Fig. 6. The initial permeate fluxes of the ceramic membranes with pore sizes are different, but pore size has little effect on the steady state flux at 40 h. It was observed that the permeate fluxes showed the same general trend when the TMP was adopted as 0.5 and 1.5 bar. The filter resistance at the start of operation

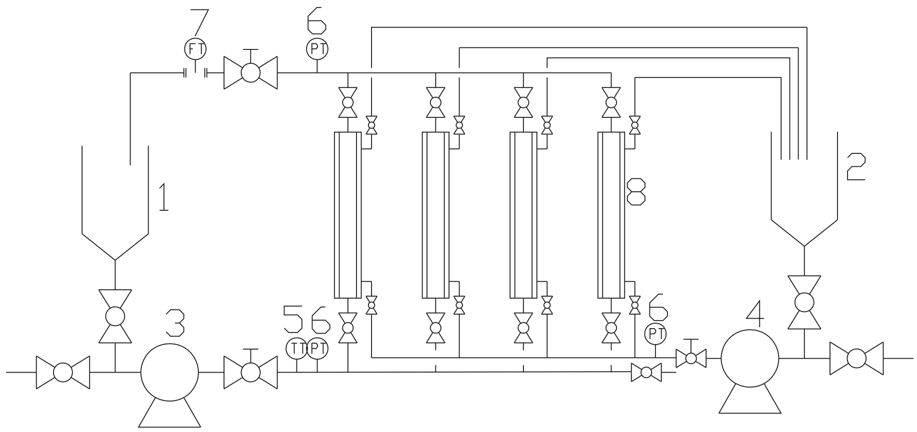


Fig. 4. Flow diagram of laboratory-scale experiment. (1) feed tank; (2) permeate tank; (3) feed pump; (4) backwash pump; (5) thermometer; (6) pressure gauges; (7) flowmeter; (8) membrane modules.

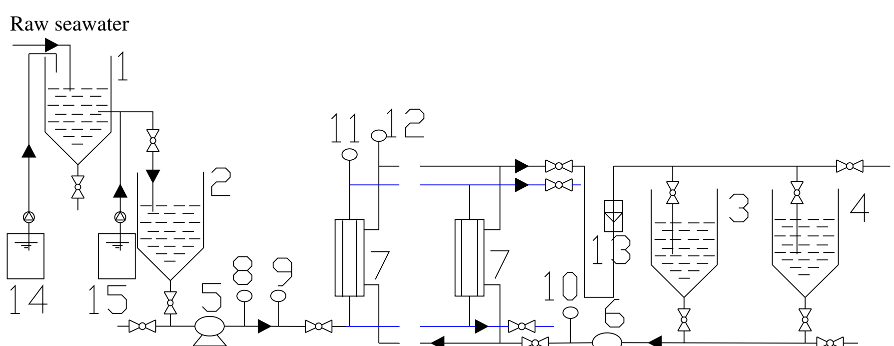


Fig 5. Flow diagram of ceramic membrane system. (1) blend tank; (2) feed tank; (3) permeate tank; (4) cleaning tank; (5) feed pump; (6) backwashing pump; (7) ceramic membrane modules; (8) temperature transducer; (9,10,11,12) pressure transducers; (13) flow transducer; (14) metering pump for $FeCl_3$; (15) metering pump for NaClO.

