Colloidal silica removal in coagulation processes for wastewater reuse in a high-tech industrial park


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Abstract Four experiments of coagulation and flocculation were conducted to investigate the characteristics of colloidal silica removal in a high-tech industrial wastewater treatment plant for reclamation and reuse of the effluent. Experimental results illustrated that poly-aluminium chloride (PACl) showed higher performances on colloidal silica removal than alum. Interestingly, the two coagulants demonstrated the same capacity on silica removal. The specific silica removal capacity was approximately 0.135 mg SiO2/mg Al2O3 when the dosage of coagulants was in the range 30–150 mg/L Al2O3. In addition, the silica was reduced significantly at the condition of pH above 8. Experimental data implied that precipitation of aluminium flocs was the major mechanism for colloid silica removal in PACl and alum coagulation, besides, charge adsorption was also important for improving removal efficiency. Moreover, the addition of polyacrylic acid (PAA) as a flocculant could slightly advance silica removal in the PACl coagulation. The combined PACl/PAA/flocs coagulation was effective for the removal of colloidal silica, soluble COD, and turbidity and also suitable as a pretreatment unit in wastewater reclamation and reuse processes.

Keywords Alum; coagulation; colloidal silica; poly-aluminium chloride; wastewater reuse

Introduction

The occurrence of high concentrations of colloidal silica in wastewater is a critical constraint for reclamation and reuse of the effluent in a wastewater treatment plant or in waste cooling, especially in a high-tech industrial park. In wastewater, amorphous silica can usually be classified into soluble, colloidal and particulate forms depending on its reactivity and suspension (Sheikholeslami and Tan, 1999). In our previous study at a high-tech industrial park, the concentration of silica in the effluent of the wastewater treatment plant was in the range 23.1–42.9 mg/L; moreover, over 95% of silica was in the colloidal category (Chuang et al., 2005). Based on silica chemistry, the solubility of colloidal silica in pure water is limited to the range of 100–140 mg/L at 25°C and at pH below 8 (Roque, 1996), the soluble species being in the form of Si(OH)4. Owing to the limited solubility of silica in water, the standard industrial guideline has been to limit the maximum silica concentration in the retentate to about 120 mg/L at 25°C in order to reduce the scaling and fouling problems in reverse osmosis (RO) (Freeman and Majerle, 1995). Therefore, this limitation becomes an indispensability of reclamation and reuse of silica-rich wastewater or waste cooling.

The chemistry of silica fouling is very complex; amorphous silica can foul the membranes by monomeric precipitation, deposition of colloidal particles or as biogenic amorphous silica (Iler, 1979; Sheikholeslami and Tan, 1999). Clearly, pretreatment is indeed required to reduce silica content and to increase the recovery of RO membranes in reclamation and reuse processes for silica-rich wastewater or in waste cooling. Various
treatment processes can be used for the removal of silica from water, such as a lime softener, hot process softener, anion exchange, membrane filtration, etc. Of these, chemical clarification is one of the most practical units employed as pretreatment for membrane desalination (Masarwa et al., 1997; Sheikholeslami et al., 2001, 2002; Al-Rehaili, 2003). Chemicals such as lime, soda ash and iron salts are used extensively for silica removal in softening processes. The research of Al-Rehaili (2003) showed that the addition of precipitation aids such as alum, sodium aluminate or ferric chloride could improve performance of the lime-soda ash process and reduce the content of silica in groundwater. Also, anionic polymer was found helpful for silica reduction at a low dosage. However, Sheikholeslami et al. (2002) reported that sodium aluminate alone was not able to reduce the silica concentration significantly; moreover, the addition of soda ash only slightly improved the efficiency. In addition, the study of Duan and Gregory (1996) concluded that coagulation by aluminium salts can be greatly affected by quite low levels of soluble silica; also, the effect is highly dependent on pH. However, studies dealing with silica removal in coagulation with aluminium salts in wastewater reported in the literature are limited. Therefore, the behaviour of silica removal by aluminium salts needs more comprehensive studies in the laboratory and field.

The study described in this article was part of extensive research aimed at wastewater reclamation and reuse in a high-tech industrial park. The objectives of this article were to investigate the characteristics of chemical coagulation processes when using aluminium salts in silica removal in the effluent of a wastewater treatment plant, and moreover, to establish the optimum conditions of coagulation for further application.

