

Development of an integrated iron oxide adsorption/membrane separation system for water treatment

K.-W. Lee*, K.-H. Choo**, S.-J. Choi* and K. Yamamoto***

* Environmental Engineering, Kyungpook National University, Daegu 701-702, Korea

** Environmental Engineering, Daegu University, 15 Naeri, Jillyang, Gyeongsan, Gyeongbuk 712-714, Korea

*** Environmental Science Center, University of Tokyo, Tokyo 113-0033, Japan

Abstract The performance of an integrated iron oxide particle (IOPs) adsorption and ultrafiltration (UF) process was investigated in terms of natural organic matter removal and membrane permeability during treatment of a drinking water source. Throughout the fractionation of raw water and subsequent UF of fractionated portions, the significance of each component in raw water affecting flux decline during IOP-UF was evaluated. Natural organic matter (NOM) removal efficiencies for the IOP-UF system increased markedly as a substantial amount of IOPs was added into suspension, without any negative effect on permeate flux. During IOP-UF testings, there was no difference in NOM removal regardless of the locations of IOPs whether they were either in suspension or deposited on the UF membrane, but significant initial flux reduction occurred with the formation of a precoat (attached) layer. However, all IOPs in suspension and in the cake were effective in both removing NOM and preventing irreversible fouling as long as they were removed by backwashing. Dissolved matter obtained from filtration through a 0.45 μm filter was more responsible for flux decline in UF than larger colloids. Particularly, IOP-adsorbable dissolved matter accounted for 60% of total flux decline, confirming the attractiveness of IOP addition to UF.

Keywords Drinking water treatment; iron oxide adsorption; membrane; natural organic matter

Introduction

Membrane processes such as reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF) are increasingly used in drinking water treatment to produce a better quality of potable water as well as to meet more stringent water treatment regulations (Odendaal *et al.*, 1996). However, the extensive use of membranes is still limited, mainly due to energy consumption and membrane fouling. Several studies of the treatment of surface, lake, and river waters have identified natural organic matter (NOM) as one of the major foulants during these membrane processes (Crozes *et al.*, 1997; Maartens *et al.*, 1999; Yuan and Zydney, 2000). Also, the reaction of NOM with halogen-containing disinfectants such as chlorine generates unwanted disinfection by-products (DBPs) (Li *et al.*, 1998). Although most of contaminants including NOM, and even some ionic species, can be eliminated by tighter membranes such as NF and RO, they are highly energy consuming. In contrast, UF and microfiltration (MF) can be operated at relatively low pressures but have some limitations in removing DBP precursors of NOM when they are used alone. In addition, membrane fouling was always a problem with any membrane, although its tendency varied with different membranes.

Thus, the combination of low pressure membrane processes such as UF or MF with powdered activated carbon (PAC) adsorption has been investigated, because PAC helps to remove dissolved organics in addition to the possibility of membrane fouling reduction (Adham *et al.*, 1991; Jacangelo *et al.*, 1997; Lee *et al.*, 2000). However, it is still relatively expensive and also the spent carbon sludge generated must be disposed of. Thus, another alternative adsorbent, such as heated iron oxide particles (HIOPs) that can be readily regenerated, is being developed for water treatment in conjunction with membranes,

demonstrating that an improvement in NOM removal and membrane fouling control could be achieved (Chang and Benjamin, 1996; Chang *et al.*, 1998). However, the use of HIOPs instead of fresh IOPs is not yet fully convincing, and its optimal dosage to remove NOM, the significance of IOP deposition at the membrane, and its interaction with NOM have not been clearly evaluated. In this work, therefore, the effects of IOP doses and its injection methods on NOM removal and UF flux were examined using a stirred cell UF unit. The influence of IOP deposition onto the membrane surface was explored with the formation of pre-coated IOP layers at the membrane before UF. Also, the dislodging of the IOP cake and fouling layers was done by backwashing and its efficiency between UF and IOP-UF systems was compared. Particularly, the fractionation of source water composition and subsequent UF of fractionated samples were investigated to find out the major fouling component during UF.

