In-line Coagulation/Ultrafiltration for Silica removal from brackish water as RO membrane pretreatment

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ABSTRACT
In this study, a brackish water containing silica concentration (30 mg/L as SiO$_2$) was studied for silica removal using in-line coagulation/ultrafiltration processes to prevent scaling problem for RO membrane. Other than pH and coagulant dosage, mixing intensity (velocity gradient, G) is also a critical factor on silica removal. Different velocity gradient (G), pH and alum dose were experimented and contour plots were used to determine the optimum silica removal. The optimum silica removal of 55 % was determined with G=2000 S$^{-1}$, pH=7.1 and alum dosage=30 mg/L as Al$_2$O$_3$, corresponding to a maximum of 87 % recovery for RO membrane plant. Silica was removed by co-precipitation of aluminium hydroxide, supported by the turbidity and silica concentration. Flux loss was observed for the cross-flow UF membrane after filtration. Streaming potential by ElectroKinetic Analyser (EKA) was used to analyze the UF membrane before and after filtration, and slightly reduction of negative charge was observed at medium pH, resulted from the positive charge coagulated particle adsorbed on the negative charge UF membrane surface. Scanning electron microscopy & Energy Dispersive X-ray Spectroscopy (SEM-EDS) also showed slight aluminum and silica signal on the used UF membrane surface.

KEYWORDS
Silica scaling; in-line coagulation; ultrafiltration; EKA; EDS

INTRODUCTION
Silica scaling is a common problem encountered in membrane separation processes due to its low solubility of about 120 mg/L in amorphous form. (Sheikholeslami and Tan, 1999; Sheikholeslami and Zhou, 2000; Koo et al., 2001; Semiat et al., 2001; Sheikholeslami et al., 2001; Al-Rehaili, 2003; Chen et al., 2006). Presence of silica in water is due to the dissolution of silica to become silicate based on the following reaction: SiO$_2$ + 2H$_2$O → Si(OH)$_4$. The most common method of silica removal is by precipitation with polyvalent metal hydroxide, such as: Fe(OH)$_3$, Al(OH)$_3$, and Mg(OH)$_2$, indicating both softening and coagulation are capable of removing silica (Darton, 1999; Sheikholeslami and Tan, 1999; Bremere et al., 2000; Sheikholeslami and Zhou, 2000; Hafez et al., 2002; Sheikholeslami and Bright, 2002; Taleb-Ahmed et al., 2002; Semiat et al., 2003; Chen et al., 2006). Although softening is capable of removing silica, it is not feasible unless raw water contains enough hardness. Coagulation is one the best options due to its low cost. However, applying coagulation along with sedimentation facilities requires a lot of footprints, which offsets the benefit of fewer footprints required for RO membrane process. Consequently, in-line coagulation/ultrafiltration is a significant methodology for silica pretreatment, where optimum silica removal was achieved in the in-line coagulation process, the remaining particle was removed by ultrafiltration and fewer footprints were required. In the present study, an in-line static mixer containing internal vanes to change the velocity pattern as well as momentum reversals were utilized to achieve the effect of in-line coagulation. Besides, the permeability of ultrafiltration would not be significantly reduced since the coagulated particle is not known as a fouling material.

Very few studies have reported silica removal by coagulation and none of them applied in-line coagulation. Al-Rehaili, (2003) reported precipitation aids such as alum and ferric chloride were found necessary for improving performance of the lime-soda ash process to reduce silica to the acceptable level. Ma et al. (2007) used enhanced coagulation and UF process and found out silica was removed from 10 mg/L to less than 2 mg/L. Chuang et al. (2007) reported using coagulation process for industrial wastewater containing silica and silica was reduced from 30 mg/L to 10 mg/L. Chen et al. (2006) demonstrated that coagulation is
effective in a jar testing experiment to enhance the silica removal, and coagulation along can remove silica to 50% at medium pH to significantly reduce the possibility of silica scaling. All the evidence demonstrates that coagulation is a feasible process for silica removal.

For in-line coagulation process, one of the most important factors is mixing intensity. However, very few studies have demonstrated this issue. Tchobanoglous et al (2003) report 1500-7500 s\(^{-1}\) and Jones et al (2002) has reported that 3000-5000 s\(^{-1}\). However, these reported values are wide ranged and no specific value can be followed. Since it is an important factor when applying in-line coagulation, the present study also intends to evaluate the optimum mixing intensity for silica removal by in-line coagulation. Besides, the impacts of these coagulated particles on ultrafiltration, including the zeta potential variation on the membrane surface, are also reported. Therefore, three major issues are discussed in this article: (1) Determination of the silica removal requirement for RO membrane by in-line coagulation/ultrafiltration process from a removal - saturation - recovery curve (2) Effects of pH, coagulant dosing and mixing intensity on silica removal for in-line coagulation (3) Impact on ultrafiltration membrane fouling due to preceding in-line coagulation.

