Evaluation of quantitative performance of the membrane filtration-differential mobility analyzer (MF-DMA) counting technique to determine suspended particles and dissolved solids in water

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Abstract

Suspended particles and dissolved solids in seawater during desalination process have been known to cause colloidal fouling in membranes. The membrane filtration-differential mobility analyzer (MF-DMA) counting technique has been developed to quantify suspended nanoparticles and dissolved solids in water in real time. Various types of suspended particles (PSL, CaCO₃, and MgCO₃) and dissolved solids (artificial seawater, NaCl, KCl, MgCl₂, and CaCl₂) were used to evaluate the MF-DMA method. By using PSL particles of known sizes and numbers in water, a linear relationship between particle number concentrations in air (particles/cm³) and in water (particles/ml) was established, which was valid independent of particle size. This relationship was used to determine number concentrations of CaCO₃ and MgCO₃ particles in water, showing good agreements with the calculated values within ∼19%. By using artificial seawater, a linear relationship between mass concentration of dissolved solids in air (μg/m³) and in water (ppm) was also found. Mass concentrations of dissolved solids (NaCl, KCl, CaCl₂, and MgCl₂) in water estimated by the MF-DMA method were in good agreements with those measured with the TDS meter within ∼15%. The current real time technique can be applied to monitor both suspended particles and dissolved solids in pre-treated seawater during RO membrane desalination process.

Keywords: Colloidal particles; MF-DMA technique; Dissolved solids; Membrane; Filtration

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1. Introduction

Colloidal particles are ubiquitous in natural waters and their size varied from a few nanometers to a few micrometers [1]. These colloidal particles have been known to cause membrane fouling by permeate flux decline, increase in applied pressure, and decrease in membrane lifetime [1–4], which has been one of the most serious considerations in membrane filtration and reverse osmosis (RO) desalination processes, and to have effects on water purification systems or water quality by aggregation and deposition of the colloidal particles [5]. To remove the colloidal fouling, water was pretreated by microfiltration (MF) or ultrafiltration (UF) membrane processes. However, the water after filtration still contained a significant amount of suspended particles passed through the filtration membrane [6,7]. In addition, some of the dissolved solids that can be changed into particle phase are survived from the filtration process, affecting membrane fouling.

Fouling of membrane by both suspended particles and dissolved solids occurred by various mechanisms [8,9]. Suspended particles can accumulate on the membrane surface due to concentration polarization, aggregations, and precipitation [10]. The dissolved solids may form a surface cake on the membrane surface, penetrate and clog the pore, and adsorb on pores reducing the pore diameter [8]. Dissolved solids are defined here as those that are able to crystallize in the form of particle phase at the membrane surface although they are originally not in particle phase in water (i.e., they are ionic phase in water) [11]. Thus, quantification of such colloidal particles and dissolved solids in water is important to predict the fouling of membrane during filtration process or desalination process using the RO membrane [12].

For methods to count and size particles in water, transmission electron microscopy (TEM) or scanning electron microscopy (SEM) [13,14], dynamic light scattering (DLS) [15], and field-flow fractionation (FFF) [16] have been used. The off-line electron microscopy measurements have a limited quantification performance for sizing and counting particles in water due to a small number data set [17]. The DLS method has an advantage to directly measure particle size and number in water in real time, while this method has been limited to accurately count small particles due to their low scattering intensity and bubble effect [18]. Lenggoro et al. [19] reported that the DLS technique was not accurate for determination of size of nanoparticles in water. The FFF technique can be used to determine the particle size in the range of 2 nm to 100 μm and can account for interaction between particles and membranes [20]. However, this method requires extensive calibration procedures to determine the absolute particle size.

Fouling indices such as silt density index (SDI) and modified fouling index (MFI) have been widely used to predict the colloidal fouling. However, the SDI or MFI method which uses a 0.45 μm MF membrane was not able to adequately deal with suspended particles smaller than 0.45 μm and dissolved solids in feed water. It was reported that these indices often fail to reflect the true fouling strength of particles in feed water [21,22]. The membrane filtration-differential mobility analyzer (MF-DMA) counting technique has been developed to measure suspended nanoparticles and dissolved solids in water in real time by our group [23]. This technique enabled us to determine size and number of particles ranging from 20 nm to 600 nm in water in real time. However, the relationship between quantity (i.e., size and number) in air and water was not fully established and the
quantitative performance of the MF-DMA method was not evaluated.