Materials and methods

Water sample and fractionation

Water samples used for this study were collected from the Nakdong River (a water supply source for the City of Daegu, Korea). Some characteristics of the samples are given in Table 1 and the values are close to the yearly average. The samples collected were stored at 4°C and equilibrated with air for about 2–3 hr to bring the samples to ambient temperature before being used in experimental runs. Fractionation of raw water was performed using 1.2 µm and 0.45 µm MF membranes and IOPs to separate dissolved, colloidal, adsorbable, and non-adsorbable matter. Raw water and permeate samples were analyzed for DOC with a TOC analyzer (Shimadzu 5000A, Japan) and for UV absorbance at 254 nm (UV₂₅₄) with a spectrophotometer (Hewlett Packard 8452A, USA), after filtration using a 0.45 µm filter (Millipore, USA) except for permeate samples.

Iron oxide particles and injection methods

An IOP slurry was generated by neutralizing a ferric chloride solution using 5 N NaOH. The precipitated IOPs were rinsed over ten times with pure water to remove excess sodium chloride. An appropriate amount of the IOP slurry was added to feed water in suspension or directly coated on the membrane surface for IOP-UF testings.

Membranes and stirred cell UF

The UF membrane used in the study was made of polyethersulfone and had a molecular weight cut-off of 100,000 and a sheet diameter of 63.5 mm. Initial and final permeabilities of the UF membrane used were checked by measuring pure water flux before and after each run. Batch experiments were performed using a 180 mL stirred cell plus an 800 mL reservoir (Amicon 8200, USA). The working volume of the batch unit was 980 mL, while the pressure applied was kept at 0.49 bar using a nitrogen gas cylinder. The stirring speed was adjusted to 160 rpm using a magnetic stirrer. During UF, the mass of permeate was continuously monitored and recorded using a balance and a personal computer to measure the flux. For backwashing experiments, when one batch of UF with feed water was completed under a predetermined condition, the stirred cell was emptied. The used membrane was placed

Table 1 Quality of raw water from the Nakdong River

Parameter	pH	Alkalinity, mg/L as CaCO ₃	Hardness, mg/L as CaCO ₃	Turbidity (NTU)	DOC (mg/L)	UV absorbance at 254 nm (cm ⁻¹)
Value	7.6–7.9	46–48	95–97	7.1–13.0	2.8–3.7	0.045–0.067

upside down in the cell and 180 mL of pure water was filtered through at 0.98 bar, and then next batch operation was begun again under the same condition. The operation was repeated to check the change of backwashing efficiency.

Results and discussion

Effect of IOP dosages and pH

Jar tests were first carried out to estimate the NOM removal efficiencies by IOP at different IOP dosages and pH. UV_{254} removal efficiencies increased markedly as IOP dosages increased from 0 to 500 mg/L as Fe and feed water pH was lowered from 8.5 to 5.5 (data not shown). Higher NOM removal efficiencies at increased IOP dosages were due to higher adsorbing surface areas, while those at lower pH levels would be caused by the more positively charged surfaces of IOPs. Since the NOM adsorption onto IOPs could be explained by the ligand exchange between carboxyl functional groups of NOM and hydroxyl functional groups of IOP surface (Gu *et al.*, 1994), a further increase in NOM removal at lower pH was expected, but decreasing the pH is limited because of the drinking water criteria and the stability of IOP. Thus, the increase of IOP dose was thought to be a better way to improve the NOM removal in practical operations as long as the IOPs added could not affect other system performances, such as membrane flux.

To investigate the performance in the combined system of IOP and UF, batch UF runs were carried out at different IOP dosages (Figure 1). In the control system (no IOP added), UF alone removed less than 10% of the NOM, which could be typically achieved by UF treatment of non-colored surface water containing low DOC concentrations. Although NOM removal for the control run was negligible, significant NOM removal was observed with addition of IOP, up to about 78% in the system receiving an IOP dose of 500 mg/L as Fe. However, further removal with larger IOP dosages was not expected because NOM removal already started leveling off at 100 mg/L as Fe. This result implied that about 20% of NOM in the Nakdong River water could be considered non-adsorbable onto IOPs. Based on the removal profiles, an appropriate IOP dose was found to be approximately 100 mg/L as Fe, which was applied for the rest of this study. The DOC removal efficiency (approximately 60%) at an IOP dose of 100 mg/L in the IOP-UF system was much higher than that required by the Enhanced Coagulation rule (US EPA, 1998).