Table 2
Operation parameters of ceramic membrane system

Parameter	Value
Designed permeate flux, L/m^2h	150
Feed pressure, bar	0.3–2.0
CVF, m/s	0.015
Filtration duration, min	30
Backwash duration, s	60
Backwash procedure	Backwash flush
Flow rate of backwash, m^3/h	27.72
Backwash pressure, bar	0.8–3.2
CEB duration, s	60
Frequency of chemical enhanced backwash (CEB), h	24
Chemical of CEB	HCl/NaClO
HCl, mg/L	200
NaClO, mg/L	400
Recovery,%	90

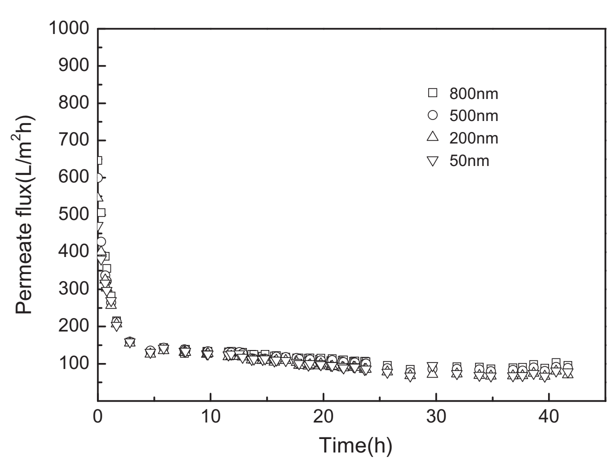


Fig 6. Permeate fluxes of ceramic membranes with different pore sizes.

represents the intrinsic membrane resistance, which is a function of the membrane properties such as pore size, porosity, and thickness. Different membranes exhibited different initial resistances, with filters with larger pore sizes displaying lower resistances and higher permeate fluxes. As the filtration process proceeded, the particles tended to enter into the larger pores, leading to an increase in the resistance and a decrease in the permeate flux. Meanwhile, the gel layer and the cake caused and contributed most of the total resistance [23]. Thus, the total final resistances with different pore sizes were close in the end, and the permeate fluxes were similar when operated at the same TMP.

The permeate fluxes of the ceramic membranes with the pore sizes of 50 and 200 nm under different TMPs are shown in Fig. 7, meanwhile, the steady state fluxes of the ceramic membranes with different pore sizes under different TMP are shown in Fig. 8. The permeate flux decreased rapidly at the beginning of the process and stabilized after 40 h. There was a similar phenomenon showed when the ceramic membranes with pore sizes of 500 and 800 nm were employed. The steady state flux at TMP of 1.0 bar is evidently larger than at TMP of 0.5 bar. But the steady state flux at TMP of 1.5 bar is less than at TMP of 1.0 bar. This may be due to the increasing compaction of the surface deposit on the membrane surface, counteracting the increasing of driving force caused by the TMP increasing.

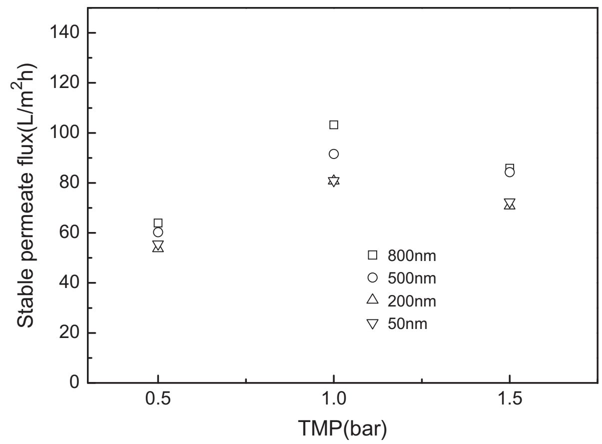
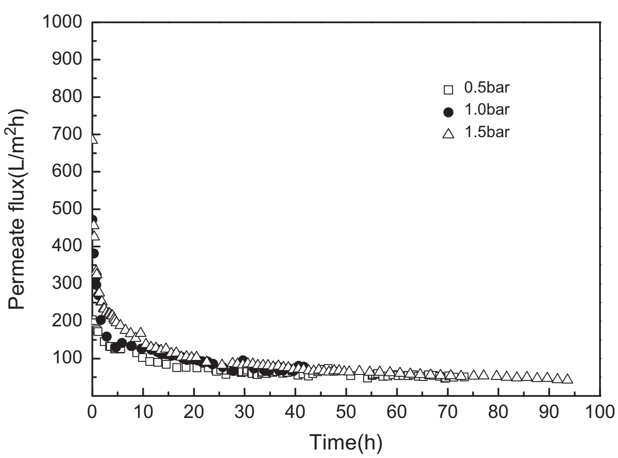
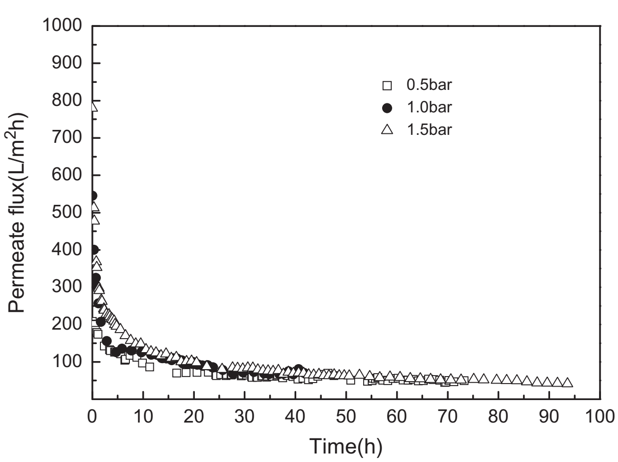


