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).

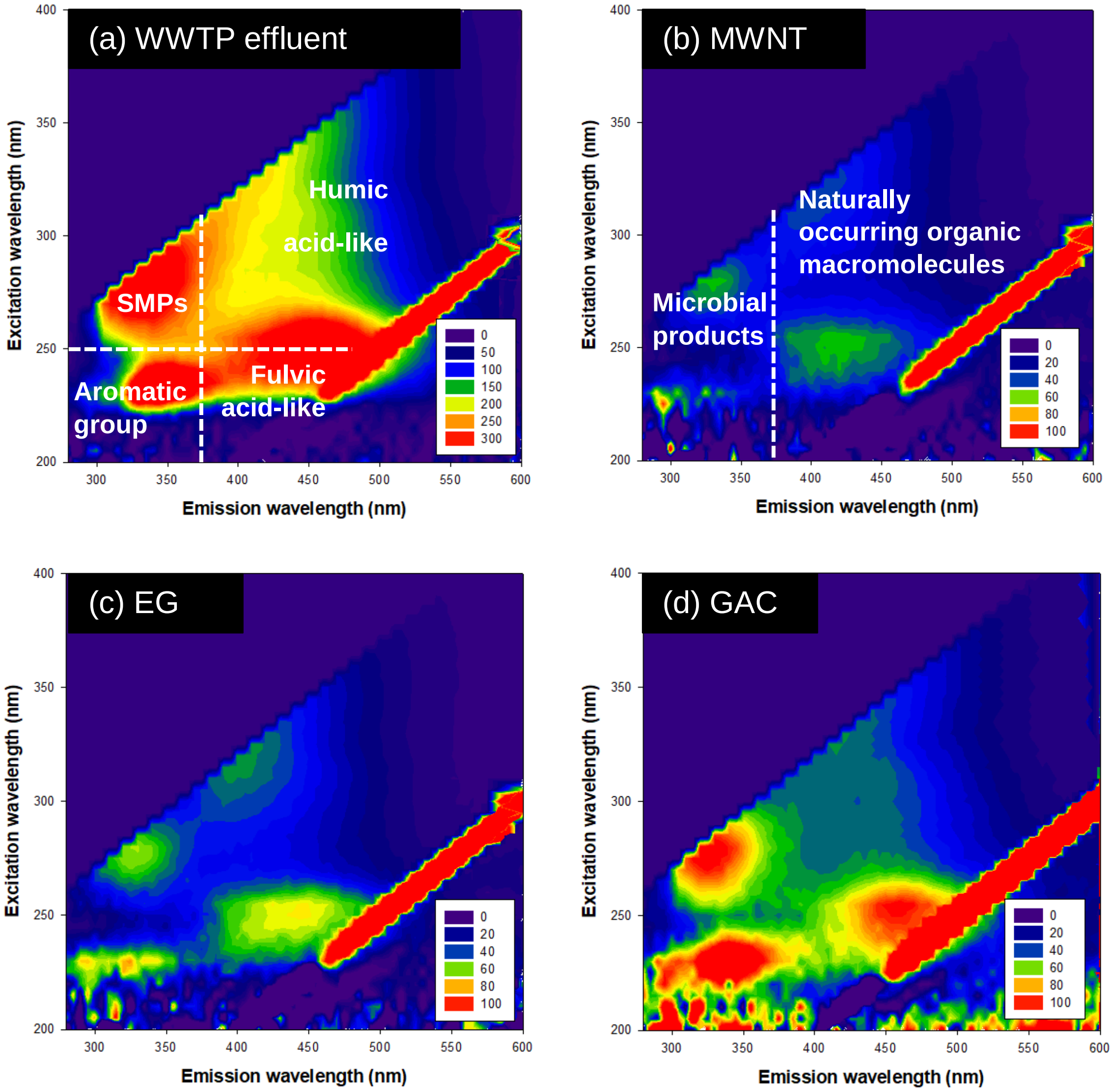

Fig. 2 Excitation−emission matrix (EEM) fluorescence spectra of the effluent of (a) wastewater treatment plant (WWTP) tertiary effluent, (b) MWNT, (c) EG, and (d) GAC adsorption.