In this study, we established a relationship between particle number concentration in air measured with the MF-DMA technique (particles/cm³) and number concentration of suspended particles in water (particles/ml). Also, the relationship between mass concentration of dissolved solids in air (μg/m³) and water (ppm) was established. Various types of suspended particles (PSL, CaCO₃, and MgCO₃) and dissolved solids (artificial seawater, NaCl, KCl, MgCl₂, and CaCl₂) were used to investigate effects of composition and size of suspended particles and dissolved solids on the quantitative performance of the MF-DMA method. With MF, UF, and RO membrane filtrations, we were able to quantify concentrations of: (1) suspended nanoparticles which survived through the MF membrane with a 0.45 μm pore size, (2) dissolved solids which passed through the MF and UF membranes, and (3) dissolved solids which passed through the RO membrane, respectively.

2. Experimental methods

A schematic of the MF-DMA counting technique is shown in Fig. 1. The target water treated by MF, UF, or RO membrane was supplied into a constant output atomizer (TSI 3076, USA) through a syringe pump at a flow rate of 2 ml/min. Then, the water solution was continuously aerosolized into ~0.35 μm droplets by a compressed air in the atomizer [24]. Droplets containing suspended particles or dissolved solids were dried out by two diffusion driers in series. The liquid droplets containing suspended particles were evaporated through driers (i.e., water solvent was evaporated), enabling only particles to be suspended in the air. For the case of dissolved solids in the droplet, they are crystallized during the drying process into

Fig. 1. Schematic of the membrane filtration-differential mobility analyzer (MF-DMA) counting technique.
particle phases in the air. Without solute in water, no particles were counted, suggesting that droplets were completely dried out in the MF-DMA counting technique. Then, those particles in the air were directly introduced into the differential mobility analyzer (DMA) (TSI 3081, USA) [25]. The DMA selected particles of a certain size and the number of those particles was counted by the condensation particle counters (CPC) (TSI 3022A, USA), which is located downstream of the DMA. The DMA voltage was scanned to select particles of different sizes with counting of particles in a continuous manner in the size range of 20–600 nm. This provides number size distribution of particles in the size range of 20–600 nm with 64 or 128 bins within ~2 min. By integrating the number size distribution, total number concentration of particles in 20–600 nm can be determined. The number size distribution can be converted to mass size distribution by using particle density, assuming that they are spherical particles. The integrated mass size distribution provides total mass concentration of particles in 20–600 nm.

For suspended particles in water, we used polystyrene latex (PSL) particles (60 nm, 135 nm, and 300 nm) (Duke Scientific, USA), CaCO₃ (Sigma–Aldrich, USA), and MgCO₃ (Sigma–Aldrich, USA), while for dissolved solids we used NaCl (Sigma–Aldrich, USA), CaCl₂ (Sigma–Aldrich, USA), KCl (Sigma–Aldrich, USA), and MgCl₂ (Sigma–Aldrich, USA). Dissolved solids and suspended particles tested in this study are summarized in Table 1. The solution was prepared by dispersing them in de-ionized water, having a conductivity less than 1 μS/cm. In case of CaCO₃ and MgCO₃, the solution was pretreated by using a 0.45 μm glass fiber filter (Whatman, USA) to remove any large residual solids greater than 0.45 μm. The total dissolved solids (TDS) were measured with the TDS meter (OAKTON, Singapore).

For MF membrane filtration, the solution was filtered through a 0.45 μm glass fiber filter (Whatman, USA). Laboratory scale cross-flow filtration unit was employed to perform UF and RO membrane filtration. A polyethersulfone (PES) UF membrane (20,000 Da, GE Osmonics, France) was used for UF filtration.

