Coagulation pre-treatment to reduce membrane fouling in the microfiltration process of Nakdong River water
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ABSTRACT
The effects of coagulation pre-treatment on microfiltration process were investigated with the Nakdong River source water. In this study, the potential membrane-fouling materials presented in the raw water were mainly attributed to particulate matters and UV254-absorbing materials. Coagulation pre-treatment mitigated the effects of these components on membrane fouling because it induced a change in the characteristics of the cake layer and a decrease in the content of UV254-absorbing materials. Even though the coagulated suspensions were not removed before MF membrane filtration, their impact on resistance to filtration was insignificant when compared with that caused by the suspensions without pre-coagulation. However, insufficient dosages of coagulant or the improper controls of coagulation pH might cause severe membrane fouling in the treatment of low turbidity water (i.e. turbidity below 10 NTU). It appeared that a selection of coagulant dosage that focused on the reduction of specific cake resistance was possibly the best way to achieve the optimal condition in this study. Also, the coagulation pre-treatment process at pH values between 5.3 and 6.8 was found to be most effective in providing the lowest specific cake resistance as well as residual UV254 absorbance.

Key words | coagulation pre-treatment, fouling reduction, microfiltration, PVDF membrane, surface water

INTRODUCTION
The incorporation of coagulation pre-treatment with the low-pressure membrane process can provide not only a higher quality water product but can also improve filtration efficiency. These benefits could be achieved through the removal of natural organic matter (NOM) as well as by the change of particle size distribution and cake layer characteristics (Farahbaksh et al. 2004; Hilal et al. 2005). However, the feasibility of coagulation pre-treatment prior to microfiltration and ultrafiltration (MF/UF) depends on the interaction of many factors. Laïmé et al. (2005) and Farahbaksh et al. (2004) reviewed the results of previous laboratory and pilot studies, and suggested that the water characteristics, pre-coagulation conditions, membrane materials, and system configuration significantly affected the membrane filtration performance.

Over the past twenty years, many studies have demonstrated that membrane fouling could mostly be reduced by coagulation pre-treatment (Wiesner et al. 1989; Carroll et al. 2000; Judd & Hillis 2001). In particular, the results reported by Carroll et al. (2000) did not reveal any significant difference in the flux decline even though pre-coagulated waters were fed into the membrane units with or without settling. On the other hand, a number of studies have shown that in some cases coagulation pre-treatment has resulted in exacerbating already severe membrane fouling (Howard & Clark 2006; Howe et al. 2006; Malgorzata 2006).
In addition, Howe & Clark (2006) compared the impacts of coagulation pre-treatment on MF and UF membrane fouling, and pointed out that, while coagulation conditions might lead to insignificant effects on UF membrane filtration performance, MF membrane fouling could become more serious under certain conditions such as pre-treatment with low coagulant dosage and settling elimination. In this context, other authors have also suggested that although coagulation pre-treatment prior to MF filtration offers some advantages compared to membrane filtration alone, the different conditions could result in divergent impacts (Lee et al. 2000; Judd & Hillis 2001). Based on the reports so far, it is evident that the impact of coagulation pre-treatment on membrane filtration performance, especially in the case of MF, is not straightforward.

In this study, a series of unstirred dead-end MF filtrations were performed to evaluate the membrane filtration performances under various coagulation conditions with different water characteristics. The major objectives were: (1) to investigate the feasibility of direct MF filtration with coagulated water; (2) to evaluate the benefit of coagulation pre-treatment on filtration performance; and (3) to determine the optimum conditions of coagulation pre-treatment for the MF membrane filtration process.

MATERIALS AND METHODS

Raw water

Surface water used in this study was collected from the Gumi drinking water works. This water represents the Nakdong River water that is a major raw water resource for the southeast part of South Korea. The waters were collected during rainy and dry seasons from July 2006 to August 2007 so that we could obtain wide variations among our water samples in terms of water characteristics. The turbidities were between 3 NTU and 230 NTU. Dissolved organic carbon (DOC) was 1.45–4.93 mg/l and represented 0.04–0.26 cm$^{-1}$ in UV$_{254}$ absorbance. The pH values of the raw water ranged from 7.1 to 7.8.