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.

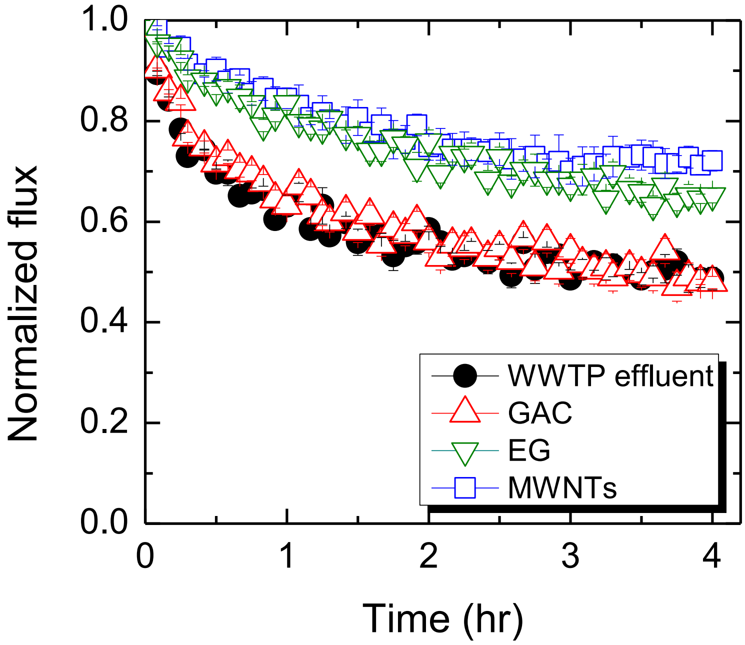

Fig. 3 The normalized flux of ceramic nanofiltration (NF) membranes using feed solutions of wastewater treatment plant (WWTP) tertiary effluent, MWNT, EG, and GAC adsorption effluent.

In **Table 2**, the rejection of DOM by ceramic NF membranes in WWTP tertiary effluent without pretreatment of adsorption was 91.0 ± 0.4%**.** The final removal efficiency of DOM by ceramic NF membranes after GAC, EG, and MWNTs adsorption was 89.0 ± 0.3%, 89.1 ± 0.5%, and 90.3 ± 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**.