Table 1
Dissolved solids and suspended particles tested in this study

<table>
<thead>
<tr>
<th>Chemical</th>
<th>MW</th>
<th>Solubility or $K_{sp}$ at 20°C</th>
<th>Density (g/cm³)</th>
<th>Concentration range (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dissolved solids</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>58.45</td>
<td>36 g/100 g</td>
<td>2.163</td>
<td>200–1800</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>74.56</td>
<td>34 g/100 g</td>
<td>1.988</td>
<td>200–1000</td>
</tr>
<tr>
<td>Calcium chloride</td>
<td>110.99</td>
<td>74.5 g/100 g</td>
<td>2.152</td>
<td>200–3500</td>
</tr>
<tr>
<td>Magnesium chloride</td>
<td>103.31</td>
<td>54.5 g/100 g</td>
<td>1.560</td>
<td>200–1000</td>
</tr>
<tr>
<td>Artificial seawater</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>30–2000</td>
</tr>
<tr>
<td><strong>Suspended particles</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>100.09</td>
<td>4.79*10⁻⁹</td>
<td>2.930</td>
<td>50–650</td>
</tr>
<tr>
<td>Magnesium carbonate</td>
<td>83.43</td>
<td>5.0*10⁻⁶</td>
<td>3.037</td>
<td>50–800</td>
</tr>
<tr>
<td>Polystyrene latex (60 nm)</td>
<td>–</td>
<td>–</td>
<td>1.05</td>
<td>10–500</td>
</tr>
<tr>
<td>Polystyrene latex (135 nm)</td>
<td>–</td>
<td>–</td>
<td>1.05</td>
<td>10–500</td>
</tr>
<tr>
<td>Polystyrene latex (300 nm)</td>
<td>–</td>
<td>–</td>
<td>1.05</td>
<td>10–500</td>
</tr>
</tbody>
</table>
and a polyamide RO membrane (Woongjin Chemical, Korea) was used for RO filtration. The UF membrane has an active area of 56.8 cm², while the area of RO membrane has 138.7 cm². Prior to membrane filtration of target solution, deionized water was filtered through the membrane for 8–10 h to obtain a stable membrane flux. The permeate flux was monitored by a digital flow meter. In case of the UF membrane, cross-flow rate, applied pressure, and permeate flow rate were 300 ml/min, 15 psi, and 8.3–8.5 ml/min, respectively, while for RO membrane, 500 ml/min, 800 psi, and 6.8–7.5 ml/min, respectively. For the RO membrane test, we used a SEPA CF II membrane element cell (Osmonics Inc., USA), which can accommodate a high trans-membrane pressure up to 1000 psi. Feed water temperature was maintained at 25°C using a re-circulating chiller during the whole experiment.

3. Results and discussion

3.1. Quantification of suspended particles in water

By using PSL particles of known sizes (90 nm, 135 nm, and 300 nm) and number concentrations in water that can be calculated from PSL size, density, and solution concentration (ppm), we established a relationship between particle number concentration in air (particles/cm³) and particle number concentration in water (particles/ml) as shown in Fig. 2. By varying solution concentration and size of the PSL, the number of particles in water can be adjusted. As shown in Fig. 2, we found a linear relationship between particle number concentration in air and particle number concentration in water with a correlation coefficient of 0.99. It also showed that the linear relationship was not affected by particle size. This relationship will be used to estimate number concentration of particles suspended in water from the measured particle number concentration in air with the MF-DMA technique (i.e., a calibration line for suspended particles). As not shown here, TEM analysis of PSL particles collected in air also confirmed that particle size in air measured with the MF-DMA was in a good agreement with the specified size within ~5%.

We applied the above relationship to determine number concentration (particles/ml) of other types of suspended particles (CaCO₃ and MgCO₃) of known concentrations (ppm) in water. The number concentrations of particles in water as a function of solution concentration are shown in Fig. 3(a). For the given solution concentration range, all data showed a linear relationship between number of particles in water and solution concentration although their slopes varied. Different densities, sizes, and solubility product (K_{sp}) between particles might lead to the different slopes of the linear relationship. Since the solution concentration (ppm) is known, we are able to estimate number concentration of particles in water using particle size and density information. The geometric mean diameter (GMD) measured with the MF-DMA...
technique was used as an approximate for particle size. Note that CaCO$_3$ and MgCO$_3$ particles are not monodisperse like PSL particles. Figure 3(b) and (c) compare number concentration of particles (particles/ml) determined by the MF-DMA technique and estimated number concentration of particles (particles/ml) for CaCO$_3$ particles, and (c) for MgCO$_3$ particles.

Fig. 3. (a) Number concentration of particles in water (particles/ml) as a function of solution concentration (ppm) for CaCO$_3$ and MgCO$_3$ particles, (b) comparison of number concentration of particles (particles/ml) determined by the MF-DMA method and estimated number concentration of particles (particles/ml) for CaCO$_3$ particles, and (c) for MgCO$_3$ particles.

