Keynote Paper

Selective adsorption of organic foulants can mediate organic fouling of ceramic nanofiltration (NF) membranes

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ABSTRACT

The influence of organic fouling on ceramic nanofiltration (NF) membranes has been characterized to reuse the tertiary treated wastewater. In order to remove organic components selectively, adsorption was conducted as a pretreatment process with various carbon-based adsorbents (CBAs). Granular activated carbon (GAC), expanded graphite (EG), and multi-wall carbon nanotubes (MWNTs) are used as CBAs. The EG and MWNT adsorbents can selectively remove the soluble microbial products (SMPs) and aromatic group in organic compounds while GAC showed non-selectivity. In this study, the flux decline and chemical cleaning period of ceramic NF membranes was improved more than twofold when the SMPs and aromatic group compounds were selectively removed by EG and MWNT adsorbents. Consequently, the application of CBAs as pretreatment processes for removing microbial products from tertiary treated wastewater effluent can provide an effective strategy to reduce organic fouling on ceramic NF membranes.

1. INTRODUCTION

Wastewater reclamation is one of the essential strategies to produce water resources for sustainable urban development and addressing water shortages. Secondary and tertiary treated wastewater has strong colour and high chemical oxygen demand (COD) and salt concentration (Liu et al. 2011). To treat and reuse secondary and tertiary treated wastewater, nanofiltration (NF) and reverse osmosis (RO) membrane processes are now being widely used as further treatment processes to guarantee acceptable water quality with a small footprint. In particular, NF membranes can reject over 90% of dissolved organic matter (DOM) with greater flux than RO membranes in the same operating conditions (Jacob et al. 2010).

Generally, NF membranes can be divided into ceramic and polymeric membranes on the basis of the raw materials. Previous studies have reported that ceramic membranes have gained popularity for the treatment of tertiary treated wastewater due to their various advantages over polymeric membranes (Kim, J. et al. 2010; Hofs, B. et al. 2011). In more detail, the advantages of ceramic membranes included superior chemical and thermal resistivity, enabling chemical or thermal

regeneration and sterilization by strong chemical or high-temperature processes. Moreover, their high mechanical stability enables high pressure back-washing. Thus, despite their higher cost, ceramic membranes are more economically feasible for use in wastewater reuse that requires strong and frequency chemical cleaning (Mustafa, G. et al. 2014).

Although ceramic NF membranes are an optimal solution to treat wastewater, their performance can be significantly degraded by membrane foulants such as DOM, soluble inorganic compounds, colloidal or particulate matters, and microorganisms in the feed solutions (Kim, E. et al. 2011). In previous studies, DOM has been identified as a major cause of membrane fouling during the filtration of secondary and tertiary treated wastewater (Kaiya, Y. et al 1996; Hong, S. and Elimelech, M. 1997).

Therefore, a suitable pretreatment process for the removal of DOM is required to reduce membrane fouling and to increase the chemical cleaning cycle in relation to operational cost and causing membrane damage. Flocculation and adsorption are the representative pretreatment processes for the feed of NF membranes (Harrelkas, F. et al. 2009). Among these technologies, the adsorption process can remove most of the solutes and organic compounds in secondary and tertiary treated wastewater. In particular, carbon-based adsorbents (CBAs) such as granular activated carbon (GAC), expanded graphite (EG), and multi-wall carbon nanotubes (MWNTs) show high adsorption capacity and selectivity toward aromatic contaminants by π - π interaction between hydrophobic adsorbents and organic foulants (Gu, Z. et al. 2005; Mauter, M. and Elimelech, M. 2008).

The purpose of this study was to evaluate the influence of organic foulants on ceramic NF membranes for reuse of tertiary treated wastewater. Various CBAs were used to remove organic components selectively. The organic fouling of ceramic NF membranes was confirmed by measurement of normalized flux and the chemical cleaning period. Also, an excitation-emission matrix (EEM) analysis using fluorescence spectroscopy was carried out to identify certain characteristics of DOM in major membrane foulants before and after selective adsorption of various CBAs.