Fig. 8. Effect of TMP on the steady state fluxes of the ceramic membranes.



a. Membrane pore size of 50 nm

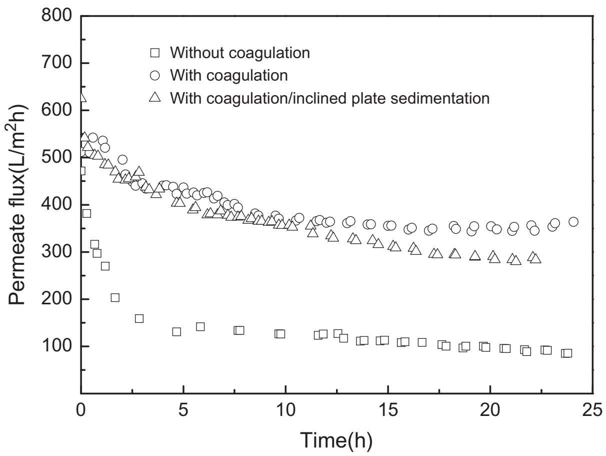


b. Membrane pore size of 200 nm

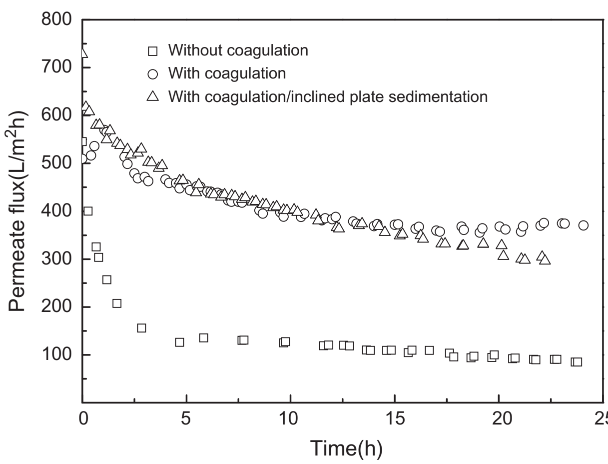
Fig. 7. Permeate fluxes of the ceramic membranes with different pore sizes.

Most of the negatively charged colloids present in seawater were neutralized by the addition of electropositive coagulant. This led to an increase in the size of the particles and colloids because of their decreased stability. Thus, coagulation can increase the size of aquatic substances to the level separable by the membrane. Fig. 9 shows the permeate fluxes of the ceramic membranes with the pore sizes of 50 and 200 nm and different treatments (without coagulation, with coagulation, with coagulation/inclined plate sedimentation) at a TMP of 1.0 bar. When no coagulation of the seawater was performed, the permeate flux through the ceramic membrane decreased rapidly, but the decline of the permeate flux was light with inline coagulation or coagulation/inclined plate sedimentation. The same general trends were observed when the ceramic membranes with pore sizes of 500 and 800 nm were used.