Experimental setup

The experimental scheme of MF membrane filtration system with coagulation pre-treatment is shown in

![Figure 1](https://iwaponline.com/ws/article-pdf/9/4/357/417203/357.pdf)

Figure 1. Poly-aluminium chloride (PACl) was used as a coagulant in pre-coagulation. The concentrated liquid PACl containing 10% Al$_2$O$_3$ was diluted to a 1% PACl solution before being added to the raw water. The coagulation process was operated at a constant hydraulic mixing condition (rapid-mix at 180 rpm for 30 seconds).

A membrane filtration unit (Amicon, model 8200) was operated in a dead-end mode. The membranes used were flat sheet poly-vinylidene difluoride (PVDF) membranes with 0.1 μm pore size (VVPP, Durapore, and supported by Millipore). The constant pressure ($\Delta P = 13.8$ kPa) as a driving force was supplied with a compressed nitrogen gas tank. Filtrations were performed under an unstirred mode and at room temperature. The permeate water was collected in a beaker placed on an electronic balance (AND, model GF-600), and the accumulated filtrate mass was recorded until the specific permeate volume reached about 52 l/m$^2$.

Evaluation of membrane fouling and resistance to filtration

A comparison of the decreases in the filtration flux during the filtering of raw and coagulated waters, as described in Equation (1), was performed in order to observe the reduction of membrane fouling potential,

$$FPR(\%) = \frac{F_c - F_r}{F_r} \times 100$$

(1)
where FPR is the fouling potential reduction in percentage; $F_r$ and $F_c$ are the ratios of final flux ($J_e$) to initial flux ($J_o$) for the cases of raw water and coagulated water filtrations, respectively (Howe & Clark 2006). Higher FPR value implies better filtration efficiency, while negative or positive values would represent an improvement or deterioration.

In order to further interpret the impact of the coagulation pre-treatment in fouling control, the resistance to filtration and the characteristics of formed cake were examined. The cake resistance ($R_c$) was computed from the Darcy’s law and the cake filtration theory, while the specific cake resistance ($r_c$) was calculated in terms of the cake resistance over the mass of cake loading per unit membrane area,

\[ J = \frac{1}{A} \times \frac{dV_p}{dt} = \frac{\Delta P}{\mu R_t} \]  
(2)

\[ R_c = R_t - R_m = \frac{\Delta P}{\mu J_e} - \frac{\Delta P}{\mu J_o} \]  
(3)

\[ R_c = r_c \frac{C_{ss} V_p}{A_m} \]  
(4)

where $R_t$ is the total resistance, $R_m$ is the intrinsic membrane resistance, $R_c$ is the cake resistance, $\Delta P$ is the transmembrane pressure, $\mu$ is the permeate viscosity, $J_o$ is the initial flux, $J_e$ is the final flux, $r_c$ is the specific cake resistance, $V_p$ is the cumulative permeate volume, $A_m$ is the membrane area, $C_{ss}$ is the concentration of suspensions, and $t$ is the filtration time (Davis & Grant 1992).

According to Equations (2) and (3), the cake resistance ($R_c$) was determined with $t$ and $V_p$ values taken at the end of the filtration experiment. When $R_c$ was plotted against the cake mass deposited on the membrane surface ($C_{ss} V_p/A_m$), a good linear correlation was observed between these two. The slope of this linear regression represented the average specific cake resistance ($r_c$).

Analysis of water quality

Water quality parameters such as pH, turbidity, suspended solid (SS), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV$_{254}$), and specific UV$_{254}$ absorbance (SUVA) were also measured to identify their impacts on coagulation and membrane fouling. Turbidity was measured using a turbidimeter (HACH, model 2100N). First, the SS concentration was experimentally determined. Thereafter, since a linear relationship between the turbidity and SS was observed ($R^2 = 0.98$), the concentration of SS was then indirectly determined on the basis of the turbidity measurement. DOC was measured by a UV spectrophotometer (Shimadzu, model UV-VIS 1240) with a 1-cm quartz cell and a TOC analyzer (Shimadzu, model TOC-VCPH) after filtration with 0.45 μm filters (PVDF w/GMF, Whatman).

