:

(2/3)

NSC93-2211-E-002-013-

93　　08　　01　　　　94　　07　　31

94　　5　　31

奈米薄膜處理對自來水中消毒副產物有機前質之去除研究(2/3)
Nanofiltration Process for Removing the Organic Precursors of Disinfection By-Products in Portable Water (2/3)

主持人：蔣本基教授　 國立台灣大學環境工程學研究所
計畫研究人員：林怡利　 國立台灣大學環境工程學研究所

1. Introduction

It has been demonstrated that nature organic matter (NOM) in raw water can react with the chlorine to form disinfection byproducts (DBPs), which may be carcinogenic or mutagenic. Evidence shown that resorcinol structures in aquatic humic materials are the major THM precursor in colored waters (Reckhow et al., 1990). On the other hand, several studies suggested that aliphatic carboxylic acids, hydroxybenzoic acids, phenols and pyrrole derivatives are reactive substrates of organic precursors for THMs formation (Korshin et al., 1997).

Most organic matters responsible for major DBP precursors in source water of Taiwan are small to medium compounds, with a molecular weight near or less than 1 K Da (Chang et al., 2001; Chiang et. al., 2002). The goal of this research is to determine the efficiency of nanofiltration in removing model compounds of resorcinol, phloroglucinol and m-hydroxybenzoic acid (chosen as major small molecular DBP precursors) and tannic acid (chosen as major medium molecular DBP precursors). The experiments were carried out with various pH values, solute concentrations and the existence of calcium to evaluate how solute type affects the result of filtration tests, and the retention mechanisms of these target compounds are also studied.

2. Materials and Methods

Three model compounds with different functional groups of benzene i.e., carboxylic and phenolic groups, were introduced to represent small molecular NOM, which are phloroglucinol (1,3,5-trihroxybenzene), resorcinol (1,3-dihydroxybenzene) and 3-hydroxybenzoic acid. Meanwhile, tannic acid represents relatively hydrophilic compounds of medium molar mass compound and is chosen as the forth model compound in this study. All model compounds were purchased from R.D.H. The DOC concentrations for model compounds were prepared as 2.0, 5.0 and 8.0 mg/L. The pH level of solutions was adjusted in the range between 3 to 10 by 0.1 M hydrochloric acid and sodium hydroxide.

The commercial NF70 membrane produced by Dow-FilmTec was used in this study. Table 1 summarizes characteristics of NF70 in this study. Fig. 1 shows the schematic diagram of the filtration module used in this study. All experiments were carried out at constant temperature ($25 \pm 1°C$) and pressure (0.48 MPa) in a recycle mode, which means that both permeate and retentate were recycled back into the reservoir.

THM was analyzed after chlorination experiment. DOC, pH and THM were performed for the water samples, following the QA/QC programs set forth in Standard Methods (APHA, 1998).

3. Results and discussion

3.1 Effect of solute type on permeate flux at neutral (pH7) condition

Experiments were conducted with four organic compounds in aqueous solution at the same transmembrnae pressure (0.48MPa) and cross flow velocity (30 cm/s). The normalized permeate flux for different model compounds as a function of time are shown in Fig. 2(a). As shown by these data, the fluxes decline rapidly in the presence of model compounds, especially for those with larger MW. As could be expected, the quality of permeate flux is best for tannic acid (Fig. 2(b)). DOC in permeate increased for resorcinol and phloroglucinol as time progressed, and only 79 and 80% was rejected at the end of experiment, respectively. The trend of THMFP is as the same trend as DOC, i.e., about 98% of THMDP exerted by tannic acid could be removed, whereas only 82% for resorcinol and phloroglucinol after 24 hours (Fig. 2(c)). There is still high THM yield in permeate for three small model compounds, although the DOC concentration in permeate is less then 1.0 mg/L (Fig. 2(d)). This means that the NF70 membrane is effective in removal DOC for molecules with a wild range of molar mass; whereas much attention is needed for small compounds with high THM yield and other treatment processes may utilized together with nanofiltraiton.

