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# The effect of deterioration of nanofiltration membrane on retention of pharmaceuticals

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**Abstract**

The retention of 8 acidic and 2 neutral pharmaceuticals in nanofiltration (NF) was investigated by a loose NF membrane and a tight NF membrane. The retention change due to the exposure to chlorine was studied. The retention of pharmaceuticals was affected by the electric repulsion effect in addition to the size exclusion effect. In the case of the loose NF membrane, the retention of pharmaceuticals was more sensitive to the exposure to chlorine than salt retention because both the decrease in electric repulsion effect and the increase in pore size affected the permeation of pharmaceuticals. On the other hand, in the case of the tight NF membrane, the retention of acidic pharmaceuticals were maintained at higher range at neutral pH range even after exposure to chlorine, though the increase in the pore size was obvious judging from the decrease in the retention of pharmaceuticals in the acidic solution environment.

*Keywords:* Pharmaceuticals; Contact to chlorine; Nanofiltration; Reverse osmosis

## 1. Introduction

Pharmaceutical substances have been recognized since 1990s as new unregulated contaminants [1–3]. On the contrary to hydrophobic and persistent compounds such as dioxins, some of pharmaceutical compounds are relatively hydrophilic and biologically persistent [4]. Their hydrophilic characteristics make it difficult to be removed in biological processes and in adsorption processes because they tend to remain in the water phase due to their hydrophilic characters [5,6]. Biological processes and adsorption processes may not be efficient on the removal of this group of substances.

The separation mechanism of nanofiltration includes both electric repulsion and size sieving [7].

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Nanofiltration membranes can easily retain solutes with larger molecular size and with electric charge, including pharmaceutical compounds. A group of pharmaceutical substances is one of the target groups for removal in treatment process considering wastewater reclamation and reuse. One of the advantages using nanofiltration is the treatment of these hydrophilic and biologically persistent compounds.

Cellulose acetate and polyamides are widely used for the materials of nanofiltration and reverse osmosis membranes. Polyamide membranes easily loose their retention characteristics by the exposure to chlorine, which is often used for the cleaning of membrane processes [8,9]. In the long term use of membranes, the change in retention characteristics by the contact to oxidants is important. This paper focuses on the change in retention characteristics by the degradation of membranes due to the contact to chlorine with taking the example of retention of pharmaceuticals. It is emphasized which effect of electric repulsion or size sieving is damaged in the contact to chlorine.

## 2. Materials and method

### 2.1. Target compounds

The target compounds in this study were clofibric acid (CA), gemfibrozil (GFZ), ibuprofen (IBP), fenoprofen (FEP), ketoprofen (KEP), naproxen (NPX), diclofenac (DCF), indomethacin (IDM), propyphenazone (PPZ) and carbamazepine (CBZ). CA is a metabolite of a certain type of lipid regulators like clofibrate, etofibrate and etofyllinclofibrate. GFZ is a lipid regulator. IBP, FEP, KEP, NPX, DCF, IDM, PPZ are commonly used non-steroidal anti-inflammatory drugs. CBZ is an antiepileptic agent. Table 1 shows the physical and chemical properties of these compounds. Two size parameters, the molecular width and the molecular radius, were calculated by the Kiso's method [10], with the use of Chem-Office software. Molecular width is the half of square root of minimum square of the objected molecule to a plane perpendicular to the line between the most distant two atoms of the target compounds. Molecular radius is the minimum diameter of the circle which includes the objected molecule to the same plane. The dipole moment of the target compounds was calculated with the same software.

### 2.2. Nanofiltration membranes

Nanofiltration membranes used in this study are C-membrane (under development by Toray) with nominal salt retention of 85% and nominal glucose retention of 95%, and ES-20 (supplied by Nitto Denko) with nominal salt retention of 99.7%. C-10T membrane module (supplied by Nittodenko with effective surface area of 60 $cm^2$) was used for the retention experiments. Virgin membranes and membranes degraded by chlorine were used. The condition for the degradation is 6 h for C-membrane and 24 h for ES-20 in 1250 mg/L sodium hypochlorite solution without pH control.

### 2.3. Nanofiltration experiment

The feed solution was prepared to contain 100 µg each of pharmaceuticals in 1 litter with the addition of 5% landfill leachate at a solid waste disposal site to simulate artificial treated wastewater and to reduce adsorption of pharmaceuticals onto membrane surface. The solution pH was adjusted by sodium hydroxide or by hydrochloric acid at 3, 5, 7 and 9. The bulk samples and permeate samples were taken at 2 and 4 h after the start of experiment to confirm that the samples were taken at steady-state condition.

### 2.4. Chemical analysis

The water samples containing target pharmaceutical substances were mixed with internal standards, 2,3-dichlorophenoxyacetic acid and chrysene-d12, and pH was adjusted at 2 by adding hydrochloric acid. This solution was