**Methods**

The raw water is obtained from a brackish groundwater source for a 600 CMD drinking water treatment plant located in Penghu County, Taiwan. This water treatment plant uses RO membrane process, but silica is the limitation for water recovery due to the possibility of scaling, and the raw water qualities were listed in Table 1.

**Table 1 Raw water qualities for the tested brackish water**

<table>
<thead>
<tr>
<th>pH</th>
<th>SiO(_2) mg/L</th>
<th>Magnesium mg/L as CaCO(_3)</th>
<th>Calcium mg/L as CaCO(_3)</th>
<th>Alkalinity mg/L as CaCO(_3)</th>
<th>chloride mg/L</th>
<th>TDS mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.8</td>
<td>30</td>
<td>333.3</td>
<td>221</td>
<td>225</td>
<td>1550</td>
<td>3451</td>
</tr>
</tbody>
</table>

Figure 1 is the schematic diagram for in-line coagulation/ultrafiltration process in this study. A static mixer containing internal vanes to change the velocity pattern as well as momentum reversals was allocated in a 10 mm diameter tube. Flowrate was varied to achieve desire mixing intensity or velocity gradient (G). For static mixer, the degree of mixing is directly related to the headloss (i.e. pressure drop) through the mixer, and the velocity gradient is calculated from Equation (1), where G=average velocity gradient (s\(^{-1}\)), P=power input(W), \(\mu\)=dynamic viscosity (N.s/m\(^2\)) and V is volume(m\(^3\)). Q is the flowrate (m\(^3\)/s) and \(\Delta P\) is the pressure drop (bar). The headloss or pressure drop through the mixer was measured by a differential electronic manometer meter (model UEI EM200, manufactured by Universal Enterprise Inc. in Oregon, USA) with measurement range of -150 to 150 mBar.

\[
G = \sqrt[3]{\frac{P}{\mu V}} = \sqrt[3]{\frac{Q \Delta P}{\mu V}}
\]  

(1)
PACl (polyaluminium chloride) was the selected coagulant in this study since it is the most popular used one in Taiwan. All chemicals used are of reagent grade. pH was adjusted by either caustic soda or hydrogen chloride. Silica was measured according to the methods 4500-SiO$_2$ listed in the 20th edition of the Standard Methods (APHA, 1999) using a UV-Vis spectrophotometer (HACH Model DR-4000). Surface charge of the membrane, represented by zeta potential measured by a streaming potential electrokinetic analyzer EKA, was purchased from Brookhaven Instrument Corp, New Jersey. Particle charge, represented by zeta potential, is measured by Zetasizer 3000JS, manufactured by Malvern Instruments Ltd, UK. Scanning electron microscopy & Energy dispersive X-ray Spectroscopy (SEM-EDS) is a S-2400 model, manufactured by Hitachi, Ltd., Japan.

RESULTS AND DISCUSSION

Determining of Optimum silica removal

The optimum operation for RO water recovery and silica removal was determined based on the solubility of silica of 120 mg/L. In other word, silica scaling will occur if the silica concentration is over 120 mg/L. From Equation (2), an optimum RO water recovery and silica removal can be determined accordingly.

\[
Solubility (mg/L) = \frac{a[SiO_2]}{1 - X} = \frac{a \times 30mg/L}{1 - X} = 120mg/L
\]  

(2)

In Equation (2), the “a” value and X represent the silica removal efficiency and water recovery for RO membrane, respectively. Figure 2 is plotted from Equation (2) for better presentation. The result shows, in raw water or 20% silica removal case, if the water recovery is high, the saturation (%) will exceed 100% and silica scaling will occur. There are two ways to solve the possible silica scaling problems (1) Decrease the recovery to 73%, where the saturation (%) will be less than 100% for raw water (2) Remove the silica concentration at least 40%, where the concentration will be less than 120 mg/L even the recovery is 85%. Consequently, in order to achieve the desired recovery 85%, the targeted SiO$_2$ concentration before entering RO is set up at 18 mg/L, which is equal to 40% removal of silica for the influent.
Effects of Velocity gradient, pH and alum dosage on silica removal