Materials and methods

Experimental methods

Coagulation and flocculation. Four different experiments, namely (1) single coagulation, (2) single flocculation, (3) combined coagulation and flocculation, and (4) combined coagulation and flocs flocculation, were designed and carried out in a modified jar test apparatus for investigating the characteristics of colloidal silica removal. Jar tests were conducted in the laboratory at room temperature (25–28°C) using 1 L plastic jars. Coagulation experiments were performed with rapid mixing at 150 rpm for 5 min with a dosage of 0–180 mg/L Al₂O₃ of coagulants. Flocculation experiments were operated with slow mixing at 20 rpm for 20 min with a dose of 0–8 mg/L of polymer. During coagulation and flocculation processes, the pH was adjusted to an appointed value using diluted sulphuric acid or sodium hydroxyl. Experiments of flocculation with addition of flocs was designed to investigate the effectiveness of flocs on silica and COD removal; the flocs was produced from previous coagulation; moreover, it was concentrated gravitationally and kept in a non-disturbed condition for use. Samples were collected and filtered after 30 min settling through 0.45 μm glass fibre filter paper for total silica and colloid silica analysis.

Analysis methods. The total silica, colloidal silica, soluble COD, turbidity, total solid and silt density index (SDI) were used to evaluate the performances in this study. The silica concentration was determined immediately using a spectrophotometer (Hitachi U2001), according to the molybdosilicate method (Standard Method, 1995). The SDI measurement conformed to the ASTM D4189-95 standards at fixed 30 psi with a time interval of 5 min.
Materials

Raw water. Table 1 shows the average characteristics of the effluent of the secondary wastewater treatment plant in a high-tech industrial park. The effluent was collected monthly for a series of jar tests during the experimental period. Table 1 shows that the effluent was neutral with a pH of 6.8 ± 0.1. The silica concentration varied from 23.1 ± 15.5 to 27.9 ± 10.7 mg/L; moreover, over 95% of silica was in the form of colloid. In addition, the average of the COD was lower than 25.0 mg/L; chloride and sulphate were the major components of anions in the effluent.

Reagents. Two commercial coagulants were used for coagulation experiments, including PACl (polyaluminium chloride, Al₂(OH)₃Cl₆−ₙ, 30% Al₂O₃) and alum (aluminium sulphate, Al₂(SO₄)₃•18H₂O, 98% Al₂O₃). Two reagent grade flocculants were selected for flocculation tests, namely PAA (polyacrylic acid, (C₃H₅NOC₃H₄O₂)n, molecular weight 1,500–5,000) and PDADMA (polydiallyl dimethylammonium chloride, (C₈H₁₆NCl)n, molecular weight 200,000–350,000). Plastic reactors and other reserved containers were used to prevent possible leaching of silica from glass.

Results and discussion

Effects of coagulants, flocculants and pH on colloidal silica removal

All single coagulation and flocculation experiments were carried out at a pH of 7.5 in jar tests. Table 2 summarises the performances of coagulation by PACl and alum. It shows that the concentration of colloid silica was significantly reduced to 14.0 mg/L at a PACl dosage of 150 mg/L Al₂O₃; moreover, the removal ratios were increased with the dosage of coagulants. Compared with alum, the coagulant PACl demonstrated a higher achievement on colloid silica removal in the dosage range of 0–150 mg/L Al₂O₃. A previous study on coagulation of aluminium salts showed that alum and PACl could precipitate to form different solid phases of flocs for colloidal removal (Van Benschoten and Edzwald, 1990a, b). Apparently, the polymeric structure of PACl could provide a more positively charged surface within the PACl precipitates and colloid, thus producing a lower silica concentration than the alum flocs in this study.

From another point of view, Figure 1 illustrates that a positive linear relationship between coagulants dosage and removed silica was established with a good correlation. This demonstrates a very interesting occurrence of coagulation of the effluent. Although PACl showed higher performance on overall colloidal silica removal than alum, the specific silica removal capacity of the two coagulants was almost the same. It was approximately 0.135 mg SiO₂/mg Al₂O₃ when the dosage of coagulants was in the range 30–150 mg/L Al₂O₃. This phenomenon implied that the precipitation of aluminium flocs
should be the major mechanism of coagulation for colloid silica removal at a neutral environment of pH 7.5; however, the higher charged precipitates of PACl can improve silica removal with charge neutralisation. Figure 2 illustrates the characteristics of single flocculation with cation polymer (PDADMA) and anion polymer (PAA). Neither PDADMA nor PAA could reduce colloid silica content, regardless of charge type and molecular weight.