Variations in permeate flux at different IOP dosages during batch UF are shown and compared in Figure 2. Permeate fluxes in the control run (UF only) decreased quite rapidly down to 30% of the initial permeate flux during stirred cell UF. However, permeate fluxes were improved substantially with an IOP dosage of as low as 10 mg/L as Fe and further flux improvements were observed with higher IOP dosages, though the degree of flux enhancement slowed down afterwards. Considering approximately 35% NOM removal at an IOP

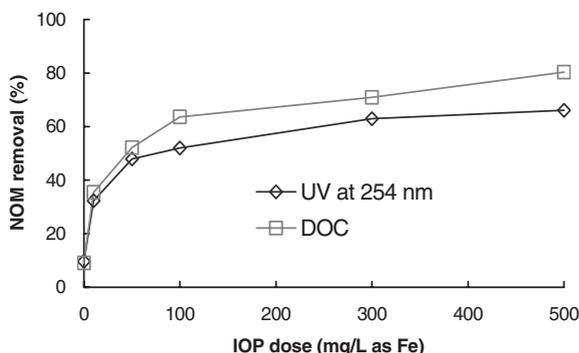


Figure 1 NOM removal efficiencies for the IOP-UF system using different IOP doses at feed pH 7.7

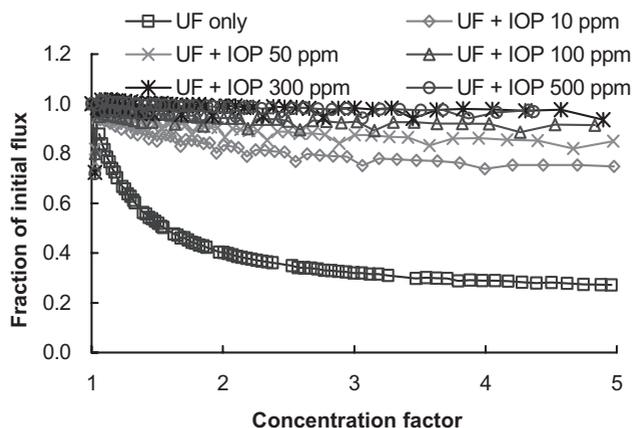


Figure 2 Effect of IOP dosages on flux during stirred cell UF (initial volume = 980 mL; feed pH = 7.7)

dosage of 10 mg/L, the flux increase at the same dosage was more than anticipated, suggesting that a portion of the NOM adsorbed onto IOPs might be more responsible for membrane fouling by adsorption. Another interesting point to note was that with an IOP dosage of 500 mg/L as Fe, there was still no adverse effect of IOP addition with respect to permeate flux, i.e. such a large amount of adsorbent particles did not show any sign of perceptible membrane fouling, but rather played a role in a continuous flux increase. Consequently, the addition of a relatively large amount of IOP to UF was effective for both removing NOM molecules from raw water and preventing the fouling of an UF membrane by them.

Effect of the deposition of IOPs

IOPs added to the UF system can exist either in suspension or at the membrane surface by their deposition during UF. Under a stirring condition that can represent crossflow operations, the IOPs attached account for a very small portion of total IOP added (about 1% in this work), while under a non-stirring condition related to dead-end operations most of IOPs accumulated at the membrane surface in the progress of UF. The effect on membrane flux and NOM removal of IOPs in suspension or at the membrane surface was thus examined (Figures 3 and 4). To simulate an attached IOP layer on the UF membrane, a slurry of IOPs was filtered (precoated) through the UF membrane under a non-stirring condition in advance. As shown in Figure 3, UF fluxes for an attached IOP system greatly decreased compared to the system with IOP in suspension, showing nearly the same flux level as that

