Effects of characteristics of softening as a pretreatment for ultrafiltration

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Abstract Softening was proposed as a pretreatment for ultrafiltration, which reduces foulants prior to membrane processes. The objectives of this research were to understand the nature of the fouling mechanisms for ultrafiltration when used for waters that either require softening or have been softened, and to use that understanding to determine promising options for the use of softening as a pretreatment before ultrafiltration (UF). Several characteristics of softening, including extent of softening, precipitation kinetics, and hydrophobicity of membrane materials, were investigated as independent variables. Because of softening, both the organic matter concentration and the particle concentration of feed water to ultrafiltration were reduced, thus reducing the degree of fouling. The slow kinetics of softening had little effect on membrane fouling although precipitation directly occurred on the membrane surface in the system during the operation. Detailed images of the membrane surface obtained by scanning electron microscopy confirmed substantial amounts of the precipitates on the surface. In contrast, the hydrophobicity of the membrane material showed a significant effect on the flux decline behavior. Overall, the integrated water treatment of softening and ultrafiltration is shown to be a promising option for hard waters.

Keywords Organic matter; precipitation kinetics; pretreatment; scanning electron microscopy; softening; ultrafiltration

Introduction
Membrane processes are widely considered for application in drinking water treatment but fouling often impedes their use. Existing treatment processes can serve as a pretreatment for membrane processes to reduce foulants and thus prevent or slow the deterioration of membrane performance. Previous research has examined the use of conventional treatment processes, particularly coagulation, as a pretreatment (Lahoussine-Turcaud et al., 1990; Laine et al., 1990; Carroll et al., 2000). However, for this application, softening has received virtually no research attention to date. Softening is traditionally designed to remove hardness ions in hard waters but it can also remove particles and organic matter, which are major foulants of membranes. Therefore, an integrated water treatment with softening and ultrafiltration is proposed as a promising option for hard waters. The objectives of this research were to understand the nature of the fouling mechanisms for ultrafiltration when used for waters that either require softening or have been softened, and to use that understanding to determine promising options for the use of softening as a pretreatment before ultrafiltration (UF). To accomplish these objectives, several independent variables were investigated, including: (1) the extent of softening, (2) precipitation kinetics, and (3) membrane characteristics such as hydrophobicity.

Experiments
The experimental protocol for this work was designed to simulate softening followed by an ultrafiltration process to investigate effects of softening pretreatment on fouling in ultrafiltration. Both polysulfone (hydrophobic) and regenerated cellulose (hydrophilic)
ultrafilters (Millipore, Inc.) with a nominal pore size of 10 kDa were used to monitor fouling in terms of specific flux decline. For source waters, two natural waters, Lake Austin (Austin, TX) and Missouri River (St. Louis, MO), were selected. Both waters are hard (with similar calcium and magnesium concentrations) and have moderate TOC values, but a striking difference is the turbidity. With a turbidity over 300 NTU, the Missouri River (MR) water is useful to investigate effects of particle concentrations on fouling; in contrast, Lake Austin (LA) has 3.4 NTU. Detailed water qualities of the two sources have been presented elsewhere (Kweon and Lawler, 2001).

In addition, synthetic water (with the same hardness ions as LA water) was used to investigate the performance without NOM effects. At first, the natural waters were characterized in terms of inorganic (especially hardness ions and alkalinity) and organic constituents. Based on the results, the synthetic waters were made to simulate those natural waters. The waters were then softened to different extents to further investigate effects of the degree of softening on membrane fouling. Standard jar tests at bench scale were used to characterize softening performance of different source waters, while softening as a pre-treatment before ultrafiltration was conducted in a batch mode. In the batch mode, a large amount of water (14 L) was softened in a 20 L cylindrical plastic reservoir at the specified softening condition. The softening performance was evaluated based on several key water parameters and effects on fouling.

The ultrafiltration performance was monitored based on flux decline behavior. The flux decline is presented using normalized values for both the dependent and independent variable, i.e. % of clean water specific flux and normalized cumulative production. The normalization accounts for variations in pore area and transmembrane pressure (TMP) between experiments in the laboratory scale system of this research. The cumulative water production (i.e. the volume of water treated per unit area of membrane) was normalized by the ratio of pore area of a standard sheet (assuming 5% porosity and Poiseuille flow in the pore) to each UF sheet. Because the clean water specific flux is proportional to pore areas, the specific flux of the clean water was used as an indicator of its pore area in this research. This normalization leads to the normalized cumulative production (NCP). Ultrafiltration was performed with approximately 10 cm/s of crossflow velocity and 90 kPa of TMP. After ultrafiltration, some fouled membranes were further investigated with scanning electron microscopy (SEM) to obtain detailed information on the surfaces of the fouled membranes.