The pH is one of the important parameters for colloidal silica control. Figure 3 shows the results of coagulation at different pH levels with the initial silica concentration of raw water at 36.2 mg/L. In experiments without adding coagulant, the variation of silica was slight at pH below 8; however, when pH increased to 9, the silica concentration dropped significantly to 21.8 mg/L. Coagulation experiments with adding PACl 60 mg/L Al₂O₃ and PAA 0.5 mg/L also showed similar behaviour; moreover, the silica concentration was reduced to about 10.4 mg/L at a pH of 9. Effects of pH on silica solubility indicate that the dissociation constants of amorphous silica increases significantly when pH is above 8; it will ionise and form more silicate ions (Roque, 1996). Therefore, with the pH below 8, the precipitation of PACl precipitates with amorphous silica performed an essential mechanism for colloidal silica removal; otherwise, the ionised silicate ions could be adsorbed on the high positively charged PACl precipitates enhancing silica removal when pH was controlled above 8.

Conductivity was an important parameter for selecting wastewater reclamation and reuse processes. Figure 4 displays a linear relationship between coagulant dosage and increased conductivity. The coagulant PACl contributed more electrolytes than alum in solution. The conductivity of the effluent used for this study was in the range 2,750–3,080 μS/cm, which is a typical quality of industrial wastewater at a treatment plant.

### Table 2 Performances of coagulants on silica removal

<table>
<thead>
<tr>
<th>Dosage of coagulant (mg/L Al₂O₃)</th>
<th>PACl</th>
<th></th>
<th></th>
<th>Alum</th>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td>T. SiO₂* (mg/L)</td>
<td>C. SiO₂** (mg/L)</td>
<td>Removal ratio (%)</td>
<td>T. SiO₂ (mg/L)</td>
<td>C. SiO₂ (mg/L)</td>
<td>Removal ratio (%)</td>
</tr>
<tr>
<td>0</td>
<td>42.3</td>
<td>41.0</td>
<td>0.0</td>
<td>42.3</td>
<td>41.0</td>
<td>0.0</td>
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<td>30</td>
<td>30.6</td>
<td>29.9</td>
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<td>38.2</td>
<td>37.2</td>
<td>9.2</td>
</tr>
<tr>
<td>60</td>
<td>26.5</td>
<td>25.4</td>
<td>38.1</td>
<td>36.4</td>
<td>35.8</td>
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<tr>
<td>90</td>
<td>22.6</td>
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<td>46.5</td>
<td>32.0</td>
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<td>23.3</td>
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<td>120</td>
<td>17.5</td>
<td>16.6</td>
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<td>24.1</td>
<td>41.2</td>
</tr>
<tr>
<td>150</td>
<td>14.3</td>
<td>14.0</td>
<td>65.9</td>
<td>23.3</td>
<td>23.0</td>
<td>43.9</td>
</tr>
</tbody>
</table>

* T. SiO₂ represents the total silica; ** C. SiO₂ represents the colloid silica

![Figure 1](https://iwaponline.com/wst/article-pdf/55/1-2/187/431001/187.pdf)  
**Figure 1** Relationship between coagulants dosage and removed colloid silica
Figure 4 illustrates that the addition of 100 mg/L Al₂O₃ of coagulants PACI and alum would increase conductivity of 174 and 96 μS/cm, respectively; it was acceptable for wastewater reclamation.

**Effects of PAA on colloidal silica removal**

All of the combined coagulation and flocculation experiments were also accomplished at pH of 7.5. Figures 5 and 6 illustrate the effects of flocculant PAA on silica removal in PACI and alum coagulation processes, respectively. In PACI coagulation, the addition of the flocculant PAA slightly increased silica removal ratios when the dosage was in the range 0.5–3 mg/L. The removal ratio was approximately 80% at the conditions of PACI dosage of 180 mg/L Al₂O₃ and PAA of 3.0 mg/L, and it seemed to approach a maximum of silica removal at a pH of 7.5.

However, compared with PACI, alum coagulation experiments demonstrated a dissimilar behaviour on silica removal. The effectiveness of the addition of flocculant PAA was not clear; moreover, the removal ratios of silica were increased linearly with the dosage of alum. The removal ratios were in the range 40–50% at an alum dosage of 180 mg/L Al₂O₃ and PAA of 0.5–3.0 mg/L.

