Removal of fluoride ions from groundwater using surface-modified ultrafiltration membrane

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Abstract. Zeolitic imidazolate framework no.8 (ZIF8), a kind of metal organic frameworks (MOFs), has potential use in water treatment due to water stability. However, there are few studies of ZIF8/polyamide as a thin-film nanocomposite (TFN) membrane. Herein, a film on the surface of ultrafiltration membrane was generated with ZIF8 nanoparticles to fabricate the TFN membrane. Thus, the objective was to investigate feasibility of the ZIF8 membrane for fluoride removal from water. A scanning electron microscopy analysis demonstrates that the ZIF8 layer was successfully made on the UF surface. The ZIF8 layer rendered an increase in the fluoride rejection, probably through size sieving by small windows of the MOFs, compared to the virgin UF membrane, while sacrificed the water permeability. It is anticipated that reducing large voids between ZIF8 particles and thickness of the ZIF8 layer improve the fluoride rejection and water permeability.

1. Introduction

Metal organic frameworks (MOFs), hybrid inorganic-organic materials, have drawn great attention for various applications due to their crystalline characteristic, porous structure, and high thermal and chemical stability [1]. Among MOFs, zeolitic imidazolate framework no.8 (ZIF8), the structure of which comprises zinc(II) ion as metal nodes and 2-methylimidazole as organic linkers, offers a good stability in water; hence, it is feasibly applied for water treatment. Moreover, ZIF8 has a robust synthetic method and high purity [2]. Recently, some researchers study on the ZIF8/polyamide thin-film-nanocomposite (TFN) membranes, pressure-driven membranes for removing dye and sodium chloride from water. The studies reported a slight increase in both water permeability and solute rejection. However, the performances of the ZIF8/polyamide TFN membranes were limited since addition of large amount of ZIF8 nanoparticles into the polyamide could cause defects on the polyamide layer [3, 4].

Since groundwater in the northern part of Thailand is contaminated with high fluoride [5], pressure-driven membranes become one of alternative processes for fluoride removal from groundwater [6]. In this study, ZIF8 was synthesised as a film on the surface of ultrafiltration (UF) membrane, a structure...
like thin-film-composite (TFC) membrane. In addition, the synthesised ZIF8-TFC-membrane is studied on the fluoride removal performance using the synthetic water, of which the fluoride concentration and pH were referred to previous studies of groundwater contamination in the northern part of Thailand.

2. Experimental methods

ZIF8 was coated as a layer on a flat-sheet polyethersulfone (PES) UF membrane via the layer-by-layer rapid synthesis method at room temperature and atmospheric pressure [7]. Since ZIF8 was hardly coated directly on the virgin PES membrane, the surface of the PES membrane was firstly prepared by coating with thin tannin layer. The tannin solution was prepared with 10 mM of tannic acid dissolved in DI water. The solution pH was adjusted with Tris base (2-Amino-2-(hydroxymethyl)-1,3-propanediol) to 7.8. The PES membrane was soaked in the tannin solution in a stirred filtration cell (Amicon, Millipore Corp., USA) and stirred at 200 rpm for 4 hours. Then, the membrane was washed by DI water. The ZIF8 solution was prepared by mixing 2 solutions: (1) zinc nitrate as a zinc(II) ion source; and (2) 2-methylimidazole solution. The zinc nitrate solution was firstly added into the stirred cell and the tannin-coated PES membrane was soaked in the zinc nitrate solution for 10 minutes (stirring at 200 rpm). The 2-methylimidazole solution was then added into the cell, and the membrane was continued soaking for another 20 minutes (stirring at 200 rpm). The ratio of zinc(II) ion to 2-methylimidazole was varied to three ratios (i.e. 1:40, 1:60 and 1:80). It was found that the ratio of 1:40 was well suited because it did not destruct the PES surface.

The virgin PES, tannin-coated PES, and ZIF8/PES membranes were characterized for the surface morphology using the field-emission scanning-electron-microscopy (FE-SEM) analysis. The ZIF8/PA membrane was confirmed on formation of ZIF8 the layer via its crystalline characteristic using x-ray diffraction (XRD) analysis.

The water permeability and fluoride rejection of virgin PES and ZIF8/PES membranes were tested in batch filtration experiments. The membrane was inserted at the bottom of the membrane cell and the solution was filtrated through the membrane under a dead-end filtration without retentate recirculation. The filtration tests on the virgin PES and ZIF8/PES membranes were operated at constant pressures of 1.4 and 2.5 bar, respectively, while testing water permeability and fluoride rejection. The water permeability was calculated from an average water flux that was obtained from collected mass of DI water filtrated in 5 minutes. According to the previous study, the fluoride concentration was found in a range of 1.5 – 12.5 mg/L as F and pH was in a range of 6–8 [5]. Thus, the synthesised fluoride solution contained 1.56, 5.32 and 13.0 mg/L as F, and the solution pH was adjusted to pH 6.6 by adding Tris base. The fluoride concentration was detected using the fluoride selective probe (US EPA method 9241).

3. Results and discussion

As shown in Figure 2, the PES surface was fully covered with ZIF8 nanoparticles. The FE-SEM images of surface of the ZIF8/PES membrane illustrate the morphology of ZIF8 crystal [7]. The thick stack of ZIF8 grains and clusters were grown unconnectedly, thereby the presence of many voids between their grains and clusters on the surface.