Results

The extent of softening

The extent of softening can alter the organic matter and particle concentration of feed water to ultrafiltration, and thus might influence the degree of fouling. During the previous study (Kweon and Lawler, 2001), the authors chose three levels of softening: “standard softening” (maximum Ca$^{2+}$ removal with no addition of soda ash), “enhanced softening” (maximum lime addition without massive precipitation of Mg(OH)$_2$), and “Mg softening” (lime dose to achieve approximately 95% Mg$^{2+}$ removal). Each condition represents a different degree of pretreatment to UF in terms of organic matter (i.e. NOM fouling) and inorganics (i.e. inorganic fouling by further precipitation). Table 1 shows the selected lime doses for Lake Austin and Missouri River waters and key water qualities at the specified lime doses. The three lime doses representing the three conditions were distinct for LA water but, for MR water, both the standard and the enhanced softening condition were 90 mg/L of CaO because Mg(OH)$_2$ started to precipitate around the same dose that calcium had the lowest concentration. The NOM (i.e. DOC) removal achieved at these three lime doses for LA water was 11%, 29%, and 37%.

The flux decline in UF experiments performed using LA water at three lime doses is
summarized in Table 2. The results showed that flux decline decreased as the extent of softening increased, indicating the removal of NOM in softening reduced fouling. The initial flux in each experiment fluctuated a little around 100% of the clean water specific flux. The variation could be caused by an operational problem like some air bubbles being trapped in the membrane apparatus during the clean water flux measurement or some differences in temperatures between distilled/deionized water and feed water, which was not caught in the measurements. In general, the fluxes continuously decreased regardless of the lime dose. The flux decline of the softened water at 125 mg/L lime dose was almost identical to that of raw Lake Austin water, despite differences in pH and Ca²⁺ concentration and some reduction in NOM. At the lime dose of 170 mg/L, the flux reduction was less than that of raw water during the whole operation. However, the improved clean water specific flux was quite small, i.e. less than 10%. At the highest dose (230 mg/L as CaO), the decline was quite gradual, so after 120 cm³/cm² of normalized cumulative production, the percent of the clean water specific flux was 88.0%, which was much better than the 61% for the raw Lake Austin water and 68% for the softened water at 170 mg/L CaO of lime.

The SEM images from the membrane fouled with the softened Lake Austin water at the lime dose of 230 mg/L are presented in Figure 1. In this experiment, soda ash (Na₂CO₃) with a dose of 105 mg/L as CaO was added to continue CaCO₃ precipitation since the precipitation would stop without carbonate ions. The images show some isolated inorganic particles and their aggregates as well as inorganic particles associated within a fibril network of organic matter. These deposits were detected over the whole area of the sampled membrane surface. Most of the inorganic particles visible within the organic matter were rhombus shapes, which are the typical morphology of calcite.
Precipitation kinetics

Lime softening has been shown to have slower kinetics than alum coagulation (Nancollas and Reddy, 1974; Alexander and McClanahan, 1975). Therefore, it is possible that the slow precipitation kinetics in lime softening could affect performance of ultrafiltration after softening. Even after lime softening removes calcium ions, the remaining calcium concentration is relatively high. Therefore, some amount of precipitation might continue to occur during settling and subsequent processes (including membrane processes), unless the precipitation is chemically stopped. The large surface area available in a membrane process can enhance the precipitation of calcium carbonate solids. Theoretically, precipitation could occur either on the surface or in the pores of the membrane. Precipitation in the pores would result in a rapid flux decline, and therefore needs to be avoided.

The precipitation kinetics was investigated by varying detention times of flocculation: 30 min for the standard condition, and 7.5 min and 1.5 min for the shorter detention times. In continuous flow experiments, the water flowed directly from a small rapid mix unit (where lime was added) through a flocculation reactor and then to the ultrafiltration (UF) unit without settling. Synthetic water with the same inorganic constituents as LA water was used to investigate the precipitation kinetics of CaCO₃ solids without any NOM interactions while the LA water was used to study effects of precipitation in the presence of NOM on fouling.