In the ceramic membrane filtration of seawater that was not coagulated, a number of colloids that were dissolved in the feed adsorbed on the membrane surface and in the membrane pores, leading the membrane pores to shrink. Additionally, suspended particles blocked the membrane pores, leading to a decrease in the porosity of the membrane and the formation of a filtrated cake layer on the surface of the ceramic membrane. These phenomena, including



a. Pore size of 50 nm



b. Pore size of 200 nm

Fig. 9. Performance of the ceramic membrane filtrating seawater with different treatments.

adsorption on the membrane surface, shrinkage of the membrane pores, decrease in the membrane porosity and the formation of a filtrated cake layer, caused the resistance to increase and the permeability to decrease.

The performance of the ceramic membrane was better for the seawater with coagulation and with coagulation/inclined plate sedimentation than without coagulation. This is because the coagulation increased the size of aquatic substances to the level separable by the membranes, and the sedimentation removed some particles and colloids.

Fig. 9 also shows that seawater with coagulation had a greater permeability through the ceramic membrane than seawater with coagulation/inclined plate sedimentation. This could be because coagulation left more large particles produced by the coagulation in the seawater than the coagulation/inclined plate sedimentation. Then for ceramic membrane filtration with coagulation, some large particles deposited and formed a filtrated cake layer on the membrane surface, thereby preventing some colloids and small particles from adsorbing and blocking the membrane surface and pores, preventing membrane fouling. Therefore, the optimal coagulation method for seawater treatment by ceramic membrane filtration is the coagulation technique without inclined plate sedimentation.

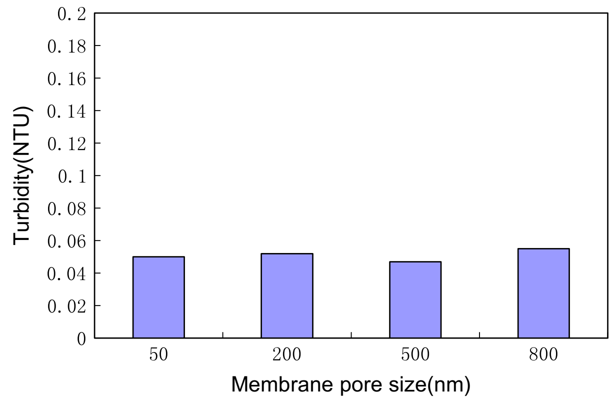


Fig. 10. Effect of ceramic membrane pore size on the turbidity of permeates.

3.2. Permeate quality under different conditions

The turbidity and SDI_{15} values of the permeate produced by the four ceramic membranes with different membrane pore sizes were measured (Figs. 10 and 11). The turbidity of the permeate varied in a narrow range from 0.04 to 0.06 NTU with different pore sizes. This shows that the removal of particles based on turbidity is efficient and that the effect of the pore size on the permeate turbidity is insignificant. The SDI_{15}

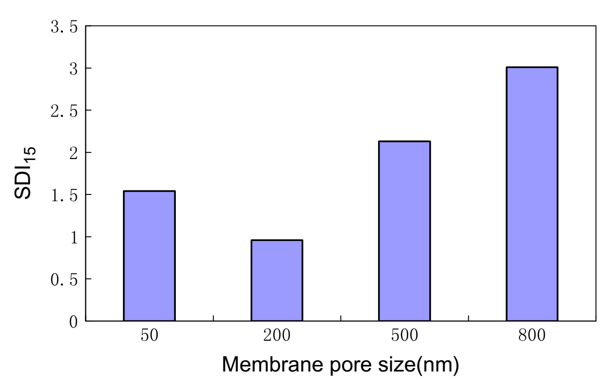


Fig. 11. Effect of membrane pore size on the SDI_{15} value of permeates.

values of the permeate produced by the ceramic membranes with 50 and 200 nm pore sizes are less than 2.0, which is beneficial for RO.