2. MATERIALS AND METHODS

2.1 Adsorption process using carbon-based adsorbents (CBAs)

To simulate the wastewater reuse system, wastewater treatment plant (WWTP) tertiary effluent (Daejeon, South Korea) was used as the raw water after filtration (Whatman GF/C-filter) for the adsorption process. The characteristics of the WWTP tertiary effluent are presented in **Table 1**. The adsorption process was conducted with the following CBAs: GAC, EG, and MWNTs. For the preparation of adsorbents, GAC (Hyundai Coma Industry Inc., Korea) was washed using deionized water and dried at 60 ± 1 °C for 24 h. The EG adsorbent (Norit, Nederland) was prepared by heat treatment at 800 ± 10 °C for 1 min to expand the graphite (Zhang, Z. and Fang, X. 2006). The MWNT adsorbent (Hanhwa Nano Tech, Korea) also was used after heat treatment at 520 ± 5 °C for 1 h. To achieve the half concentration of dissolved organic carbon from the initial concentration after 30 min of each adsorption process, 5.0 ± 0.2

g/L of GAC, 1.9 \pm 0.2 g/L of EG, and 1.7 \pm 0.2 g/L of MWNT were added as adsorbents in each glass bottle-containing WWTP tertiary effluent with stirring at 23 \pm 1 °C.

The morphology of the adsorbent surface was analyzed by scanning electron microscopy (SEM) (Magellan 400, FEI Co., USA). The specific surface area and pore size of the individual adsorbents were measured by a Brunauer-Emmett-Teller (BET) analysis (BELSORP-max (MP), BEL, Japan). The amount of adsorbed DOM on the CBAs (q) (mg/g) was calculated by Eq. (1) (Lu, C. and Su, F. 2007)

$$q = \frac{(C_0 - C_e)V}{m} , \qquad (1)$$

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of dissolved organic carbon (DOC) in the WWTP tertiary effluent, respectively. V (L) is the volume of the WWTP tertiary effluent and m (g) is the added mass of each CBA.

The changes of DOC concentration in the WWTP tertiary effluent after the adsorption process were measured by a TOC analyzer (TOC-L, Shimadzu, Japan) (Kimura, K. et al. 2008). In addition, a qualitative analysis of the composition of organic substances was conducted by EEM fluorescence spectroscopy (RF5301PC, Shimadzu, Japan) (Li, W. et al. 2013)

Parameter	Description	
DOC (mg/L)	6.0 ± 0.2	
SUVA (L/mg⋅m)	1.9 ± 0.1	
Ca (mg/L)	30.8 ± 0.4	
Mg (mg/L)	6.8 ± 0.2	
Conductivity (µs/cm)	490.1 ± 9.2	
рН	7.3 ± 0.2	
Temperature (°C)	23.0 ± 1.0	
Soluble T-P (mg/L)	0.2 ± 0.1	
Soluble T-N (mg/L)	1.9 ± 0.2	

Table 1. Properties of a wastewater treatment plant (WWTP) tertiary effluent in South Korea for the adsorption process.

2.2 Evaluating impact of fouling on ceramic NF membrane

Lab-made ceramic NF membranes were used to evaluate the impact of fouling on each effluent of the adsorption process. The properties of the ceramic NF membranes were provided in our previous study (Chung, Y. et al. 2018). The important characteristics of ceramic NF membranes are a specific flux of 4.9 ± 0.4 LMH/bar and a molecular weight cut-off (MWCO) of 980 Da.

