



# Effects of hydrodynamic conditions (diffusion vs. convection) and solution chemistry on effective molecular weight cut-off of negatively charged nanofiltration membranes



Eunyoung Kang<sup>a</sup>, Yunho Lee<sup>a</sup>, Kangmin Chon<sup>b</sup>, Jaeweon Cho<sup>c,\*</sup>

<sup>a</sup> School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), 261 Cheomdan-gwagiro, Buk-gu, Gwangju 500-712, Republic of Korea

<sup>b</sup> Jeju Global Research Center (JGRC), Korea Institute of Energy Research (KIER), 200 Haemajihae-ro, Gujwa-eup, Jeju-si, Jeju-do 695-971, Republic of Korea

<sup>c</sup> Department of Civil and Environmental Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea

## HIGHLIGHTS

- Nominal MWCO may not be suitable to predict rejection rates of various solutes.
- Higher J/k ratio yields reduced solute rejection and a higher MWCO.
- Nominal MWCO values at varying J/k ratios are lower than the effective MWCO values.
- Ionizable functional groups are crucial in the determination of an effective MWCO.
- The apparent MWCO should be determined under actual filtration conditions.

## ARTICLE INFO

### Article history:

Received 17 March 2014

Received in revised form 18 August 2014

Accepted 18 August 2014

Available online 7 September 2014

### Keywords:

Molecular weight cut-off

Nanofiltration

Natural organic matter

Polyethylene glycol

Diffusion to convection ratio

## ABSTRACT

The apparent and effective molecular weight cut-off (MWCO) values of negatively charged nanofiltration (NF) membranes were determined using the fractional rejection of solutes of interest, including neutral polyethylene glycols and natural organic matter (NOM) containing ionizable functional groups. Varying the hydrodynamic operating conditions, denoted by the J/k ratio (where J represents the permeate water flux/convectional transport and k represents the mass transfer coefficient/back diffusional transport), produced changes in both the nominal and effective MWCO. Consequently, a higher J/k ratio resulted in reduced solute rejection and a higher MWCO. It was confirmed that the nominal MWCO provided by the membrane manufacturers might not be capable of predicting performance with respect to the different characteristics of various solutes (i.e., contaminants) since the predicted nominal MWCO values were nearly twice as high as those measured in this investigation. The effective MWCO values of the NF membranes with respect to NOM were slightly higher than the corresponding nominal MWCO when the NOM was relatively hydrophilic.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Membrane processes, such as microfiltration, ultrafiltration, nanofiltration (NF), reverse osmosis, and membrane distillation have been employed in a wide range of industrial applications including water and wastewater treatment, desalination, concentration, food purification and separation, dairy, beverage processing, and petrochemical technologies owing to their relatively high performance and cost effectiveness [1–5]. In addition, the utilization of membranes allows these industries to become more eco-friendly by facilitating resource recovery and recycling of waste materials that can contribute to a reduction in waste production [6]. However, proper selection of the membranes

based on the membrane molecular weight cut-off (MWCO) is considered a key step in achieving specific concentrations, purities, and separations since the removal performance of membranes is closely associated with pore sizes in terms of MWCO [7]. The pore size and pore size distribution of a membrane have been known to play a crucial role in membrane transport mechanisms, especially size exclusion, and have a direct impact on the separation characteristics of various solutes by the membrane [6].

Several analytical methods, including the fractional rejection method, bubble point method, soluble probe techniques, thermo porosimetry, liquid replacement, and visual observation techniques (e.g., atomic force microscopy, scanning electron microscopy, and transmission electron microscopy) are commonly employed in the measurement of the pore sizes of membranes [8,9]. Each of these methods has its own advantages and limitations for various types of membranes containing different materials and pore sizes. However, some of these techniques are not

\* Corresponding author. Tel.: +82 2 2123 8296; fax: +82 2 364 5300.  
E-mail address: [chojw@yonsei.ac.kr](mailto:chojw@yonsei.ac.kr) (J. Cho).

useful in the determination of pore size (in terms of MWCO) of membranes since they cannot actually predict the sieving effects based on the removal of particles and solutes by membranes under actual operating conditions such as varying hydrodynamic conditions [8,10,11]. Among the previously mentioned methods, the fractional rejection method is an effective technique to investigate the separation characteristics of various solutes by membranes because it measures fractional rejection using actual filtration experiments with non-ionic solutes of a known molecular weight, such as polyethylene glycol (PEG) or dextran. Therefore, different hydrodynamic conditions may provide different MWCO values even when the same membrane and solute is under examination [7,12–19].