Velocity gradient, pH and alum dosage all affect the mixing intensity and coagulation, and furthermore affect the efficiency of silica reduction. Figure 3 demonstrates the isopleths for silica removal rate vs. pH and velocity gradient for the four different coagulant dosages. First of all, from the four diagrams, the optimum G value is around 2000 s\(^{-1}\) regardless of alum dosages. Tchobanoglous et al. (2003) report 1500-7500 s\(^{-1}\) and this study suggests the optimum value for silica removal by in-line coagulation was around 2000 s\(^{-1}\). Secondly, the optimum pH was shifted down as the alum dosage was increased. The optimum pH was 7.1 for alum dosage of 30 mg/L (all alum dosages were as Al\(_2\)O\(_3\) throughout the manuscript) decreased to 6.9 for dosage of 60 mg/L and to 6.4 for dosage of 90 mg/L. The reduction of optimum pH for the in-line coagulation for silica removal can be attributed to the generated proton when alum was added. Since the highest silica removal was observed at 30 mg/L of alum dosage, the optimum silica removal of 55\% was determined with G=2000 S\(^{-1}\), pH=7.1 and alum dosage=30 mg/L, corresponding to a maximum of 87\% recovery for RO membrane plant. Besides, silica removal was not increased as dosage increase, due to the destabilization of the coagulated particle to decrease the silica reduction.
Figure 3 Silica removal for different pH and velocity gradient for different coagulant dosages (a) 30 mg/L (b) 60mg/L (c) 90mg/L (d) 120mg/L

The silica was removed by co-precipitation aluminum hydroxide, supported by the results of turbidity and silica removal in Figure 4. In Figure 4, using an example of alum dosage of 30 mg/L at G= 2000s⁻¹, higher turbidity due to the formation of aluminum hydroxide resulted in higher silica removal, indicating silica was removed during the process of co-precipitation of aluminum hydroxide. From solubility diagram of freshly precipitated aluminum hydroxide, the lowest solubility was located at pH 7(Snoeyink and Jenkins, 1980); therefore, the turbidity was gradually increased as pH increased until around 7. But after pH 7, the turbidity was decreased since solubility was increased for pH >7 from solubility diagram.

Figure 4 Silica removal and remaining turbidity for different pHs at 30 mg/L and G=2000 s⁻¹
Ultrafiltration fouling potential by coagulation

Flux loss was observed for the cross-flow UF membrane after filtration, as shown in Figure 5. The gel layer resistance was evaluated using resistance-in-series model. Other than lower mixing intensity at $G=1000 \text{ s}^{-1}$, the resistance was increased significantly for the rest three mixing intensity. This phenomenon was evaluated by measurement of membrane and particle surface charge, and both were represented by their zeta potentials.

![Figure 5](image.png)

**Figure 5** Membrane resistances versus filtration time throughout the experiment

Figure 6 presents the membrane surface charge (zeta potential) measured by EKA for fresh and used membrane. In Figure 6, for the fresh membrane, the pH of zero charge ($\text{pH}_{zpc}$) was 4.4 with higher negative charge at medium pH. After the membrane was used, the negative charge was less since the particle of silica-aluminum hydroxide was attached on the membrane surface. The indication of less negative charge on the membrane surface was supported by the particle zeta potential data, as reported in Figure 7. Figure 7 shows zeta potential for different dosages at $G$ of 2000 $\text{s}^{-1}$ before and after membrane filtration. For the water before membrane filtration, the particle zeta potential increases as the dosage increases, resulted from the positive charge coagulated particle. Therefore, the reduction of negative charge in Figure 6 was attributed to the positive charge coagulated particle attaching onto the membrane surface. After the membrane filtration, the zeta potential stayed negative, due to the removal of those positive particles and small amount of negative charge of silica particle remaining. Another evidence of the coagulated particle attachment is shown in Figure 8 by EDS for used membrane, where a significant peak was observed for aluminum and silica, indicating the attachment of the coagulated particle onto the membrane.
Figure 6 Alternation of membrane surface charge for fresh and used membrane

Figure 7 Zeta potential for different dosages before and after membrane filtration (G=2000 s⁻¹)

Figure 8 EDS for used membrane in the in-line coagulation/ultrafiltration processes

Conclusions
Silica was successfully removed in these in-line coagulation/ultrafiltration processes. Other than pH and coagulant dosage, mixing intensity (velocity gradient, G) is also a critical factor on silica removal. The
optimum silica removal of 55% was determined with G=2000 s⁻¹, pH=7.1 and alum dosage=30 mg/L as Al₂O₃, corresponding to a maximum of 87% recovery for RO membrane plant. Flux loss was observed for the cross-flow UF membrane after filtration. Streaming potential by EKA was used to analyze the UF membrane before and after filtration and slightly reduction of negative charge was observed, resulted from the positive charge coagulated particle adsorbed on the negative charge UF membrane surface. EDS images also showed also showed slight aluminum and silica signal on the UF membrane surface.

References