The performance of the ceramic NF membrane was assessed using a closedloop lab-scale system containing a tubular-type membrane module. The ceramic NF membrane had an effective membrane area of 4.17×10^{-4} m² and was placed inside the membrane module. The feed solution was contained in a stainless steel vessel that can be pressurized to 20 bar by nitrogen gas (99.99% purity) and circulated at a cross-flow velocity (CFV) of 10 cm/s. The membrane system was operated in a closed loop so that the pressure on the feed side was stable during the experiment. During the operation of the ceramic NF membrane system, each effluent of the adsorption process was used as a feed solution. A digital pressure gauge was connected to measure the transmembrane pressure (TMP) between the feed and permeate sides during the operation. In addition, the flux data were calculated using Darcy's law (Eq.2) and loaded into a computer in real time (Fagkaew, P. et al. 2017):

$$J = \frac{\Delta P}{\mu R_m} \quad , \tag{2}$$

where J denotes the water flux (L/m²h, LMH), $\triangle P$ is the TMP (bar), R_m represents the membrane resistance (/m), and μ is the dynamic viscosity of water (1.0×10⁻³ kg/m/s at 23 °C).

The changes in normalized flux were monitored for 4 h with initial flux of 50 ± 1 LMH in each experiment. To confirm reproducibility, all experiments were performed at least three times. The changes of DOC concentration and composition of organic substances in the feed and permeate were also analyzed by a TOC analyzer and EEM fluorescence spectroscopy, respectively.

2.3 Chemical cleaning

To compare the chemical cleaning cycle of the ceramic NF membranes, the treated effluents by GAC and MWNT adsorbents were used as feed solutions. The chemical cleaning was conducted when the measured flux was decreased to $65 \pm 1\%$ of the original flux. During the chemical cleaning, 1 wt% of NaOH solution and 1 wt% of HCl were used to remove the organic and inorganic scales, respectively, on the ceramic NF membranes for 1 h each at room temperature (Madaeni, S. et al. 2012). The chemical cleaning cycle was conducted three times between each experiment using feed solutions of the effluents treated by GAC and MWNT adsorbents.

3. RESULTS AND DISCUSSION

3.1 Adsorption process using carbon-based adsorbents (CBAs)

Fig. 1 shows SEM images of the EG, GAC, and MWNTs. The EG surface shows a worm-like texture and clearly reveals abundant graphene interstices formed during the thermal expansion, in contrast to the irregular appearance of the GAC surface. The MWNT composite nanofibers are represented in **Fig. 1**. From the results of the BET

analysis, the specific surface area of EG, GAC, and MWNT was 93 m²/g, 961 m²/g, and 290 m²/g, respectively. In addition, the average pore size of the EG, GAC, and MWNTs was 6.7 nm, 2.1 nm, and 9.5 nm, respectively.



Fig. 1. Scanning electron microscopy (SEM) images of EG, GAC, and MWNT adsorbents.

Table 2. The changes of dissolved organic carbon (DOC) concentration after adsorption of carbon-based adsorbents (CBAs) and filtration of ceramic NF membrane.

Effluent samples	After adsorption		After ceramic NF membranes		
	DOC (mg/L)	SUVA (L/mg⋅m)	Removal efficiency (%)	DOC (mg/L)	Final removal efficiency (%)
WWTP	6.0 ± 0.1	2.0	-	0.5 ± 0.0	91.0%
GAC	2.9 ± 0.1	1.6	51.6%	0.3 ± 0.1	89.0%
EG	3.0 ± 0.1	1.3	49.8%	0.3 ± 0.1	89.1%
MWNT	2.9 ± 0.1	2.1	52.0%	0.3 ± 0.0	90.3%

In **Table 2**, the removal efficiency of DOC by adsorption for pretreatment of the ceramic NF membrane process using various CBAs (GAC(51.6 \pm 0.8%), EG (49.8 \pm 1.1%), and MWNTs (52.0 \pm 0.9%)) was approximately 50%. Furthermore, the MWNTs showed the largest amount of adsorbed DOM on the adsorbents (q) in the same time period at 1.84 mg/g, compared to 1.58 mg/g for the EG and 0.62 mg/g for the GAC, as determined by Eq.1. Although GAC is known to have the largest specific surface area (960.7 m²/g) among the CBAs including the MWNTs (289.7 m²/g) and EG (92.5 m²/g), the amount of DOM adsorbed per unit mass on GAC was less than 50% of that of the MWNTs and EG. The GAC shows the smallest average pores at 2.1 nm, which provide adsorption sites. This indicates that the diffusion of DOM into GAC pores takes more time than in the case of MWNTs and EG, which respectively have 9.5 nm and 6.7 nm average pore size.