The main factor affecting the turbidity is the existence of large particles. All of the turbidity removal ratios for the four kinds of ceramic membranes used in this experiment were high, especially when the membranes were fouled and the filtered cake formed. The turbidity did not vary significantly with the change in membrane pore size. However, the colloids and small particles also contributed to the SDI_{15} value. The efficiency of the ceramic membrane in removing the colloids is less than that in removing the large particles. Thus, pore size has a significant effect on the SDI_{15} value.

Chlorine can be added to the feedwater to suppress the growth of micro-organisms and to maintain oxidative conditions in the water. The turbidities of the ceramic membranes with different pore sizes under different NaClO additions are shown in Fig. 12. The results show that the turbidity fluctuated in a narrow range from 0.05 to 0.07 NTU and that NaClO addition had a minor effect on the turbidity for the four ceramic membranes with different membrane pore sizes. Fig. 13 presents the SDI_{15} values of the ceramic membranes with different pore sizes and with different amounts of NaClO. This figure illustrates that as the NaClO addition increased from 3.0 to 30 mg/L, the SDI_{15} values increased from 0.9 to 4.8 for the 50 nm pore size, from 1.2 to 3.2 for the 200 nm pore size, from 1.9 to 3.0 for the 500 nm pore size, and from 1.9 to 4.9 for the 800 nm pore size.

The addition of NaClO had two effects. The NaClO became alkaline after hydrolysis, which is beneficial for the production of $Fe(OH)_3$ from the Fe^{3+} of

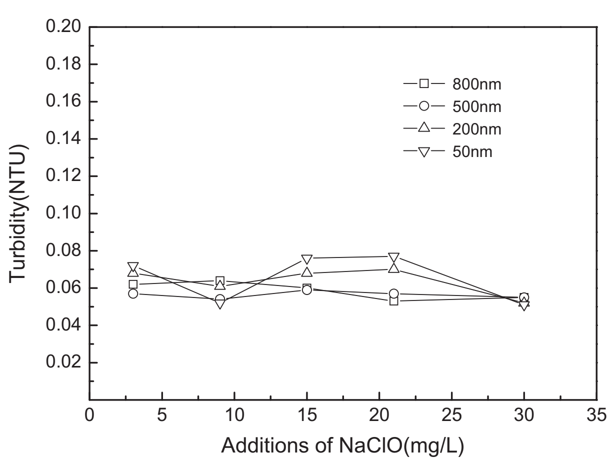


Fig. 12. Effect of NaClO addition on the turbidities of permeates.

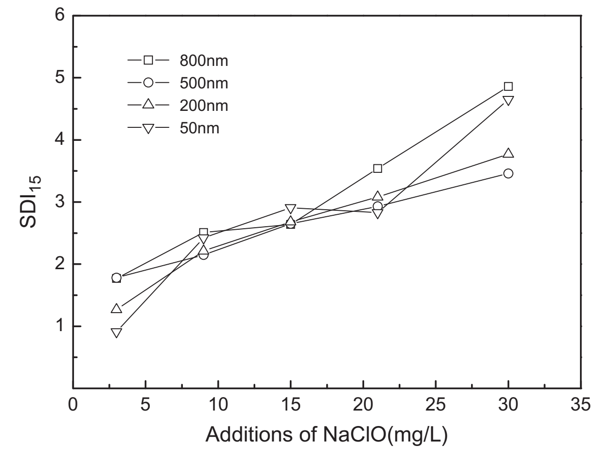


Fig. 13. Effect of NaClO addition on the SDI_{15} values of permeates.