Fig. 3 presents the influence of feed concentration on rejection of model compounds without the presence of calcium at pH 7.0. It is obviously that the removal efficiency of tannic acid is the highest (89-94%) owing to its large molecular size compared to the pore radius of NF70 membrane. For the other three small model compounds, 3-hydrobenzoic acid has a little higher compound rejection (about 83-86%) compared to phloroglucinol and resorcinol (having similar rejection about 80%). This is because of the hydrolysis of carboxyl group on 3-hydrobenzoic acid (pK_1=4.06) at pH 7 condition so that this compound carries negative charge and can be excluded by NF70 membrane (with

negative charge at neutral pH) owing to the electrostatic repulsive interaction with NF70 membrane (Xu and Lebrun, 1999). However, for phloroglucinol and resorcinol with pKa values higher than 7, these two compound are unhydrolyzed at pH 7 so that they are neutral and can only be rejected owing to the sieve effect of NF70 membrane. As a result, although these three small model compounds are very similar in MW (which is much less than the MWCO of NF70 membrane), the compound rejection of 3-hrdrobenzoic acid is the highest. Meanwhile, there is a similar trend for the tannic acid and 3-hrdrozenzoic acid that the compound rejection increase to the highest as the compound concentration reaching 5 mg/L, and the compound rejection decrease a little as the compound concentration still raising. For phloroglucinol and resorcinol, the compound rejection increase as the compound concentration increase. The mechanism needs further studied and this information might imply that we can pretest the feed water and find an optimum concentration range of compound rejection.

3.2 Effect of pH on compound rejection and permeate flux

Rejection of all four model compounds increase with the increase in pH (shown in Fig. 4). This is due to the polyelectrolyte character of chosen model compounds and NF70 negatively charged membrane characteristics. For tannic acid with medium MW, at pH values lower than its ionization constant, the molecule is neutral and may form a compact coiled conformation because of the suppression of dissociation of ionogenic groups as the same as humic acid and fulvic acid studied by Kabsch-Korbutowicz, et al. (1999). This leads a restriction of electrostatic intra-chain repulsion, and thus, a reduction in the tannic acid molecular size under acidic conditions so that the there is only one rejection mechanism based on "sieve effect". However, at pH values higher than the ionization constant of tannic acid, the

molecule unfolds because of the ionization of ionogenic groups leading to electrostatic repulsion between macromolecule segments. The tannic acid molecule now is negatively charged with larger molecular size so that it can be rejected more effectively not only by "sieve effect" but also the "charge effect" on NF70 membrane. As a result, the removal efficiency increased to 98.5%. For the other three small model compounds, at pH values lower than the ionization constant of each compound, the only mechanism of compound rejection is based on "sieve effect". For 3-hydrobenzoic acid, it has a little higher compound rejection compared to phloroglucinol and resorcinol; at pH values larger than its pK_1 and pK_2, we can see the increase in compound rejection because of the hydrolysis of carboxyl and phenolic groups leading to the electrostatic repulsive interaction with NF70 membrane (Xu and Lebrun, 1999). The trend of compound rejection vs. pH is very similar for resorcinol. Meanwhile, for phloroglucinol rejection at pH > 9.2, two phenolic functional groups are dissociated. In this situation, the charge density and molecular size are similar to that of 3-hydrobenzoic acid so that the rejection efficiency is very close to each other (about 92%).

Fig. 5 shows that the transmemrnbane flux increase with pH rise during nanofiltration of the solutions containing model compounds. The decrease of membrane fouling with the increase of pH should be related to many factors. As mentioned above, at low pH value model compounds are neutral and coiled compacted so that boundary layers at the membrane surface with higher hydraulic resistance are formed and reduce the permeate flux (Alpatova, et al., 2004). Under this kind of situation, they become less soluble and have a tendency to adsorb on hydrophobic materials. NF70 membrane is a strong hydrophobicity membrane made of polyamide materials, which may cause greater decrease of permeability

(Kabsch-Korbutowicz, et al., 1999). This influence is stronger for tannic with medium MW than for the other three small MW model compounds. When pH value is higher than 7.0, the dissociation of carboxyl and phenolic functional groups increase so that the negative charge density on model compounds rise; meanwhile, the negative charge density on NF70 membrane also increases. Malluhotla, et al. (1999) indicated that phenomena of membrane swelling and charge effects were evident as a function of varying the pH during membrane filtration. Dissociation of the functional groups on membrane and model compounds intensifies the electrostatic interaction between NF70 and mode compounds so that membrane fouling is reduced.