3.2. Quantification of dissolved solids in water

By using an artificial seawater of a known amount of dissolved solids, we established a relationship between mass concentration of dissolved solids in air (μg/m$^3$) determined by the MF-DMA method and mass concentration of dissolved solids in water (ppm). The solution was filtered by the MF membrane. Figure 4 shows mass concentration of particles in air measured with the MF-DMA versus mass concentration of dissolved solids measured with the TDS meter for the artificial
As the dissolved solids in water increased, mass concentration of particles in air increased linearly from 81 μg/m³ to 1100 μg/m³. We repeated measurements five times and their standard deviations were shown as error bars. The linear relationship was valid for the concentration range up to 2000 ppm. Above 2000 ppm, the measured concentration in air did not increase linearly with increasing solution concentration. Thus, for the case of highly concentrated solution, the solution should be diluted into the above concentration range (30–2000 ppm) where the linear relationship is valid. Note that the artificial seawater consists of several dissolved salts such as chloride, sodium, sulfate, magnesium, and potassium. The relationship can be used to determine mass concentration of other types of dissolved solids in water (i.e., a calibration line for dissolved solids).

Using the above relationship, we determined mass concentrations of dissolved solids (NaCl, KCl, CaCl₂, and MgCl₂) in water and compared them with the TDS meter as shown in Fig. 5. The mass concentration of dissolved solids in air was calculated from number concentration measured with the MF-DMA technique, assuming that they are spherical particles with a known density. In case of NaCl, the dynamic shape factor of 1.08 [26] was used to account for their cubic shape when the mass concentration in air was calculated. Figure 5 showed that they agreed well within 15%, suggesting that the MF-DMA method can also be used to determine mass concentration of dissolved solids in water. When the artificial seawater was further filtered by the UF membrane, mass concentration of dissolved solids decreased only by 0.6%. This suggests that penetration of the artificial seawater through the current UF membrane was 99.4%.

We also determined concentration of dissolved solids in seawater (Taean, Korea) that passed through MF, UF and RO membranes. Figure 6 shows the dissolved solids which passed through the UF membrane and dissolved solids which passed through the RO membrane. Also, mass concentrations of dissolved solids measured with the TDS meter were included. Since the seawater consists of suspended particles and dissolved solids, they need to be separated. The seawater was filtered by the MF membrane to remove large
particles, and then we further filtered the seawater using the UF membrane [27]. The UF membrane-filtered seawater will contain only dissolved solids with most of suspended particles removed. The value after UF filtration would represent only dissolved solids. Using the relationship derived from the previous section for dissolved solids, we determined mass concentration of dissolved solids for the UF membrane-filtered seawater, resulting in 26,358 ppm, which was in an excellent agreement with the value (27,600 ppm) measured with the TDS meter. When the seawater was further treated by the RO membrane, the dissolved solids decreased to 469 ppm. The difference before and after the RO membrane filtration represents dissolved solids remaining in the RO membrane or recalculating in feed water as retentate, which may significantly affect membrane fouling. We found that the difference was about 25,889 ppm. In addition, we determined size of dissolved particles in air formed from dissolved solids in water. The geometric mean diameters (GMD) of dissolved particles in seawater (Taean, Korea) that passed through MF, UF and RO membranes were 102.81 nm, 102.94, and 69.18 nm, respectively. We observed that a significant amount of dissolved solids in water can be crystallized during drying process in the MF-DMA technique after the MF and RO treatments. This indicates that they can cause membrane fouling by various processes of precipitation and aggregation and the formation of surface cake on the membrane surface.

4. Conclusions

Quantitative performance of the MF-DMA counting technique to determine number concentration of suspended particles and mass concentration of dissolved solids in water was evaluated by using suspended particles (PSL, CaCO₃, and MgCO₃) and dissolved solids (artificial seawater, NaCl, KCl, MgCl₂, and CaCl₂) in water. Relationships between concentrations of particles and dissolved solids in air measured with the MF-DMA method and those in water were established by using PSL particles of known sizes and numbers and artificial seawater of known concentrations. The relationships were applied to determine number concentration of suspended particles and mass concentration of dissolved solids in water. Results showed that the MF-DMA method was able to estimate particle number concentration in water within 19% for suspended CaCO₃ and MgCO₃ particles and mass concentration of dissolved solids (NaCl, KCl, CaCl₂, and MgCl₂) within 15%. Furthermore, we determined dissolved solids which passed through the UF and RO membranes. We found that mass concentration of dissolved solids in the UF membrane-filtered seawater was 26,358 ppm and after RO membrane filtration it decreased to 469 ppm. Also, we observed that the geometric mean diameters (GMD) of dissolved particles passed through MF, UF and RO membranes were 102.81 nm, 102.94 nm, and 69.18 nm, respectively.
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References