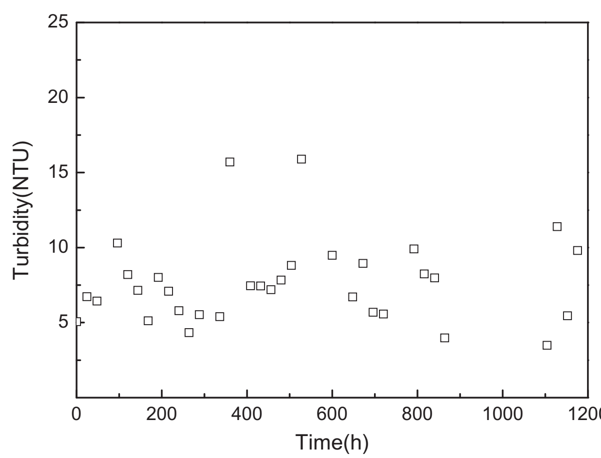


Fig. 14. Turbidity of the feed for the ceramic membrane device.

the coagulant, thus enhancing the effect of the coagulant. This is beneficial for the decrease in the turbidity and the SDI_{15} value. However, the strong oxidation of the NaClO partially oxidized some organic matter and destroyed the filtered cake on the membrane surface. This destruction of the cake reduced the effect of filtration and adsorption, leading to a decrease in the removal ratio for some small particles and organic matter. The ceramic membrane has a high removal ratio for the large particles, which make the greatest contribution to the turbidity, so this ratio was not affected significantly by the NaClO addition. But the increase in the permeate ratio of the organic matter and small particles caused by the strong oxidation of NaClO led to an increase in the SDI_{15} value of the permeate.

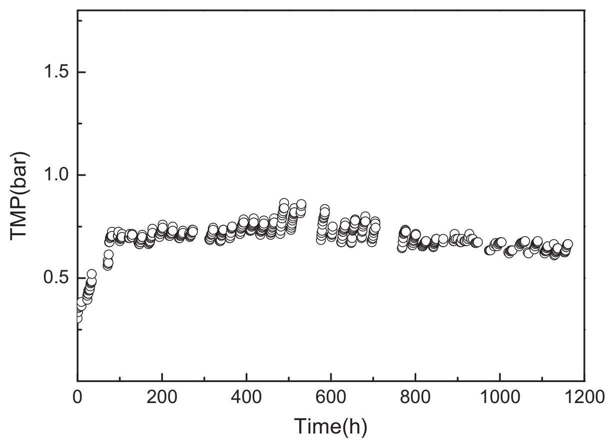


Fig. 15. Long-term run performance of the pilot-scale device.

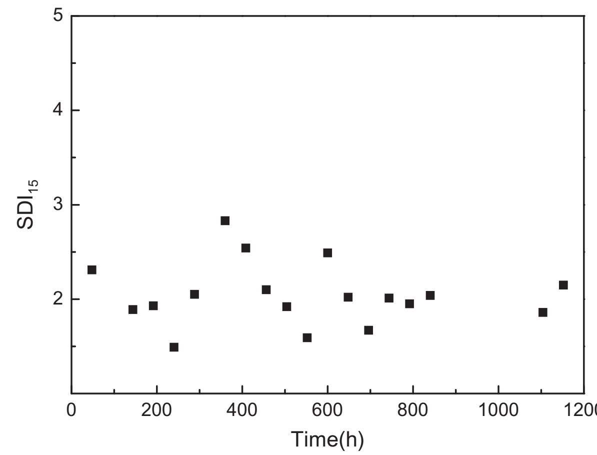


Fig. 17. SDI_{15} values of the permeate.

3.3. *Long-term run performance of ceramic membrane filtration*

A pilot-scale study was carried out to investigate the long-term performance of the ceramic membrane system. Parameters such as permeate flux, pressure, and permeate quality were monitored during the testing period.