Observation of the membrane surface

A specimen of membrane that was cut off from the membrane sheet was dried (10 minutes) and coated with platinum (2 minutes) using an ion sputter (Hitachi, model E-1010). The membrane surface was then observed using a scanning electronic microscope (Hitachi, model S-3000H).

RESULTS AND DISCUSSION

Effect of the coagulation pre-treatment without pH adjustment on MF membrane filtration

Effect of the coagulant dosage

The impacts of different coagulant dosages on MF filtration performance were evaluated for several kinds of raw waters. For each experiment, the coagulation process was operated at the original pH (7.3 ± 0.5) without any adjustment. As shown in Figure 2, the reductions of fouling potential
(FPR) increased as the coagulant dosage increased up to the certain optimum values, and after that point the effectiveness of pre-coagulation on membrane fouling tended to decrease with further increases of coagulant dosages. On the other hand, most of the FPR data shown in Figure 2 showed positive values with the exception of the negative FPR value for low turbidity water (10 NTU) pre-coagulated at 5 mg/l PACl. Thus, the addition of different PACl dosages significantly impacted on the reduction of membrane fouling in the case of mid-to-high turbidity water (43–230 NTU). However, the effect of coagulant dosage became more important when coagulation pre-treatment was applied for the low turbidity water (10 NTU) since the fouling potential of coagulated water at an insufficient dosage might be greater than that of the raw water.

Figure 3 describes variations in cake resistance ($R_c$) and specific cake resistance ($r_c$) as a function of coagulant dosage. Both the $R_c$ and $r_c$ decreased with the increase of coagulant dosages up to an optimal reduction point, and increased thereafter. When the low turbidity water (10 NTU) was coagulated with 5 mg/l PACl, its $r_c$ value was noticeably even higher than that of low turbidity water without coagulation pre-treatment. Similar observations were reported previously by Judd & Hillis (2001), Howe & Clark (2006), Howe et al. (2006) and Malgorzata (2006). To explain this phenomenon, they proposed that it could be attributed to the incomplete aggregation of colloidal particles as well as the precipitation of humic materials. Accordingly, these flocs, which have a similar size to the membrane pore possibly caused the internal fouling of membrane or provided the denser filter cake. As a result, coagulation pre-treatment resulted in the increase in specific cake resistance.

The removal of NOM (in terms of DOC and UV$\text{}_{254}$) by coagulation pre-treatment with various coagulant dosages is depicted in Figure 4. The data suggested that with a higher dosage of coagulant a greater reduction of DOC/UV$\text{}_{254}$ was achieved. However, the increase of coagulant dosage proved to be more significant impact for improving the removal efficiency with mid-to-high turbidity water than with the low turbidity water. On the other hand, the removal rates of DOC and UV$\text{}_{254}$ showed similar trends.
Selection of the coagulant dosage for the best filtration performances

Many researchers have mainly focused on mitigating the negative effects of NOM on membrane fouling (Judd & Hillis 2001; Howe & Clark 2006), while others have paid more attention to controlling the effects of floc aggregation on membrane performance (Pikkarainen et al. 2004; Lee et al. 2006). However, in another previous study (Park et al. 2002), it was reported that both the floc characteristics and the removal rate of NOM provided by coagulation pre-treatment affected the filterability of the dead-end membrane filtration system. Thus, a smaller $r_c$ value incorporated with a higher DOC/UV$_{254}$ removal rate is expected to gain a better membrane filtration performance. However, the data shown in Figures 3 and 4 suggests that an optimum coagulant dosage for the $r_c$ reduction does not coincide with that for the removal of DOC/UV$_{254}$. For example, when mid turbidity raw water (43 NTU) was treated at the dosage of 60 mg/l PACl, the DOC/UV$_{254}$ was removed more effective than at 40 mg/l PACl which was the optimum dosage for the $r_c$ reduction. Therefore, the selection of an appropriate coagulant dosage depends not only upon the quality of the source water, but also upon the intended purposes during the coagulation stage, such as removal of NOM or reduction of cake resistances.