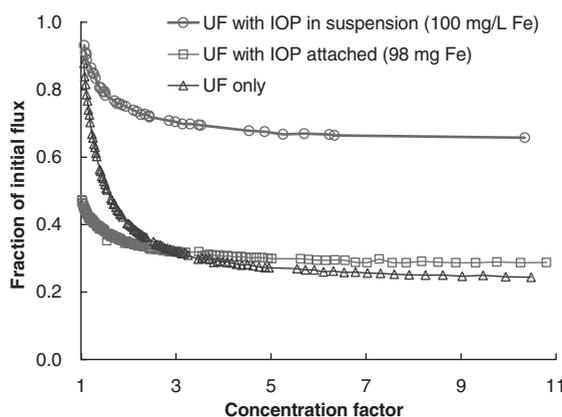


Figure 3 Effect of IOP injection methods on flux during UF (initial volume = 980 mL; feed pH = 7.8). UF with IOP attached was done without stirring after forming a precoat IOP layer on the membrane

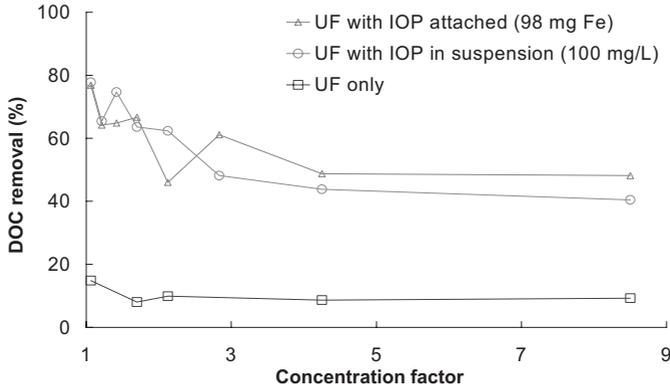


Figure 4 Effect of IOP injection methods on DOC removal during UF (initial volume = 980 mL; feed pH = 7.8). UF with IOP attached was done without stirring after forming a precoat IOP layer

of UF only. Two possible causes of that flux decline were an increase of the cake layer resistance and a reduction of the adsorption capability in the attached IOP system. In Figure 4, NOM removal efficiencies for the two IOP systems showed almost the same trends at a lot higher level compared to that of UF only. This revealed that IOPs in the attached layer on top of the UF membrane can also sorb NOM as much as those in suspension, possibly because of the rapid reaction of IOPs with NOM molecules. As a result, sharp flux reduction could be mainly attributed to the build-up of an IOP cake layer, which is different from that of UF only caused by NOM fouling. It was thus believed that dead-end UF operations with IOPs would bring about flux decline as much as UF alone (no IOP added), although it could be effective in removing NOM, but this flux reduction might be reversed while dislodging the cake layer from the membrane by backwashing.

Effect of backwashing on flux recovery

In stirred cell UF, backwashing was performed after each batch run to compare the extent of flux recovery between UF only and IOP-UF systems (Figure 5). In the control system, only less than half the initial permeate flux was recovered by backwashing after the first run, and from the second run UF fluxes were in the same trend or became a little bit worse. This implies that in the control run significant irreversible fouling might be caused at the first run by the monolayer adsorptive reaction of NOM with the UF membranes, and multiple fouling layers that can offer additional resistance above the monolayer could be controlled by backwashing. A wide spread irreversible fouling layer on the membrane surface was observed on a SEM image of the membrane in the control run (data not shown). With the

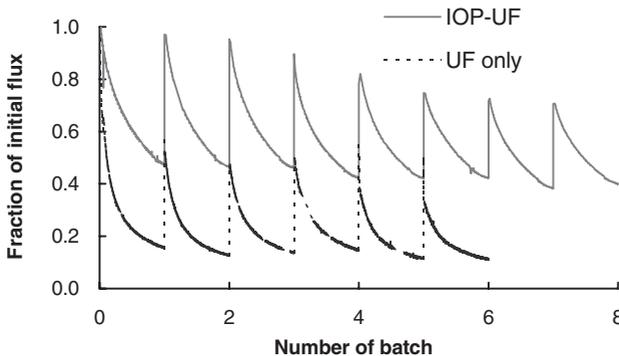


Figure 5 Flux recovery by backwashing during UF with and without IOP addition (initial volume for each batch = 980 mL; feed pH = 7.8; IOP dosage for IOP-UF = 100 mg/L as Fe)