Seawater was fed to a ceramic membrane system from the middle of the blend tank after coagulation, and the turbidity of the feed for ceramic membrane is shown in Fig. 14. The turbidity was controlled in the range from 4.0 to 15.9 NTU.

As shown in Fig. 15, the TMP increased from 0.30 bars and then plateaued from 0.60 to 0.80 bar while the backwash and CEB were utilized. The TMP decreased slightly after 600 h, perhaps because of the increase in temperature. This result suggests that the fouling can be controlled and that the system can run stably under these experimental conditions.

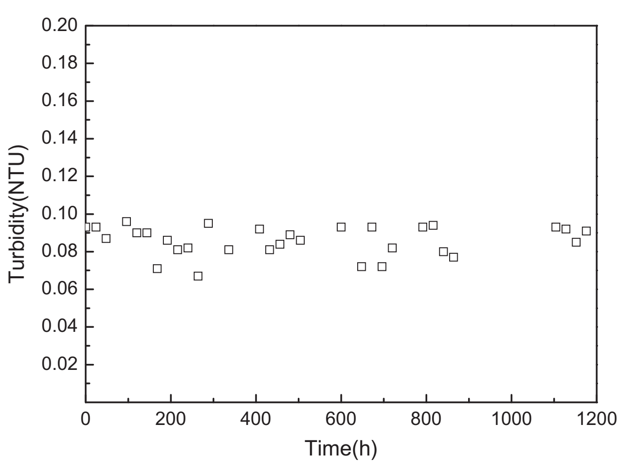


Fig. 16. Turbidity of the permeate.

The permeate qualities such as turbidity and SDI_{15} were measured to determine whether the permeate could meet the demands of the SWRO process.

As shown in Fig. 16, the turbidity of the permeate ranged from 0.06 to 0.10 NTU, and the average value was 0.082 NTU. As shown in Fig. 17, the SDI_{15} value ranged from 0.5 to 2.8, with 80% of the values less than 2.0. These excellent turbidities and SDI_{15} values indicated that the permeate produced by ceramic membranes can meet the demands of the SWRO process.

4. Conclusions

To exploit ceramic membrane filtration as a pretreatment of seawater for SWRO processes, the performance of the ceramic membrane was investigated with different pore sizes under different conditions, and a pilot test was carried out to investigate the stability of the permeability and the permeate quality. The following conclusions were obtained.

The permeate flux was significantly affected by the coagulation method. Coagulation leads to better ceramic membrane performance than coagulation/inclined plate sedimentation. The pore size of the ceramic membrane and NaClO addition have insignificant effects on the turbidity of the permeate but a clear effect on the SDI_{15} value.

The ceramic membrane system with a capacity of 330 m^3/d ran stably for 1,200 h with a permeate flux of 150 L/m^2h, without chemical cleaning. Most fouling can be removed from ceramic membranes by employing the cleaning in place (CIP). The turbidity and SDI_{15} values of the permeate produced by these ceramic membranes are reliable, and the permeate is suitable for feeding into an SWRO process.

In summary, the permeate flux of a ceramic membrane device is sufficiently stable for application to the pre-treatment of seawater for an RO process, and the permeate quality is high enough to be fed into RO.

References

[1] C.J. Vörösmarty, P.B. McIntyre, M.O. Gessner, A. Prusevich, P. Green, S. Glidden, S.E. Bunn, C.A. Sullivan, C.R. Liermann, P.M. Davies, Global threats to human water security and river biodiversity, Nature 467 (2010) 555–561.

[2] A.D. Khawaji, I.K. Kutubkhanah, J.M. Wie, Advances in seawater desalination technologies, Desalination 221 (2008) 47–69.

[3] A.D. Khawaji, I.K. Kutubkhanah, J.M. Wie, A 13.3 MGD seawater RO desalination plant for Yanbu industrial city, Desalination 203 (2007) 176–188.