Although the calculation of the nominal MWCO of membranes using the fractional rejection method with non-ionic solutes may still be a reliable way to select suitable membranes for various applications, there are some limitations on its use [6]. The separation characteristics of non-ionic solutes by membranes may vary, depending on the ratio of molecular size of the solute (i.e., MW) to the membrane pore size [18, 20,21]. The solution chemistry (e.g., ionic strength and calcium concentration) may affect the removal of PEG using negatively charged membranes. However, the removal of PEG increased significantly at high ionic strengths and high levels of calcium, which is likely due to the double layer compaction of the membrane surface and/or pore walls [22,23]. Furthermore, non-ionizable solutes such as PEG may not be able to effectively demonstrate the effects of electrostatic repulsion between ionic solutes (including humic substances (acids)) and the charged membrane surfaces upon the rejection of the solutes [24]. Cho et al. [24] introduced the concept of the effective MWCO. Unlike the nominal MWCO, the effective MWCO concept incorporates all factors affecting the rejection of natural organic matter (NOM) (i.e., ionic solutes) including the physicochemical properties of NOM (e.g., dissolved organic carbon concentration, specific UV absorbance at 254 nm, and contents of hydrophobic fractions), water characteristics (e.g., pH and ionic strength), membrane characteristics (e.g., contact angle, surface zeta potential, and nominal MWCO), hydrodynamic operating conditions (i.e.,  $J/k$  ratio, which is the ratio of the permeate flux ( $J$ , cm/s) to the mass transfer coefficient ( $k$ , cm/s)), and interactions between NOM and membranes (e.g., size exclusion, electrostatic repulsion, and hydrophobic interactions) into MWCO calculations to estimate an apparent MWCO of a charged membrane [23,25]. Despite this advantage, the effective MWCO concept has not been utilized in most previous studies.

The main goal of this study was to determine the influential factors for the transportation of non-ionic (i.e., PEG) and ionic solutes (i.e., NOM) and their corresponding rejections by negatively charged membranes. The effective MWCO values of three different NF membranes (i.e., NE20, NE70, and NE90) with different properties in terms of nominal pore size and surface potential were determined by fractional rejection methods for both PEG and NOM under various hydrodynamic (i.e.,  $J/k$  ratio) and water conditions (including pH and calcium levels). These values were also correlated to the observed separation characteristics to provide valuable insights into the utilization of effective MWCO over nominal MWCO.

## 2. Materials and methods

### 2.1. Analytical methods

The concentrations of dissolved organic carbon (DOC) and calcium ions were measured using a combustion type total organic carbon analyzer (TOC-V<sub>CPH</sub>, Shimadzu, Kyoto, Japan) and an ion chromatograph (ICS-90, Dionex, Sunnyvale, CA, USA) equipped with an IonPac CS12A column (Dionex, Sunnyvale, CA, USA) [26,27]. The UV absorbance at 254 nm (UVA<sub>254</sub>) of the samples was determined using a UV spectrophotometer (UV-1601, Shimadzu, Kyoto, Japan) and the specific UV absorbance (SUVA) was defined as the ratio of UVA<sub>254</sub> to the concentration of DOC [28]. The surface zeta potentials of the membranes were evaluated

by an electrophoretic light scattering spectrophotometer (ELS-Z-2, Otsuka Electronics, Osaka, Japan) using a plate sample cell, a 10 mM NaCl electrolyte solution (Sigma-Aldrich, St. Louis, MO, USA), and polystyrene latex particles (diameter: 520 nm) (Otsuka Electronics, Osaka, Japan) at various pH values (pH = 4, 7, or 9) [29].

