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Efficient removals of tris(2-chloroethyl) phosphate (TCEP) and perchlorate using NF membrane filtrations

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Abstract

Perchlorate and tris(2-chloroethyl) phosphate (TCEP), which have been widely detected micropollutants in rivers and wastewater effluents, were investigated in terms of removals by nanofiltration (NF) membranes under different membrane feed water conditions. For this study, NF membranes with different characteristics, including molecular weight cutoff (MWCO), relative hydrophobicity, and roughness, were used. To demonstrate the effect of electrostatic repulsion between the membrane surface and investigated compounds, the conductivity of membrane feed solutions were altered using sodium chloride; the effects of natural organic matters on removal efficiencies of tested compounds were also demonstrated using synthetic model solutions and the Youngsan River water. Filtration tests with seawater were conducted to investigate applicability of NF membranes for desalination. A relatively loose NF membrane with lower hydrophobicity and lower roughness exhibited lower removal efficiencies for both perchlorate and TCEP than the other tight NF membranes with lower MWCO. When comparing removal efficiencies of perchlorate and TCEP for the loose NF membrane, removals of uncharged TCEP were less affected by differences in solution chemistry variations than those of perchlorate. The tight NF membranes exhibited higher removal efficiencies for both perchlorate and TCEP than the loose NF membrane, as expected, under tested conditions, including seawater.

Keywords: NF; Micropollutant; Perchlorate; TCEP; Desalination

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1. Introduction

In the last decades, anthropogenic micropollutants such as endocrine disrupting compounds, pharmaceuticals, and personal care products (PPCPs) have been frequently found in surface waters, wastewater effluents, and even seawater. Although most micropollutants have not been regulated yet as worldwide drinking water criteria, the potential risk of these chemicals to human health cannot be ignored. Tris(2-chloroethyl) phosphate (TCEP), widely used for fire retardant, and perchlorate, a rocket-fuel additive, frequently detected in wastewater effluents and rivers at ppb levels. It has been revealed that TCEP causes kidney and liver cancers and perchlorate prevents thyroid hormones from regulating the metabolism by disrupting iodide uptake. In this study, three NF membranes were used to investigate removal efficiencies of both TCEP and perchlorate. Effects of membrane properties and solution chemistries on removal efficiencies of TCEP and perchlorate were also demonstrated.

2. Materials and methods

2.1. Membranes

Three NF membranes with different characteristics were used in this study. Membranes were characterized using various methods. The molecular weight cutoff (MWCO) of the membranes was measured using the fractional rejection method with polyethylene glycols [1]. The membrane surface charge was measured using an electrophoresis method (ELS-8000, Otsuka, Japan) employing polystyrene latex particles, with a nominal size of 520 nm (Otsuka Electronics, Japan), coated with hydroxyl propyl cellulose having a molecular weight of 300,000 [2]. The contact angel of the membranes was measured using the sessile drop method with a contact angle meter (ráme-hart, standard goniometer with drop image, 200-00, NJ, US). And the roughnesses of membranes were measured using atomic force microscopy (XE-100, PSIA, Korea) equipped with ACTA-10 cantilever (Applied NanoStructures, USA).

2.2. Membrane filtration test

Flat-sheet type of membranes was used with a typical bench-scale cross-flow membrane unit. The experiment were operated in a recycle mode in which all retentate and permeate were returned to feed water reservoir. For each experiment, a new membrane coupon was used. The effective membrane area in the tested unit was 58.2 cm^2. In all of the experiment, the applied pressure was fixed 320–400 kPa and resulted in an average permeate flux of 3.5 mL/min. Feed flow rate was adjusted at an appropriate value 500 mL/min. Each membrane filtration test was conducted at ambient temperature (25 ± 2°C). Whole membranes were washed with distilled water prior to the initiation of new series of experiment.

2.3. Chemicals and reagents and analyses

The feed concentrations of perchlorate and TCEP were 200 and 100 μg/L, respectively. The conductivities of feed solutions were controlled at 150 μS/cm using sodium chloride. To investigate the effect of natural organic matters on removal efficiencies of tested compounds, both the Youngsan River surface water (350 μS/cm, 4.2 mg C/L) and synthetic model water (150 μS/cm, 3.0 mg C/L) with humic acids (Aldrich, USA) were used. Collected perchlorate samples were analysed using ion chromatograph (DX-120, Dionex) equipped with AS11 column and AG11 guard column (REICTM), with eluent of 12 mM NaOH. For TCEP concentration measurements, solid-phase microextraction (SPME) coupled with gas chromatography-mass spectrometric detection (HP 5890 series, Hewlett Packard) was used. 65 μm PDMS-DVB (Supelco, USA) fiber was directly immersed into 15 mL of samples containing 300 mg/mL of NaCl, with a magnetic bar