Figure 5 shows a comparison of the coagulant dosages required to achieve the optimal fouling potential reduction (FPR), the specific cake resistance reduction, and the DOC/UV$_{254}$ removals against the raw water turbidities. As can be seen, the dosages needed for the best $r_c$ reductions were well matched to those for the best FPR; meanwhile the dosages that produced the highest DOC removals were similar to the optimal dosages for UV$_{254}$ removals. Consequently, to control membrane fouling in the case of direct filtration of coagulated water, optimizing coagulant dosage based on the $r_c$ reduction data could be more appropriate than based on the DOC/UV$_{254}$ removals. On the other hand, it appears that the coagulant dosage for the best FPR has a good correlation with the turbidity concentration in the raw water ($R^2 = 0.90$). Thus the turbidity could be used as a representative parameter of raw water characteristics as a mean to estimate the dosage demand for fouling control.

Effectiveness of proper coagulation pre-treatment without pH adjustment

Changes in fouling characteristics

The particulate matters and NOM are considered as two major components that cause membrane fouling because they can accumulate on the membrane surface to form a cake or gel layer, and can also be adsorbed within the membrane pores (Laîné et al. 2005). In order to determine the relationship between the fouling grade and the feed water quality, the property of the cake formed after the filtration against the turbidity as well as NOM concentration (in terms of DOC, UV$_{254}$, and SUVA) was plotted as shown in Figure 6. The data presented in this figure was obtained by experiments carried out with nine raw water samples including the four samples mentioned above. Based on $R_c$ data, it was found that, while the MF membrane fouling with the raw water strongly correlated to the level of turbidity ($R^2 = 0.90$) and UV$_{254}$ absorbance ($R^2 = 0.89$), it was slightly dependent on variations of DOC ($R^2 = 0.56$) and SUVA ($R^2 = 0.50$). This implied that particulate matters and UV$_{254}$-absorbing materials have had a more significant contribution to fouling. As also shown in Figure 6, the $R_c$ of raw water increased linearly with the turbidity, while the $r_c$ behaved in the opposite direction. The reason for this is because, while the $R_c$ was dictated by the total mass of suspensions that will be deposited on the membrane surface, the $r_c$ was dictated by the size of
particulate matters and the porosity of the cake layer. Thus, without coagulation pre-treatment, the level of turbidity seemed to involve the total cake mass deposited on the membrane surface as well as the cake layer properties such as cake resistance and specific cake resistance. These results suggested that the effectiveness of pre-coagulation on the reduction of membrane fouling would be mediated by controlling the effects of particulate matters and UV\textsubscript{254}-absorbing materials.

Examining the differences between the raw and coagulated water filtrations (Figure 6), it can be seen that the correlation between \( R_c \) and turbidity shows a decrease from \( R^2 = 0.90 \) (raw water filtration) to \( R^2 = 0.04 \) (coagulated water filtration). This indicated that \( R_c \) had significantly reduced independently of the raw water turbidity. A possible explanation can be found in the previous works of several researchers, where it was speculated that the cake layer was modified to be more filterable with a low \( r_c \) value. Lee et al. (2003) suggested that more porous flocs could reduce the specific cake resistance of coagulated flocs. Similarly, Cho et al. (2005) investigated the relationship between the membrane filterability and the fractal dimension of flocs in a batch filtration system as well as in a dead-end or submerged MF hybrid system. They reported that the membrane permeability improved with coagulated flocs of lower fractal dimensions, which tend to have higher porosity and aggregate relatively loosely. In conclusion, by using coagulation pre-treatment, the negative effect of a high level of turbidity-causing particulate matter was insignificant compared to the positive effect of the decreasing \( r_c \). Concomitantly, the degree of membrane fouling (based on \( R_c \)) with coagulated water was not proportional to the residual UV\textsubscript{254} \( (R^2 = 0.11) \). This result implied that the removal of UV\textsubscript{254}-absorbing materials from the raw water by coagulation pre-treatment also contributed to the reduction of membrane fouling.

Enhancement of permeate quality

The removal efficiencies of turbidity and NOM during MF membrane filtration, both with and without coagulation pre-treatment, were investigated. All the coagulation pre-treatments were conducted at the optimum coagulant dosages and the results are presented in Figures 7 and 8.