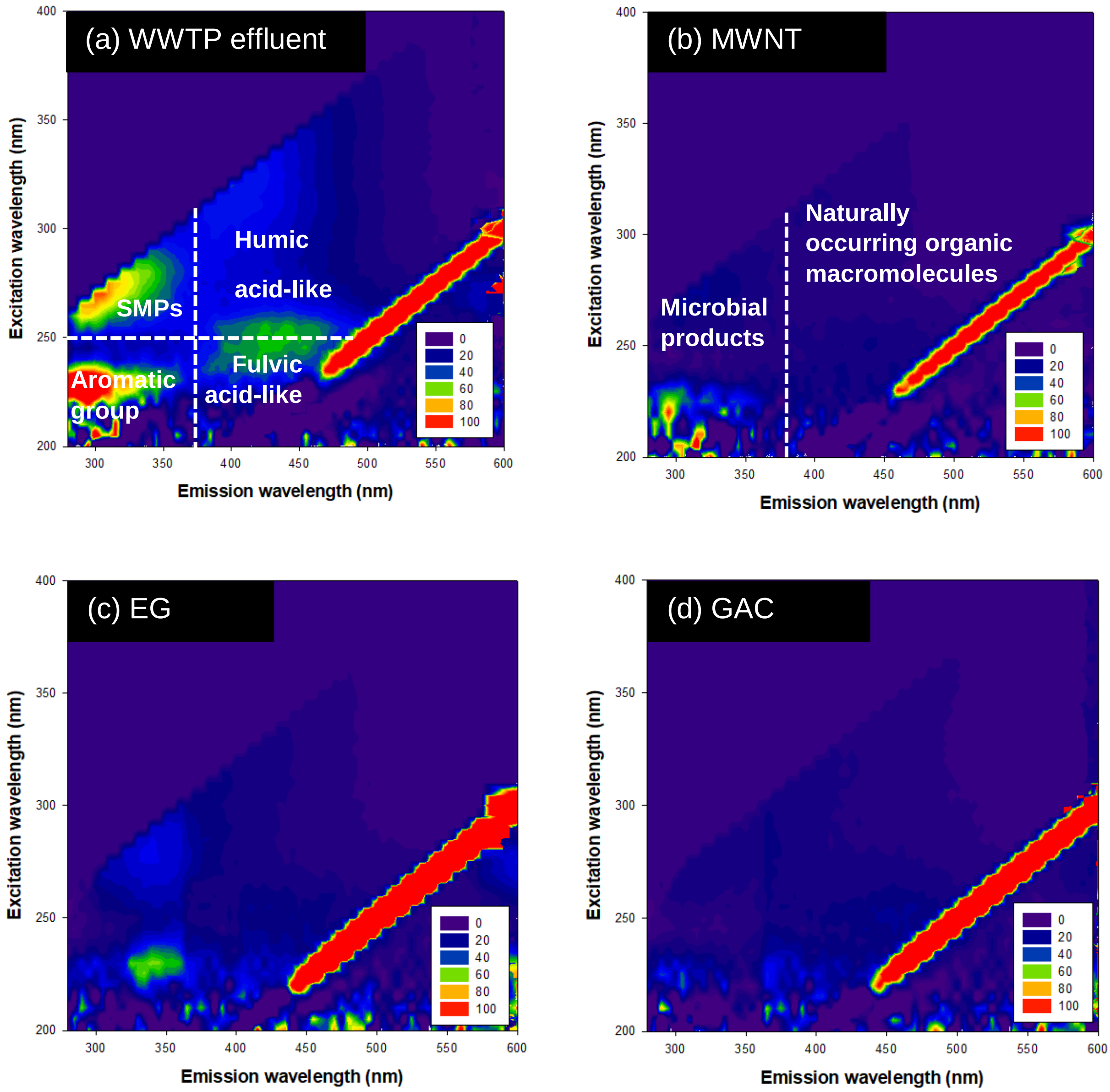

Fig. 4 Excitation−emission matrix (EEM) fluorescence spectra of the permeate from ceramic nanofiltration (NF) membranes using feed solutions of (a) wastewater treatment plant (WWTP) tertiary effluent, (b) MWNT, (c) EG, and (d) GAC adsorption effluent.

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 HCl, 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).

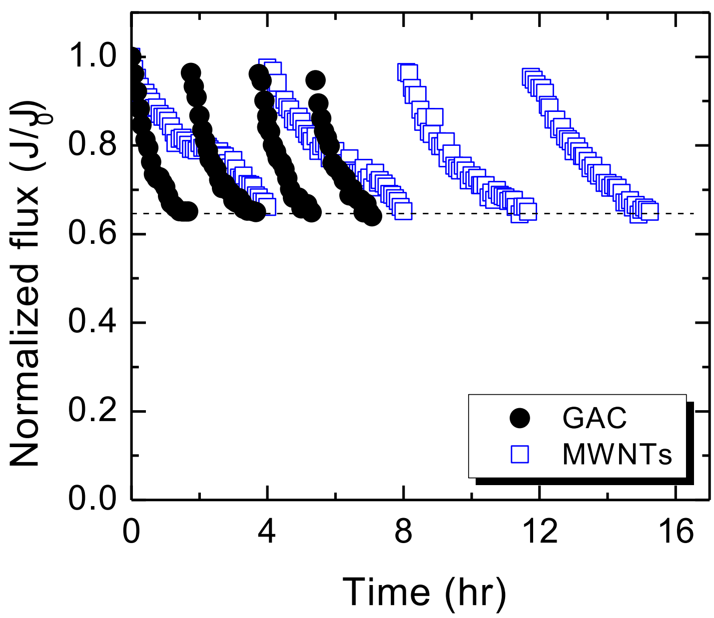

Fig. 5 Normalized flux of ceramic nanofiltration (NF) membranes with the effluent from GAC and MWNT adsorption (Chemical cleaning with 1 wt% of NaOH and HCl, respectively, when the flux reaches 65% of the original flux).

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 multi-excitation/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.