The water permeability of the ZIF8/PES membrane was determined as ca. $1.2 \times 10^{-12} \text{m}^2/\text{s}\cdot\text{Pa}$, which is considered to be in the range of ultrafiltration and nanofiltration membranes [8], in comparison to that of the virgin PES membrane of ca. $6.8 \times 10^{-11} \text{m}^2/\text{s}\cdot\text{Pa}$. For the fluoride rejection, the ZIF8/PES membrane performs the rejection of 22.6%, which markedly increased from the rejection of 3.9% for the virgin PES membrane. It is anticipated that the fluoride removal is based on the size sieving mechanism by narrow windows of ZIF8 crystalline structure. The window size of ZIF8 was 0.34 nm, small enough to retain fluoride ion with a hydrated ion size of 0.70 nm, while allowing permeation of water molecules with a size of 0.28 nm. As shown in Figure 2 (c), the presence of many large voids between ZIF8 grains and clusters probably results in the observed small fluoride rejection. Jeong et al. [9] suggested that superhydrophilic, negatively charged nanoparticles provide preferential flow paths for water permeation and maintain solute rejection through a combination between steric and Donnan exclusion. The Donnan exclusion might be enhanced for the ZIF-8 UF membrane, compared to the virgin UF membrane, due
to its more negative charge. In brief, in this study both size sieving and Donnan exclusion might be contributed to the fluoride rejection by the ZIF-8 UF membrane.

Meanwhile the pH of the permeate from the ZIF8/PES membrane was about pH 8.1, which increased compared to the feed solution pH. The increase in the permeate pH might be explained by the wash-out of remaining base on ZIF8 into the permeate, and at higher filtered volume the permeate pH gradually declined.

![Figure 1. Set-up of membrane filtration.](image1)

**Figure 1.** Set-up of membrane filtration.

![Figure 2. FE-SEM images of the surface of the ZIF8/PES membrane at different magnifications: 2k (a); 5k (b); 20k (c)](image2)

**Figure 2.** FE-SEM images of the surface of the ZIF8/PES membrane at different magnifications: 2k (a); 5k (b); 20k (c)

| Membrane   | Operating pressure (bar) | Water permeability ($\times 10^{-11}$ m/s·Pa) |
|------------|--------------------------|---------------------------------------------|
| Virgin PES | 1.4                      | 6.8                                         |
| ZIF8/PES   | 2.5                      | 0.12                                        |

**Table 1.** Summary of water permeability at 25°C of the virgin PES and ZIF8/PES membranes

| Initial Fluoride concentration (mg/L as F) | Fluoride rejection percentage (%) |
|-------------------------------------------|----------------------------------|
| 1.56                                      | 26.7 ± 4.1                       |
| 5.32                                      | 18.5 ± 0.4                       |
| 13.0                                      | 23.0 ± 5.6                       |

**Table 2.** Summary of fluoride rejection percentage of the ZIF8/PES membrane
To confirm stability of the ZIF8 layer, the permeate has been collected and analyzed for Zn concentration that helps to determine whether the ZIF8 particles slip out of the ZIF8 layer and contaminate into the permeate.

4. Conclusions
In this research, ZIF8, a type of MOFs stable in water, was lab-synthesised and coated as a film on the surface of PES UF flat-sheet membrane, through the layer-by-layer rapid synthesis method. The experimental result shows that the water permeability of the PES membrane decreased substantially after coating with the ZIF8 layer, indicating the presence of dense layer on the UF membrane. The fluoride was rejected from the water, probably by the size sieving mechanism of the dense ZIF8 layer. A small fluoride removal might be caused by the fluoride leakage through large voids between ZIF8 particles. Further improvement requires in order to reduce large voids between the ZIF8 particles to increase the fluoride rejection while reducing the coating layer thickness is expected to increase water permeability.

5. References
[1] Kumar, P., K. Vellingiri, K.H. Kim, R.J.C. Brown, and M.J. Manos. 2017. Modern progress in metal-organic frameworks and their composites for diverse applications. Microporous and Mesoporous Materials. 253:251-256.
[2] Leus, K., T. Bogaerts, J.D. Decker, H. Depauw, K. Hendrickx, H. Vrielink, V.V. Speybroek, and P.V.D. Voort. 2016. Systematic study of the chemical and hydrothermal stability of selected “stable” Metal Organic Frameworks. Microporous and Mesoporous Materials. 226:110-116.
[3] Duan, J., Y. Pan, F. Pacheco, E. Litwiller, Z. Lai, and I. Pinnau. 2015. High-performance polyamide thin-film-nanocomposite reverse osmosis membranes containing hydrophobic zeoliticimidazolate framework-8. Journal of Membrane Science. 476:303-310.
[4] Aljundi, I.H. 2017. Desalination characteristics of TFN-RO membrane incorporated with ZIF-8 nanoparticles. Desalination. 420:12-20.
[5] Matsui, J. 2007. Fluoride removal from groundwaters using nanofiltration process. Ph.D. diss., The University of Tokyo.
[6] Shen, J., and A.I. Schäfer. 2015. Factors affecting fluoride and natural organic matter (NOM) removal from natural waters in Tanzania by nanofiltration. Reverse osmosis. Science of the Total Environment. 527-528:520-529.
[7] Kida, K., K. Fujita, T. Shimada, S. Tanaka, and Y. Miyake. 2013. Layer-by-layer aqueous rapid synthesis of ZIF-8 films on a reactive surface. Dalton Trans. 42:11128-11135.
[8] Shon, H., S. Phuntsho, D.S. Chaudhary, S. Vigneswaran, and J. Cho. 2013. Nanofiltration for water and wastewater treatment-a mini review. Drink. Water Eng. Sci. 6:47-53.
[9] Jeong, B.H., E.M.V. Hoek, Y. Yan, A. Subramani, X. Huang, G. Hurwitz, A.K. Ghosh, and A. Jawor. 2007. Interfacial polymerization of thin film nanocomposites: a new concept for reverse osmosis membranes. J. Membr. Sci. 294: 1-7.

Acknowledgement
This work has been partially supported by the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through its Research Network NANOTEC (RNN) program.