Figure 2 shows that the flux decline was not substantial with the synthetic water softened at 125 mg/L of lime using the shorter precipitation times. The scatter in the experiment with 7.5 min of precipitation stems from the combination of high solids content and low
crossflow velocity. Despite the scatter, the results are sufficiently clear to see that the flux decline was quite small, a surprising result given the high turbidity (449 NTU). The small flux decline in both experiments indicated that the pores were not blocked by precipitation within them. It had been hypothesized that precipitation could occur in the membrane system and, if it occurred inside the pores, would severely foul the membrane. However, it seems that precipitation either was completed prior to reaching the membrane or occurred entirely on the external surface, not inside the pores. The SEM (scanning electron microscopy) images from the experiment in Figure 3 show well the precipitates on the membrane surface and give no indication of pore blockage. The petal-shaped image in the left portion of the figure might be interpreted as precipitation that occurred on the membrane surface. These results confirm that NOM, not CaCO₃ solids, cause the fouling.

The precipitation kinetics test with the softened LA water using 1.5 min and 30 min precipitation times is shown in Figure 4. Note that the LA water experiment with 30 min of precipitation time was not a continuous but a batch mode operation. In a batch experiment, a large batch of approximately 14 L of LA water was softened with the standard softening jar test, i.e. 2 min of rapid mixing, 30 min of slow mixing, and 30 min of settling, and then it was introduced to the UF system. This large reservoir of water and the ability to recycle the batch meant the UF experiment could have a high crossflow velocity. The other (continuous flow) experiments were limited to a low crossflow velocity since recycling was impossible and the UF filtration rate had to match the feed flow from the earlier units. Despite this major difference, the comparison seems to be reasonable as this experiment was meant to simulate a long time for precipitation, and the extra time after the flocculation before processing in the membrane only increased this time.

![Figure 3](https://iwaponline.com/ws/article-pdf/3/5-6/429/419249/429.pdf)

Figure 3  SEM images of membranes fouled with softened inorganic water at 125 mg/L CaO (7.5 min of precipitation time, 200,000× of resolution)

![Figure 4](https://iwaponline.com/ws/article-pdf/3/5-6/429/419249/429.pdf)

Figure 4  Flux decline: effect of precipitation kinetics with the softened Lake Austin water at 125 mg/L lime dose
At the beginning of the experiment with 1.5 min of precipitation time, the percent of clean water specific flux was much less than the test with 30 min of precipitation time. However, the fluxes of two tests became almost the same at the end of the runs. The small flux decline in the 1.5-minute test is another indication that neither the relatively high solids content of the feed (264 NTU vs. the 23.3 NTU in the 30 minute test) nor precipitation in the pores was a real problem. Therefore, the slow precipitation kinetics in softening showed little significance in the membrane fouling in terms of inorganic (i.e. results from the water only with inorganic constituents) and organic fouling (i.e. results from the LA water).

Hydrophobicity
Two different membrane materials, one hydrophobic and the other hydrophilic, were used for this research. Hydrophobicity of the membrane affects fouling rate because NOM is more easily adsorbed on a hydrophobic membrane than a hydrophilic membrane (Laine et al., 1989). The choice was regenerated cellulose for the hydrophilic material and polysulfone for the hydrophobic material. The experiments with the different membrane materials were performed with LA water, and results for the flux decline are shown in Figure 5. The polysulfone material showed much more rapid flux decline than regenerated cellulose, as expected. The very little flux decline using the regenerated cellulose membrane made it difficult to examine any advantages of the softening process.

Conclusions
Softening pretreatment significantly reduces fouling in ultrafiltration. For Lake Austin water, increasing the extent of softening continually reduced the fouling, but the extent of the improvement of water flux was dramatic at the highest lime dose (i.e. 230 mg/L CaO). This significant flux improvement might imply that the Mg(OH)$_2$ precipitation has better removal of natural organic matter, which has a great role in fouling.

Inorganic fouling by CaCO$_3$ precipitates shows negligible effect on membrane fouling. The experiment to investigate the effects of the slower precipitation kinetics showed that precipitation could be initiated in the membrane system. The SEM images confirmed the substantial amount of precipitation, but very little flux decline occurred. The precipitation occurred on the surface, not inside the pores, and the precipitates were big enough not to cause a resistance to water flux in ultrafiltration.

The integrated treatment with softening and ultrafiltration proves to be a promising option for hard waters. The degree of softening required to improve water flux should be determined with the raw water to be applied.
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