4. References

1. Alpatova, A.; Verbych, S.; Bryk, M.; Nigmatullin, R. and Hilal, N., Ultrafiltration of water containing natural organic matter: heavy metal removing in the hybrid complexation-ultrafiltration process, *Sep. Purif. Technol.*, **40**(2), 155-162, 2004.
2. APHA, Standard methods for the examination of water and wastewater, 20th ed., American Public Health Association, Washington, DC., 1998
3. Chang, E.E.; Chaing, P.C.; Ko, Y. W. and Lan, W.S., Characteristics of organic precursors and their relationship with disinfection by-products, *Chemosphere*, **41**(5), 1231-1236, 2001.
4. Chiang, P.C.; Chang, E.E.; Liang, C.H., NOM characteristics and treatabilities of ozonation processes, *Chemosphere*, **46**(4), 929-936, 2002.
5. Kabsch-Korbutowicz, M; Majewska-Nowak, K. and Winnicki, T., Analysis of membrane fouling in the treatment of water solutions containing humic acids and mineral salts, *Desalination*, **126**(1-3), 179-185, 1999.
6. Korshin, G.V.; Li, C.W.; Benjamin, M.M., Monitoring the Properties of

Natural Organic Matter Through UV Spectroscopy: A Consistent Theory, Wat. Res., 31(7), 1787, 1997.

7. Malluhotla, H.; Schmidt, M.; Lee, K.H. and Belfort, G., Flux enhancement during Dean vortex tubular membrane nanofiltration: 13 effects of concentration and solute type, *J. Membr. Sci.*, **153**(2), 259-269, 1999.

8. Reckhow D.A.; Ssinger, P.C. and Malcolm, R.L., Chlorination of humic materials: byproduct formation and chemical interpretation, *Environ. Sci. Technol.*, **24**(11), 1655-1664, 1990.

9. Xu, Y. and Lebrun, R.E., Investigation of the solute separation by charged nanofiltration membrane: effect of pH, ionic strength and solute type, *J. Membr. Sci.*, **158**(1-2), 93-104, 1999.

Table 1   Characteristics of the NF70 membrane

| Parameter	Characterisitcs
Manufacture	Dow-FilmTec
MWCO (Da)[a]	250
Materials	0.2 μm crosslinked aromatic polyamide + 0.46 μm polysulfone
Charge (neutral pH)	Negative
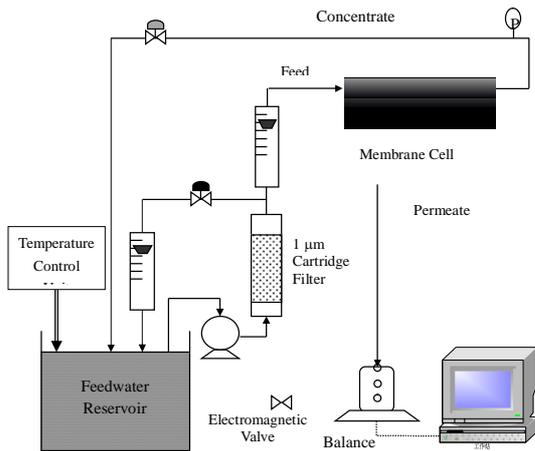
Fig. 1   Schematic diagram of cross-flow nanofiltration experiment setup
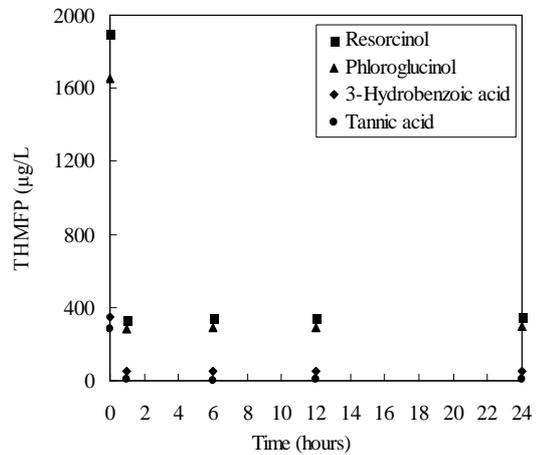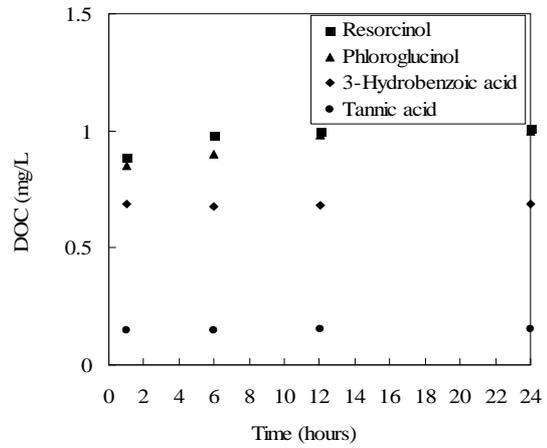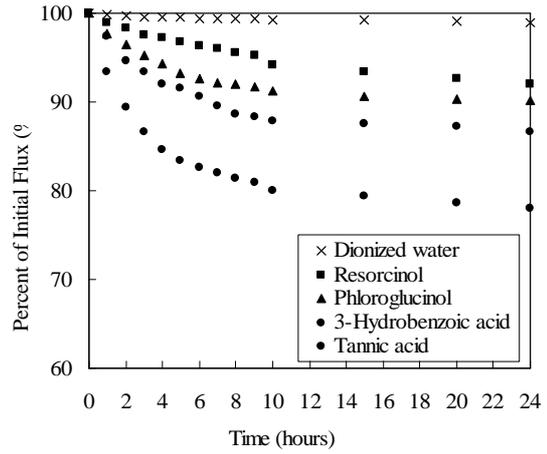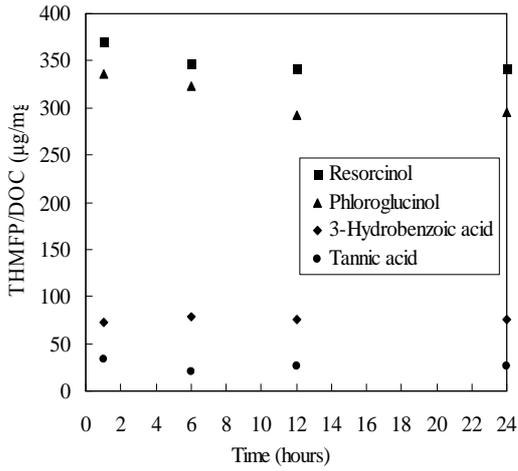
Fig. 2　Permeate quality and flux of model compounds (pH=7, concentration=5.0 mg/L): (a) flux, (b) DOC, (c) THMFP and (d) THM yield.
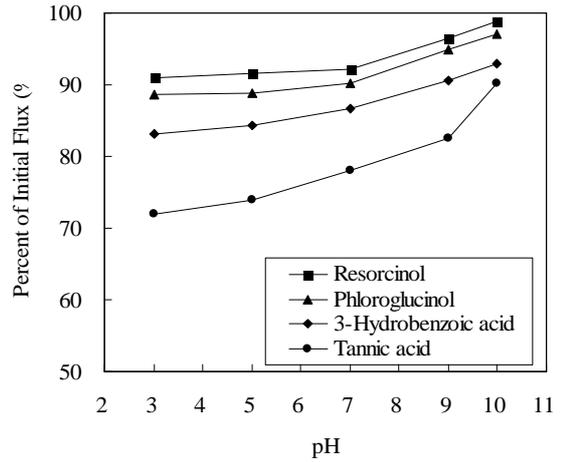