The spectral contour plots and excitation and emission spectra of each identified DOM component are shown in **Fig. 2**. From the peak results of fluorescence EEM in **Fig. 2a**, the Humic acid-like (HL), fulvic acid-like (FL), aromatic protein group (AP), and soluble microbial products (SMPs) were detected in the WWTP tertiary effluent (Chen, W. et al. 2003). **Figs. 2b, 2c, and 2d** present the results of treated effluents by MWNT, EG, and GAC adsorption. After the adsorption process, the signal intensity of the organic components in the WWTP tertiary effluent was reduced in all cases. In particular, in **Figs. 2b and 2c**, SMPs and the aromatic group are significantly removed by the MWNT and EG adsorbents compared to the GAC adsorbent in (**Fig. 2d**) where all the peaks of the organic components still remain. The selective adsorption phenomena between functional groups (e.g., carbonyl, aromatic, and carboxyl) in DOM and the surface of the MWNT and EG adsorbents are driven by π - π interaction (Hyung, H. and Kim, J. 2008).



Fig. 2 Excitation-emission matrix (EEM) fluorescence spectra of the effluent of (a) wastewater treatment plant (WWTP) tertiary effluent, (b) MWNT, (c) EG, and (d) GAC adsorption.

3.2 Normalized flux of ceramic NF membranes

The normalized flux of ceramic NF membranes using feed solutions, which are pretreated by various CBAs, is shown in **Fig. 3**. Among the GAC, MWNT, and EG adsorbents, the MWNT adsorbent was the most effective in terms of decreasing fouling on the ceramic NF membranes, achieving a 30% decrease of the initial flux after 4 h. The highest flux decline of the ceramic NF membranes was represented in the GAC adsorbents with a 30% decrease of the initial flux within around 30 min. In **Fig. 2**, the results of normalized flux were not significantly different between the GAC adsorbent and raw water without a pretreatment process as a result of containing a greater amount of SMPs and aromatic groups than MWNTs and EG in the feed solution. This indicates that the performance of ceramic NF membranes is significantly affected by the composition of organic matter in feed solutions.



Fig. 3 The normalized flux of ceramic nanofiltration (NF) membranes using feed solutions of wastewater treatment plant (WWTP) tertiary effluent, MWNT, EG, and GAC adsorption effluent.

In **Table 2**, the rejection of DOM by ceramic NF membranes in WWTP tertiary effluent without pretreatment of adsorption was $91.0 \pm 0.4\%$. The final removal efficiency of DOM by ceramic NF membranes after GAC, EG, and MWNTs adsorption

was $89.0 \pm 0.3\%$, $89.1 \pm 0.5\%$, and $90.3 \pm 0.4\%$, respectively. **Fig. 4** shows that the ceramic NF membranes could reject all components of the DOM. The removal efficiency of the ceramic NF membranes was not improved by the pretreatment process. However, the permeability was significantly affected by adsorption pretreatment. The residual SMPs in the feed solution of the ceramic NF membranes are known to have a bimodal distribution with less than 1 kDa of molecular weight or greater than 10 kDa (Jarusutthirak, C. and Amy, G. 2006). The residual SMPs with molecular weight less than 1 kDa could be crucial compounds that can cause fouling on ceramic NF membranes with 1000 Da of MWCO in this study. Therefore, the permeability of the ceramic NF membranes using effluents that have less SMPs by MWNT and EG adsorption was superior to that of membranes with the effluent after GAC adsorption, as presented in **Fig. 3**.