### 2.2. Preparation of the non-ionic and ionic solute samples

Seven different PEG solutions (Sigma-Aldrich, St. Louis, MO, USA) with a wide range of molecular weights (200, 400, 600, 1.0 K, 3.4 K, 4.6 K, and 8.0 K Da) were prepared at a concentration of 1,600 mg/L in deionized (DI) water (resistivity: 18.3 MΩ-cm). The molecular weight distribution of the PEG solutions was measured using high-performance size-exclusion chromatography (HPSEC) with an Ultra hydrogel 120 column (Water, Milford, MA, USA), a refractive index (RI) detector (RID-6A, Shimadzu, Kyoto, Japan), and a phosphate buffer solution (0.096 M NaCl (Sigma-Aldrich, St. Louis, MO, USA) + 0.0024 M NaH<sub>2</sub>PO<sub>4</sub> (Sigma-Aldrich, St. Louis, MO, USA) + 0.0016 M Na<sub>2</sub>HPO<sub>4</sub> (Sigma-Aldrich, St. Louis, MO, USA, total ionic strength: 0.1 M, pH: 6.8) [7]. The manufacturer reported that the polydispersities of PEG (the ratio of the weight-averaged molecular weight ( $M_w$ ) to number-averaged molecular weight ( $M_n$ )) range from 1.1 to 1.2. Surface water sampled from the Yeongsan River (Gwangju, Korea) was used as the NOM source and was filtered using regenerated cellulose micro filters with a pore size of 0.45 μm (Advantec, Tokyo, Japan) and stored in a refrigerator at 4 °C prior to the experiments. The feed water characteristics were as follows; pH: 7, DOC: 3.16 ± 0.28 mgC/L, SUVA: 1.04 ± 0.09 L/mgC m, and calcium level: 20 mg/L. The molecular weight distribution of NOM was measured using an HPSEC equipped with a Protein-Pak 125 column (Waters, Milford, MA, USA), UV detection at 254 nm (SPD-10AVP, Shimadzu, Kyoto, Japan), a phosphate buffer solution (0.096 M NaCl + 0.0024 M NaH<sub>2</sub>PO<sub>4</sub> + 0.0016 M Na<sub>2</sub>HPO<sub>4</sub>, total ionic strength: 0.1 M, pH: 6.8), and polystyrene sulfonate standards (molecular weight: 210, 1.0 K, 4.6 K, 8.0 K, 18.0 K Da) (Polysciences, Warrington, PA, USA) [30,31]. The  $M_w$ ,  $M_n$ , and polydispersity ( $M_w/M_n$ ) of NOM from the Yeongsan River water were estimated from the following equations [32]:

$$M_n = \sum_{i=1}^N h_i / \sum_{i=1}^N (h_i/M_i) \quad (1)$$

$$M_w = \sum_{i=1}^N (h_i \times M_i) / \sum_{i=1}^N h_i \quad (2)$$

where  $h_i$  is the height of molecular weight peak with respect to elution time. The PEG and NOM from the Yeongsan River were employed as non-ionic and ionic solutes to measure the effective MWCO of the negatively charged NF membranes at various pH values (pH = 4, 7, or 9) [7]. To investigate the role of calcium complexation with NOM in the calculation of the effective MWCO, 130 mg/L of CaCl<sub>2</sub> was added to the Yeongsan River water based on the classification of water hardness proposed by the United States Geological Survey (USGS; general guidelines for classification of water are as follows: 0 to 60 mg/L (milligrams per liter) as calcium carbonate is classified as soft; 61 to 120 mg/L as moderately hard; 121 to 180 mg/L as hard; and more than 180 mg/L as very hard) [33].

### 2.3. Membrane filtration tests

All experiments were conducted using a lab-scale cross flow filtration unit containing a flat-sheet type membrane cell (effective surface area of 96 cm<sup>2</sup>, channel height of 0.04 cm) equipped with the NF membranes (NE20, NE70, and NE90), one magnetic gear pump (Micropump, Vancouver, WA, Canada), and two reservoirs for feed and permeated water (volume: 4 L for each reservoir) (Fig. 1). The physicochemical properties and performance of the NF membranes (i.e., rejection rates of ions and permeate flux of DI water) are listed in Table 1.

Download English Version:

<https://daneshyari.com/en/article/623417>

Download Persian Version:

<https://daneshyari.com/article/623417>

[Daneshyari.com](https://daneshyari.com)