[4] Y. Dreizin, Ashkelon seawater desalination project – off-taker's self costs, supplied water costs, total costs and benefits, Desalination 190 (2006) 104–116.

[5] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature 452 (2008) 301–310.

[6] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: Water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348.

[7] I.C. Karagiannis, P.G. Soldatos, Water desalination cost literature: Review and assessment, Desalination 223 (2008) 448–456.

[8] M. Kumar, S.S. Adham, W.R. Pearce, Investigation of seawater reverse osmosis fouling and its relationship to pretreatment type, Environ. Sci. Technol. 40 (2006) 2037–2044.

[9] N. Prihasto, Q.F. Liu, S.H. Kim, Pre-treatment strategies for seawater desalination by reverse osmosis system, Desalination 249 (2009) 308–316.

[10] D.F. Halpern, J. McArdle, B. Antrim, UF pretreatment for SWRO: Pilot studies, Desalination 182 (2005) 323–332.

[11] O. Lorain, B. Hersant, F. Persin, A. Grasmick, N. Brunard, J.M. Espenan, Ultrafiltration membrane pre-treatment benefits for reverse osmosis process in seawater desalting: Quantification in terms of capital investment cost and operating cost reduction, Desalination 203 (2007) 277–285.

[12] P.H. Wolf, S. Siverns, S. Monti, UF membranes for RO desalination pretreatment, Desalination 182 (2005) 293–300.

[13] A. Brehant, V. Bonnelye, M. Perez, Comparison of MF/UF pretreatment with conventional filtration prior to RO membranes for surface seawater desalination, Desalination 144 (2002) 353–360.

[14] G.K. Pearce, The case for UF/MF pretreatment to RO in seawater applications, Desalination 203 (2007) 286–295.

[15] F. Knops, S. van Hoof, H. Futselaar, L. Broens, Economic evaluation of a new ultrafiltration membrane for pretreatment of seawater reverse osmosis, Desalination 203 (2007) 300–306.

[16] J. Feng, Y. Fan, H. Qi et al., Co-sintering synthesis of tubular bilayer α-alumina membrane, J. Membr. Sci. 288 (2007) 20–27.

[17] M. Qiu, S. Fan, Y. Cai, Y. Fan, N. Xu, Co-sintering synthesis of bi-layer titania ultrafiltration membranes with intermediate layer of sol-coated nanofibers, J. Membr. Sci. 365 (2010) 225–231.

[18] A. Bottino, C. Capannelli, A. Del Borghi, M. Colombia, O. Conia, Water treatment for drinking purpose: Ceramic microfiltration application, Desalination 141 (2001) 75–79.

[19] T. Matsushita, Y. Matsui, N. Shirasaki, Y. Kato, Effect of membrane pore size, coagulation time, and coagulant dose on virus removal by a coagulation-ceramic microfiltration hybrid system, Desalination 178 (2005) 21–26.

[20] K. Konieczny, M. Bodzek, M. Rajca, A coagulation – MF system for water treatment using ceramic membranes, Desalination 198 (2006) 92–101.

[21] S.G. Lehman, L. Liu, Application of ceramic membranes with pre-ozonation for treatment of secondary wastewater effluent, Water Res. 43 (2009) 2020–2028.

[22] W. Li, L. Zhou, W. Xing, N. Xu, Coagulation–microfiltration for lake water purification using ceramic membranes, Desalin. Water Treat. 18 (2010) 239–244.

[23] J. Xu, C.Y. Chang, C. Gao, Performance of a ceramic ultrafiltration membrane system in pretreatment to seawater desalination, Sep. Purif. Technol. 75 (2010) 165–173.

[24] Z. Cui, W. Xing, Y. Fan, N. Xu, Pilot study on the ceramic membrane pre-treatment for seawater desalination with reverse osmosis in Tianjin Bohai Bay, Desalination 279 (2011) 190–194.