As shown in Figure 7, even though the turbidity of raw water varied widely from around 3 to 230 NTU, the
turbidities of all filtrates without coagulation pre-treatment were lower than 0.3 NTU and the turbidity removal reached more than 95%. The difference between the effect of MF membrane process, with and without pre-coagulation, becomes more obvious with the high turbidity raw water (230 NTU). With the pre-treatment the turbidities of filtrate decreased to below 0.1 NTU.

Figure 8 shows the removal efficiencies of NOM, which were measured in terms of UV$_{254}$ and DOC removals. In this study, we observed that MF could remove 18.8 ± 6.8% of UV$_{254}$ absorbance and 13.5 ± 10.3% of DOC (± value is based on a 95% confidence interval), and this concurs with the previous reports stating that the MF process can only remove a small amount of NOM (Van der Bruggen & Vandencaesteel 2003). When coagulation was applied prior to the MF process, the overall removal efficiencies for UV$_{254}$ absorbance and DOC were 48.5 ± 13.4% and 35.9 ± 16.1%, respectively. These results are consistent with the previous results that indicated that employing coagulation before the MF process tends to enhance the removal of NOM (Vickers et al. 1995; Farahbakhsh et al. 2004; Pikkarainen et al. 2004).

**Impact of coagulation pH adjustment on MF membrane performance**

**Fouling potential reduction**

The impact of pH on the coagulation pre-treatment was also investigated, because it is another important factor that can directly influence the coagulation efficiency as well as the membrane filtration performance (Wiesner et al. 1989; Judd & Hillis 2001). Figure 9 shows the FPR data of various turbidity raw waters treated at the given dosages and different pH values. The given dosages were 20 mg/l PACI for the raw waters with a turbidity of 10 NTU and 43 NTU, and 40 and 60 mg/l PACI for the raw waters with a turbidity of 100 NTU and 230 NTU, respectively. From this study, the pH range of 5.3 to 6.8 was selected as the optimum pH for the coagulation since these values align with the highest FPRs. Once the coagulation pre-treatments were not within the optimum pH range, they resulted in lower reduction efficiencies. It is important to note that at pH 8.5, the pre-coagulation of low turbidity water (10 NTU) had a negative effect on the reduction of fouling potential. This is similar to the situation when the coagulant dosage is much lower than that for effective coagulation. Therefore, it can be suggested
that the coagulation pre-treatment at very high pH values is not effective in controlling membrane fouling.

When compared to the results obtained for the coagulation pre-treatment without pH adjustment, the pre-coagulation at the optimum pH exhibited less than 8% improvement of FPR for treating mid-to-high turbidity raw water while the same treatment could improve FPR up to 25% for low turbidity raw water. This suggests that pH adjustment is more effective for improving the treatment efficiency for low turbidity water treatment compared to mid-to-high turbidity water treatment.

Examination of cake properties and NOM removal

Figure 10 shows the properties of cake formed (presented as cake and specific cake resistance) and Figure 11 shows the NOM removal efficiency (expressed in terms of DOC and UV$_{254}$) when performing coagulation at different pH values. It can be seen that both the resistances and the NOM contents were lowest in the optimum pH range (pH 5.3 to 6.8). This result could be explained by the good interaction between coagulant and contaminants during the pre-coagulation stage. It is well known that PACl is present as Al$_{13}^{7+}$ species at a similar pH range to that shown above (Van Benschoten & Edzwald 1990; Pernitsky & Edzwald 2003). At a pH below 5.3 or above 6.8, PACl is present mainly as Al(OH)$_2^+$ or Al(OH)$_4^{-}$, respectively. Thus, at a pH between 5.3 and 6.8, it is likely that more colloids will be aggregated as more Al$_{13}^{7+}$ is available. Furthermore, it has been demonstrated by Wiesner et al. (1989) that the coagulation pre-treatment at pH values between 4 and 8 could produce a cake layer with low specific cake resistance due to the increasing size of colloids and macromolecules in the suspension to be filtered. They also found that the largest flocs were formed near pH 7 and pH 8 depending on the aluminium dosage of 10$_{-4.00}^{+3.60}$ and 10$_{-3.93}^{+3.93}$ M, respectively. In the present study, the coagulant dosages used (20–60 mg/l PACl) correspond to 10$_{-4.41}^{+4.00}$–10$_{-3.60}^{+3.93}$ M of aluminium, hence the optimum pH range observed is likely to be appropriate for providing the largest flocs. Another possible reason could be the removal of NOM. The removal rates of DOC and UV$_{254}$ were highest at the optimum pH range. This result is similar to the findings of a previous