addition of IOPs to UF, backwashing brought the permeate flux nearly back to the initial level, though a minimal decrease in flux recovery occurred in later stages of operation. SEM pictures showed that in the IOP-UF system a cluster of IOP deposit cakes appeared partly on the membrane surface, but it looked like most of the used membrane surfaces remained clean after eight batches of filtration (data not shown). As a result, it was likely that in IOP-UF foulants were adsorbed mainly on the surface of IOPs, rather than they directly deposited on the membrane surface. That was why backwashing in the IOP-UF system could help restore the membrane permeability more efficiently than that in the control run. Thus, although IOPs did not seem to completely eliminate the need for additional chemical cleaning during long-term operations, the frequency of such cleaning steps would be reduced a lot and so make that system more feasible in practical applications.

Effect of raw water composition

In the previous sections of this study, we focused mainly on NOM removal and flux reduction with and without IOP addition to UF. Thus, in order to further investigate the effect of the components of raw water on flux and NOM removal, fractionation of raw water was done on the basis of particle size and adsorption ability using several MF membranes and IOPs. The effects of the fractionation on NOM removal and UF flux are shown in Figures 6 and 7. No change in UV removal was observed with prefiltration using MF membranes, confirming that NOM was only controlled by IOP adsorption. However, prefiltration did affect the UF fluxes, probably due to the removal of colloidal matter, and so those results are summarized in Figure 7. The dissolved portion that includes all DOC adsorbable (61% flux reduction) and non-adsorbable (10% flux reduction) onto IOP contributed to approximately 71% of the overall flux decline, so it was found that dissolved matter, particularly IOP-adsorbable portion was most responsible for flux decline. Next, colloidal particles with a size $> 1.2 \mu\text{m}$ occupied about 25% of overall flux decline, while the particles between $0.45 \mu\text{m}$ and $1.2 \mu\text{m}$ in size gave only 4% of flux reduction whose effect was lower than that of non-adsorbable portions (10%). Consequently, it was obvious that dissolved matter remaining in $0.45 \mu\text{m}$ filtrate was the primary factor affecting flux decline in UF only, but it could be effectively controlled with the integration of IOP adsorption into UF. Also, in IOP-UF, non-adsorbable NOM and colloidal matter should be considered regarding flux reduction, although its severity might be small, because they would not be removed by IOP adsorption.

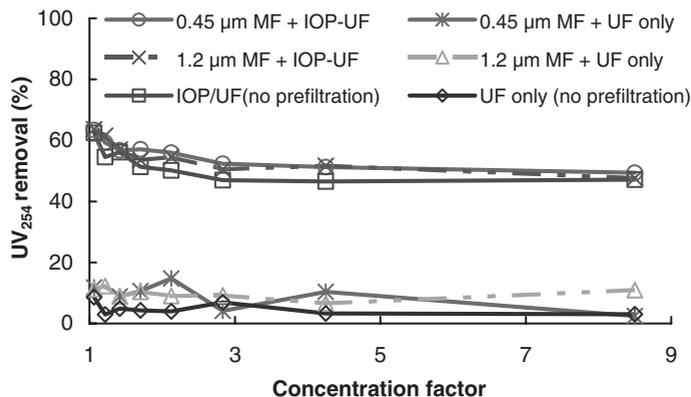


Figure 6 Effect of prefiltration using $1.2 \mu\text{m}$ and $0.45 \mu\text{m}$ filters on UV removal (initial volume = 980 mL; feed pH = 7.8; IOP dosage for IOP-UF = 100 mg/L Fe)

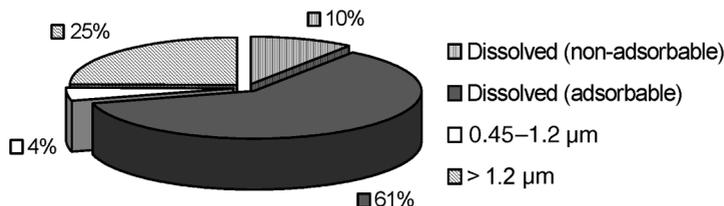


Figure 7 The extent of flux reduction caused by different fractions of raw water

Conclusions

In the conjunctive use of IOP adsorbents and UF membranes for treatment of the Nakdong River water, the effects of IOP dosages, dosing methods, backwashing, and fractionation of raw water components were investigated in terms of NOM removal and membrane permeability, and the following conclusions could be drawn.