Fig. 5　Influence of the solution pH on the permeate flux for filtration of solutions containing model compounds.　Initial concentration: 5 mg/L.
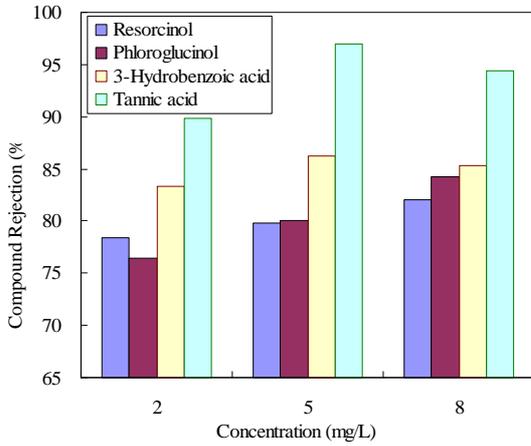

Fig. 3　Influence of feed concentration on rejection of model compounds.　Initial pH: 7.
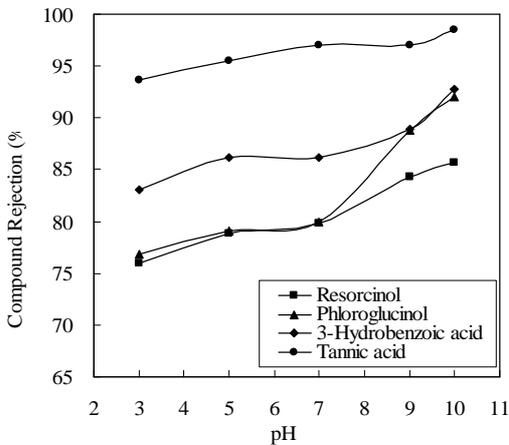
Fig　4　Influence of the solution pH on rejection of model compounds.　Initial concentration: 5 mg/L.