Fig. 4 Excitation-emission matrix (EEM) fluorescence spectra of the permeate from ceramic nanofiltration (NF) membranes using feed solutions of (a) wastewater treatment plant (WWTP) tertiary effluent, (b) MWNT, (c) EG, and (d) GAC adsorption effluent.

3.3 Chemical cleaning

Fig. 5 presents the normalized flux of ceramic NF membranes with the effluent from GAC and MWNT adsorption. The chemical cleaning was conducted three times with 1 wt% of NaOH and HCl, respectively, when the flux reaches 65% of the original flux. By the chemical cleaning with NaOH and HCI, the initial flux of the ceramic NF membranes was successfully recovered, as seen in Fig. 5. The use of high acid and base chemical agents can remove the foulants including SMPs and other irreversible foulants on ceramic NF membranes, which are known to have superior chemical resistance (Adadi, S. et al. 2011). When the MWNT adsorption process is included as a pretreatment process, the chemical cleaning period of the ceramic NF membranes can be increased more than twofold as compared with the feed containing SMPs. This implies that the ceramic NF membrane process, combined with an adsorption process using MWNTs and EG adsorbents, can reduce operating costs for wastewater reuse by reducing the chemical cleaning cycle by removing organic compounds such as SMPs in the feed. Although the additional adsorption process can increase capital costs, a reduction of the total cost can be expected as the semi-permanent and stable ceramic NF membrane can be used without replacement (Durham, B et al. 2001).



Fig. 5 Normalized flux of ceramic nanofiltration (NF) membranes with the effluent from GAC and MWNT adsorption (Chemical cleaning with 1 wt% of NaOH and HCI, respectively, when the flux reaches 65% of the original flux).

3. CONCLUSIONS

We proposed an effective pretreatment process for ceramic NF membranes using CBAs. MWNT and EG adsorbents, which have relatively large pores, can decrease the fouling of ceramic NF membranes by removing the SMPs and aromatic groups from the WWTP tertiary effluent. Moreover, the ceramic NF membranes can be operated by an adsorption process with extension of the chemical cleaning cycle, which can reduce the operating cost. Consequently, MWNT and EG adsorbents to remove microbial products of organic foulants can be applied as an effective strategy to reduce ceramic NF membrane fouling to reuse secondary and tertiary treated wastewater effluent containing various organic compounds.

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REFERENCES

- Liu, M., Lü, Z., Chen, Z., Yu, S., & Gao, C. (2011). Comparison of reverse osmosis and nanofiltration membranes in the treatment of biologically treated textile effluent for water reuse. *Desalination*, *281*, 372-378.
- Jacob, M., Guigui, C., Cabassud, C., Darras, H., Lavison, G., & Moulin, L. (2010). Performances of RO and NF processes for wastewater reuse: tertiary treatment after a conventional activated sludge or a membrane bioreactor. *Desalination*, *250*(2), 833-839.
- Kim, J., & Van der Bruggen, B. (2010). The use of nanoparticles in polymeric and ceramic membrane structures: review of manufacturing procedures and performance improvement for water treatment. *Environmental Pollution*, *158*(7), 2335-2349.
- Hofs, B., Ogier, J., Vries, D., Beerendonk, E. F., & Cornelissen, E. R. (2011). Comparison of ceramic and polymeric membrane permeability and fouling using surface water. *Separation and Purification Technology*, *79*(3), 365-374.
- Mustafa, G., Wyns, K., Vandezande, P., Buekenhoudt, A., & Meynen, V. (2014). Novel grafting method efficiently decreases irreversible fouling of ceramic nanofiltration membranes. *Journal of Membrane Science*, *470*, 369-377.
- Kim, E. S., Liu, Y., & El-Din, M. G. (2011). The effects of pretreatment on nanofiltration and reverse osmosis membrane filtration for desalination of oil sands process-affected water. Separation and purification technology, 81(3), 418-428.
- Harrelkas, F., Azizi, A., Yaacoubi, A., Benhammou, A., & Pons, M. N. (2009). Treatment of textile dye effluents using coagulation–flocculation coupled with membrane processes or adsorption on powdered activated carbon. *Desalination*, 235(1-3), 330-339.