- IOP addition to UF improved both NOM removal and membrane flux even at a high IOP dosage of up to 500 mg/L. This supported the fact that such a large amount of IOP was contributing to the adsorptive removal of NOM and subsequent fouling reduction, sufficiently compensating a possible adverse effect on flux that may arise from the formation of a thicker IOP cake layer at the membrane.
- Whether IOPs were in suspension or attached at the membrane surface, it did not affect NOM removal but did significantly affect UF flux. However, during dead-end UF the accumulation of IOPs at the membrane surface could be controlled by backwashing, and also NOM molecules would not foul the membrane itself while being sorbed onto the IOP cakes.
- Through the fractionation of raw water using MF membranes and IOPs, dissolved matter, particularly which is adsorbable onto IOPs, was most responsible for a decrease in UF flux. This implies that the addition of IOP to UF was effectively controlling the fouling of the membrane, but non-adsorbable and colloidal matter might be brought into play in IOP-UF.

Acknowledgements

Support for this research work was provided by the Korea Research Foundation (Grant 2000-042-E00086). The authors thank public servants of the Maegok Water Utility for their help in obtaining water samples.

References

- Adham, S.S., Snoeyink, V.L., Clark, M.M. and Bersillon, J.L. (1991). Predicting and verifying organics removal by PAC in an UF system. *J. AWWA*, **83**, 81–91.
- Chang, Y.J. and Benjamin, M.M. (1996). Iron oxide adsorption and UF to remove NOM and control fouling. *J. AWWA*, **88**(12), 74–88.
- Chang, Y.J., Choo, K.H., Benjamin, M.M. and Reiber, S. (1998). Combined adsorption-UF process increases TOC removal. *J. AWWA*, **90**, 90–102.
- Crozes, G.F., Jacangelo, J.G., Anselme, C. and Laine, J.M. (1997). Impact of ultrafiltration operating conditions on membrane irreversible fouling. *J. Membr. Sci.*, **124**, 63–76.
- Gu, B., Schmitt, J., Che, Z., Liang, L. and McCarthy, J.F. (1994). Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. *Environ. Sci. Technol.*, **28**, 38–46.
- Jacangelo, J.G., Adham, S.S., Cummings, E.W. and Laine, J.M. (1997). UF with pretreatment for removing DBP precursors. *J. AWWA*, **87**(3), 100.
- Lee, S.J., Choo, K.H. and Lee, C.H. (2000). Conjunctive use of ultrafiltration with powdered activated carbon adsorption for removal of synthetic and natural organic matter, *J. Ind. Eng. Chem.*, **6**(6), 356–363.
- Li, C.W., Korshin, G.V. and Benjamin, M.M. (1998). Monitoring DBP formation with differential UV spectroscopy. *J. AWWA*, **90**(8), 88–100.

- Maartens, A., Swart, P. and Jacorbs, E.P. (1999). Removal of natural organic matter by ultrafiltration: characterisation, fouling and cleaning. *Wat. Sci. Tech.*, **40**(9), 113–120.
- Odendaal, P.E., Wiesner, M.R. and Mallevalle, J. (1996). *Water Treatment Membrane Process*. McGraw-Hill, New York, USA.
- US EPA (1998). Stage 1: disinfectants and disinfection byproducts rule. *EPA 815-F-98-010*, United States Environmental Protection Agency, North Carolina, USA.
- Yuan, W. and Zydney, A.L. (2000). Humic acid fouling during ultrafiltration. *Environ. Sci. Technol.*, **34**, 5043–5050.