論文の内容の要旨

Abstract of Dissertation

# Effects of Membrane Fouling on Fluoride Removal from Groundwater by Ultra-Low-Pressure Reverse Osmosis Membrane

（超低圧逆浸透膜による地下水中のフッ素除去における膜ファウリングの影響）

ウォンルエン アノップ

Residents of Chiang Mai and Lamphun Provinces, Thailand, have been suffering from dental and skeletal fluorosis due to drinking water from the groundwater resource that contains an excessive amount of fluoride. Fluoride concentration commonly found in this region is higher than WHO's guideline value of 1.5 mg/L and Thailand fluoride standard for drinking water of 0.7 mg/L, set by The Ministry of Industry in Thailand. Although defluoridation using membrane filtration process is a new technology, it is increasingly used due to the advancement of membrane manufacturing. However, accumulation of suspended and dissolved compounds on the membrane surface results in membrane fouling such as concentration polarization and gel-layer formation. These phenomena are problems in membrane separation processes: namely, a permeate flux decline, deterioration in permeate quality and membrane degradation.

Applicability of an ultra low pressure reverse osmosis (ULPRO) membrane (UTC-70U) for groundwater defluoridation was investigated using groundwater samples obtained in Lamphun Province, Thailand. The used membrane achieved high fluoride rejections of 94.4-98.4%. Thus, the ULPRO membrane was expected to produce permeate water with a lower fluoride concentration than the standard for drinking water in Thailand (0.7 mg/L).

Effect of feed water pH on fluoride rejection was studied. The isoelectric point of the UTC-70U membrane was found at pH 5.7. This result well explained why the percentage rejection of fluoride by the charged membrane decreased at the bulk water pH below 7.0. According to the Nernst-Planck equation, the electrical potential across UTC-70U membrane ($\Delta\Psi$) at the initial feed water pH of 7.9, 7.0, 6.0, 5.0, and 4.0 was determined to be 49.1, 49.1, 44.2, 0.0, and -116 mV, respectively. Diffusion coefficient of fluoride through the membrane ($D_{i(m)}$) was estimated to be $7.79 \times 10^{-13}$ $m^2/s$.

When groundwater samples were filtered, a fouling gel-layer was formed on the membrane surface. As a result, the rejections went up or down over the course of filtration. Fluoride

concentrations at the gel-layer surface ($C_G$) and at the membrane surface ($C_M$) were estimated. When the fouling gel-layer is porous and can be regarded to be similar to the fluoride concentration in bulk water. Hence, back diffusion of fluoride within the gel-layer forms concentration polarization as in the water film. In this case, the ratio of $C_M/C_G$ is higher than unity. On the other hand, if the gel-layer is very tight, the ratio of $C_M/C_G$ is less than unity, fluoride transports by diffusion are considered to be dominant. Hence, the ratio of $C_M/C_G$ can be used to estimate the characteristics of the fouling gel-layer.

Using the electrical potential across UTC-70U membrane ($\Delta\Psi$) and the diffusion coefficient of fluoride through the membrane ($D_{i(m)}$), $C_G$ and $C_M$ were obtained. The change of $C_M/C_G$ ratios during the filtration suggested that the difference in gel-layer structure and thickness resulted in the different trends of the fluoride rejections within groundwater samples.

Besides, the fluoride mass-transport models via diffusion mechanism were verified by filtering NaF solutions. The mass transfer coefficient of fluoride ($k$) in water was estimated to be $3.20 \times 10^{-5}$ m/s and the solute mass transfer coefficient through UTC-70U membrane ($k_i$) was $1.06 \times 10^{-7}$ m/s. Using these mass transfer coefficients, $C_G$ and $C_M$ were estimated as well to analyzed fouling gel-layer.

Consequently, transport mechanisms of fluoride through UTC-70U membrane applied for the fouling gel-layer analysis were evaluated by considering both diffusion mechanism and the Nernst-Planck equation. The results indicated that the diffusion mechanism could be applied for the fouling gel-layer analysis of UTC-70U membrane at the feed water pH of 7.0 or higher.

Silica fouling in membrane filtration was investigated. Fouling by silica polymerization on the membrane surface without colloidal silica at the feed solution pH of 7.1 and 9.6 was not significantly different based on the permeate flux, mass of silica attached on the membrane surface, and thickness of fouling gel-layer. Silica polymerization in the presence of colloidal silica on the membrane surface at pH 9.6 is more severe than that at pH 7.1 when considering the mentioned parameters, e.g. permeate flux, mass of attached silica, and so on. Based on the evaluation of $C_M/C_G$ ratios, since the ratios were higher than 1, the fouling gel-layers were fouled with loose gel-layers and the fouling gel-layer became looser when the feed water contained colloidal silica.

Although the analysis on the $C_M/C_G$ ratio is a qualitative approach, the measurement of pore size and pore volume using nitrogen adsorption method was used to strengthen the application of the $C_M/C_G$ ratio. The obtained results on pore size and pore volume of the fouling gel-layer

were consistent with the $C_M/C_G$ ratio. Thus, it was concluded that the $C_M/C_G$ ratio can be applied to estimate the fouling gel-layer structure.

For a foulant extraction on the used membrane surface by ultrasonication with chemicals in series, two foulants including calcium ($Ca^{2+}$) and silica ($SiO_2$) were significantly observed. Therefore, possibility and effectiveness of fouling control including pre-filtration using microfiltration (MF) membrane with or without adding ethylenediaminetetraacetic acid (EDTA) were evaluated. It was found that EDTA addition to MF-filtered groundwater samples, i.e., twice as high as the molar concentration of divalent cations, did help to prevent $Ca^{2+}$ attached on the membrane surface efficiently but did not affect silica fouling. Addition of EDTA to groundwater samples did not significantly affect to permeate fluxes, which implied that $Ca^{2+}$ was not a determinant factor of the membrane fouling.

In summary, ULPRO membrane produced permeate water with a lower fluoride concentration than the standard for drinking water in Thailand at the feed water pH 7.0 or higher. The fouling gel-layer was formed on the membrane surface at filtration of groundwater samples. The $C_M/C_G$ ratio was found useful in evaluating the fouling gel-layer structure. The experimental results demonstrate that colloids present in the feed water were noxious since they intensified the flux decline and gel-layer formation which deteriorated the rejection of fluoride. Hence, it is suggested that pre-filtration using MF membranes or other fouling controls could potentially minimize the colloidal fouling and improve the fluoride removal efficiency of the ULPRO process.