- Gu, Z., Fang, J., & Deng, B. (2005). Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal. *Environmental science & technology*, *39*(10), 3833-3843.
- Mauter, M. S., & Elimelech, M. (2008). Environmental applications of carbon-based nanomaterials. *Environmental Science & Technology*, *42*(16), 5843-5859.
- Zhang, Z., & Fang, X. (2006). Study on paraffin/expanded graphite composite phase change thermal energy storage material. *Energy Conversion and Management*, *47*(3), 303-310.
- Lu, C., & Su, F. (2007). Adsorption of natural organic matter by carbon nanotubes. Separation and *Purification Technology*, 58(1), 113-121.
- Li, W. T., Xu, Z. X., Li, A. M., Wu, W., Zhou, Q., & Wang, J. N. (2013). HPLC/HPSEC-FLD with multiexcitation/emission scan for EEM interpretation and dissolved organic matter analysis. *Water research*, 47(3), 1246-1256.
- Kimura, K., Maeda, T., Yamamura, H., & Watanabe, Y. (2008). Irreversible membrane fouling in microfiltration membranes filtering coagulated surface water. *Journal of Membrane Science*, 320(1-2), 356-362.
- Chung, Y., Lee, M. Y., Park, H., Park, Y. I., Nam, S. E., Lee, P. S., ... & Kang, S. (2018). Novel preparation of ceramic nanofiltration membrane for the removal of trace organic compounds. *DESALINATION AND WATER TREATMENT*, *101*, 31-36.
- Fagkaew, P., Ruengruehan, K., Chung, J., & Kang, S. (2017). Relating intrinsic membrane water permeability and fouling propensity in forward osmosis processes. *DESALINATION AND WATER TREATMENT*, 77, 122-128.
- Madaeni, S. S., Monfared, H. A., Vatanpour, V., Shamsabadi, A. A., Salehi, E., Daraei, P., ... & Khatami, S. M. (2012). Coke removal from petrochemical oily wastewater using γ-Al2O3 based ceramic microfiltration membrane. *Desalination*, 293, 87-93.
- Chen, W., Westerhoff, P., Leenheer, J. A., & Booksh, K. (2003). Fluorescence excitation- emission matrix regional integration to quantify spectra for dissolved organic matter. *Environmental science & technology*, 37(24), 5701-5710.
- Hyung, H., & Kim, J. H. (2008). Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters. *Environmental science* & *technology*, *42*(12), 4416-4421.
- Jarusutthirak, C., & Amy, G. (2006). Role of soluble microbial products (SMP) in membrane fouling and flux decline. *Environmental science* & *technology*, *40*(3), 969-974.
- Abadi, S. R. H., Sebzari, M. R., Hemati, M., Rekabdar, F., & Mohammadi, T. (2011). Ceramic membrane performance in microfiltration of oily wastewater. *Desalination*, *265*(1-3), 222-228.
- Durham, B., Bourbigot, M. M., & Pankratz, T. (2001). Membranes as pretreatment to desalination in wastewater reuse: operating experience in the municipal and industrial sectors. *Desalination*, *138*(1-3), 83-90.
- Kaiya, Y., Itoh, Y., Fujita, K., & Takizawa, S. (1996). Study on fouling materials in the membrane treatment process for potable water. *Desalination*, *106*(1-3), 71-77.
- Hong, S., & Elimelech, M. (1997). Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *Journal of membrane science*, *132*(2), 159-181.