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Figure 10 | Effects of coagulation pH on properties of cake formed by coagulated water.

Figure 11 | DOC and UV$_{254}$ residuals after coagulation pre-treatment at various pH values.
study (Qin et al. 2006), where it was observed that the optimum condition for NOM removal was at pH 5.2 and at an alum dosage of 5 mg/l aluminium when treating reservoir water. Also, UV$_{254}$-absorbing materials have been known to be more coiled in structure and less negatively charged at low pH values (Ghosh & Schnitzer 1980). Therefore, the effectiveness of coagulation pre-treatment with PACI seems to agree with the general consensus that colloidal organic matters have been controlled at a pH of around 6.0 due to the adsorption and enmeshment mechanisms (Qin et al. 2006; Yan et al. 2008).

**SEM micrographs**

In order to visually examine the different impacts of coagulation conditions on the cake formed during the membrane filtration, images of the virgin and fouled membranes were taken with a scanning electron microscopic (SEM). Raw water with a turbidity of about 100 NTU (turbidity level at mid range during the experiment duration) was used for this test. As can be seen from Figure 12A and B, the clear surface of the virgin membrane have been covered completely with foulants after being filtered with raw water indicating that all of the membrane pores were obscured. However, the SEM images reveal that the cake layer of coagulated water at pH $\approx 5.8$ (Figure 12D) seemed to be more porous compared to that of either raw water or coagulated water at pH $\approx 7.3$ (Figure 12B or C). The feature was observed on the image of membrane fouled with coagulated water at pH $\approx 5.8$, which was identified as the membrane pores were being viewed in some places. These images are consistent with the filtration results presented above. Consequently, it is believed that the reduction of membrane fouling by coagulation pre-treatment was

![Figure 12](image_url)

**Figure 12** | SEM images of (A) virgin PVDF membrane and membranes fouled with the Nakdong River water (100 NTU): (B) without coagulation pre-treatment; (C) pre-coagulated with 40 mg/l PACI; (D) pre-coagulated with 40 mg/l PACI, pH 5.8.
achieved through the modification in cake layer properties and the removal of UV$_{254}$-absorbing materials.

CONCLUSIONS

Based on the filtration performances under various coagulation conditions with different source water characteristics, the main conclusions for this study are as follows:

1. Coagulation pre-treatment using PACl coagulant was effective in preventing the fouling of MF membrane filtration of the Nakdong River water. It is mostly applicable for the treatment of water that has mid-to-high turbidity (about 40 to 230 NTU). When treating the low turbidity water (below 10 NTU), the efficiency of coagulation pre-treatment strongly depends on the coagulation conditions (i.e. coagulant dosage and pH).

2. The influences of two major foulants (particulate matters and UV$_{254}$-absorbing materials of raw waters) on the MF membrane fouling could be prevented by coagulation pre-treatment. The cake layer formed by coagulated flocs exhibited less resistance to filtration compared to the cake layer formed by uncoagulated suspensions. The reduction in content of NOM (in terms of UV$_{254}$ and DOC) by coagulation pre-treatment could also facilitate the improvement of MF filtration performance.

3. The reduction of specific cake resistance was found to be a better candidate as a parameter choice for the proper dosage of coagulant to control membrane fouling. This proper dosage could be estimated on the basis of the raw water turbidity. At the given coagulant dosage, the optimum coagulation pH was found to be between a pH of 5.5 to 6.8. Noticeably, in the case of low turbidity water, the low coagulant dosage or high coagulation pH would result in somewhat negative impacts on the membrane fouling.

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