Table 1
Membrane characterizations

Membrane code	Contact angle	Zeta potential at pH 7 (mV)	MWCO	Roughness (nm)
NE70 (loose), Saehan Corp.	22.6	–46.2	350	8.7
NE90 (tight), Saehan Corp.	41.5	–36.4	210	34.3
NF90 (tight), Filmtec	43.8	–21.6	200	84.9

being stirred. The pH of samples was not adjusted and the processes were conducted at a room temperature for 30 min. TCEP samples extracted with the fiber were separated in DB-5MS capillary column (Agilent Technologies; 30 m × 0.25 mm i.d. × 0.25 μm film thickness). Helium was used as the carrier gas at a flow rate of 0.6 mL/min. The column temperature was programmed from 50°C (holding time of 2 min) to 150°C (holding time of 5 min) with heating rate of 20°C/min, then the temperature increased to 280°C with rate of 5°C/min, and finally increased to 300°C with rate of 25°C/min.

3. Results and discussion

The properties of tested membranes are presented in Table 1. The NE70 membrane provided relatively hydrophilic, relatively higher MWCO, and lower roughness, as compared to the other membranes.

Fig. 1 depicts the comparisons of the removal efficiencies of perchlorate and TCEP with different feed waters. Removal efficiencies of perchlorate and TCEP by the NF90 and NE90 membranes were not significantly affected by different feed characteristics. Both the tight NF membranes provided removal efficiencies higher than 90% for perchlorate and TCEP under tested different solutions condition. According to the prior research by Kim et al. [3], the NE90 membrane exhibited high removal efficiency (~95%) of TCEP included in effluent treated by a membrane bioreactor. This suggests the solution chemistries of feed water might little affect on TCEP removal efficiency. As shown in Fig. 1, the NE70 membrane did not provide good removal efficiencies compared to the other two

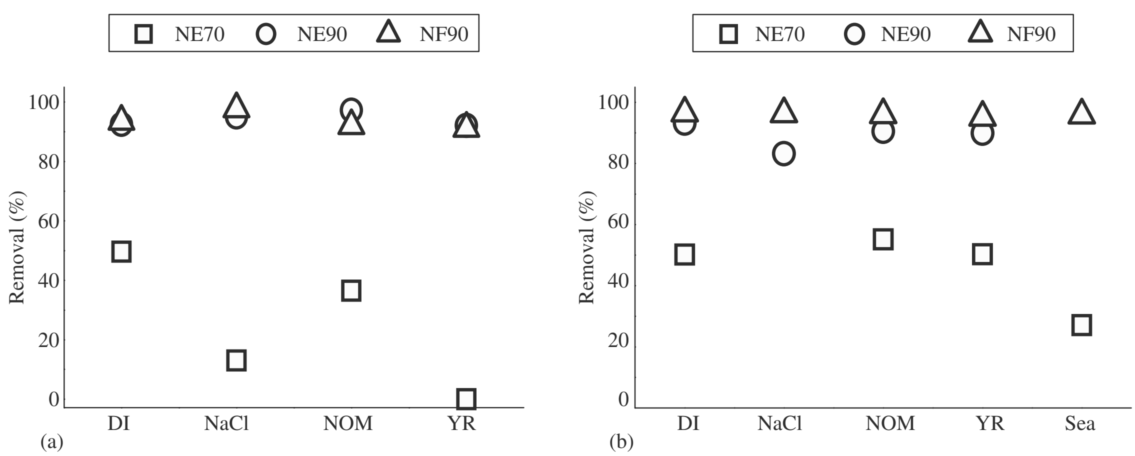

Fig. 1. Removal efficiencies trend of (a) perchlorate and (b) TCEP under different feed waters condition.

tight NF membranes. Especially, the NE70 membrane provided very low perchlorate removal efficiencies for NaCl controlled and the Youngsan River surface water solutions, which was probably due to reduced electrostatic repulsion resulted from higher conductivities. These trends were not found for TCEP as TCEP is neutral compound without any ionizable functional groups. Furthermore, filtration tests using seawater were conducted to investigate applicability of the NF membranes to desalination. It was found that the tight NF90 membrane exhibited relatively high removal efficiency for TCEP.

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