From the results of the coagulation and flocculation experiments, it seems that the positively charged aluminium precipitates initially contributed a chance for charged neutralisation of amorphous silica on the surface of precipitates. The highly charged PACI precipitates demonstrated higher performance on silica removal than alum and produced...
lower concentrations of silica. Then, when the complex flocs of aluminium precipitates and amorphous silica was formed, precipitation of the complex flocs became the major mechanism of silica removal; meanwhile, the flocs developed from PACl or alum showed the same specific capacity on silica reduction. Moreover, adjusting pH to above 8 for increasing silica ionisation was one of the effective operations for improving colloidal silica removal in the aluminium coagulation processes.

Effects of addition of waste flocs on colloidal silica and COD removal

Experiments with the addition of waste flocs in PACl coagulation were designed to investigate the extended performances of waste flocs on silica and COD removal at a pH of 8 and PACl of 60 mg/L Al₂O₃. Figure 7 shows that the addition of waste flocs could moderately increase the efficiency of colloidal silica removal with about 8.8% when the dosage of flocs was at 90 mg/L; meanwhile, the soluble COD removal ratios were increased by approximate 22.0%. However, overdosage of waste flocs at 120 mg/L resulted in the decrease of silica removal; contrarily, soluble COD removal was increased significantly. It revealed that the precipitation of waste PACl–silica complex flocs demonstrated more effectiveness on organic matters removal than on colloid silica reduction. From the view of application, the silica illustrated good potential as a coagulation aid for improving organics reduction. Therefore, addition of an adequate amount of flocs could be useful for moderately extending silica and COD removal.
Table 3 summarises the performances of combined PACI/PAA/flocs coagulation at different pH levels with PACI of 60 mg/L Al₂O₃, PAA of 0.5 mg/L, and flocs of 90 mg/L. This demonstrates that single coagulation of PACI was useful for the removal of turbidity, colloid silica and solids, although the fouling index SDI₅ was still higher than 20. The combined PACI/PAA/flocs coagulation showed remarkable improvement on soluble organics removal and fouling index; nevertheless, the SDI₅ was still very high and the treated water was still inadequate to flow into the membrane process for further reclamion. Besides, the addition of waste flocs resulted in a slight increase on turbidity and total solids.

Figure 8 illustrates the comparisons of performances of combined PACI/PAA/flocs coagulations under the conditions of pH 7 and 8. It shows that experiments had excellent results on turbidity reduction in different pH situations. Compared with the experiment at pH 7, the experiment at pH 8 demonstrated a better performance on colloidal silica and soluble COD removal; the removal ratios increased approximately 10–12%. However, the performance of total solids was reduced in the condition of pH 8. In summary, the combined PACI/PAA/flocs coagulation was suggested as a pretreatment unit for improving the removal of turbidity, silica and SCOD in wastewater reclamation processes; the optimal conditions of operation were determined at PACI of 60 mg/L Al₂O₃, PAA of 0.5 mg/L, waste flocs of 90 mg/L and pH of 8 in this study.
Conclusion

The objectives of this study were to investigate the characteristics of colloidal silica removal in chemical coagulation processes by using aluminium salt, and moreover, to establish the optimum conditions of coagulation for further application on wastewater reclamation and reuse in a high-tech industrial park. Based on the results of this research, conclusions were made as follows:

1. The PACl showed higher performances on colloidal silica removal than alum. Interestingly, the two coagulants demonstrated the same capacity on silica removal. The specific silica removal capacity was approximately 0.135 mg SiO2/mg Al2O3 when the dosage of coagulants was in the range 30–150 mg/L Al2O3.

2. Adjusting pH to above 8 for increasing silica ionisation was one of the effective operations for improving colloidal silica removal in aluminium coagulation processes.

3. The precipitation of aluminium flocs was the major mechanism for colloid silica removal in PACl and alum coagulation; besides, charge adsorption was also important for improving removal efficiency. Moreover, the addition of polyacrylic acid (PAA) as a flocculant could slightly advance silica removal in the PACl coagulation.

4. Combined PACl/PAA/flocs coagulation was suggested as a pretreatment unit for improving the removal of turbidity, silica and SCOD in wastewater reclamation processes; the optimal conditions of operation were determined at PACl of 60 mg/L Al2O3, PAA of 0.5 mg/L, waste flocs of 90 mg/L and a pH of 8 in this study.

Table 3 Performances of combined PACl/PAA/flocs coagulation

<table>
<thead>
<tr>
<th>PACl/PAA/flocs (mg Al2O3/mg/mg)</th>
<th>pH</th>
<th>Cond. (µS/cm)</th>
<th>Turbi. (NTU)</th>
<th>Colloid SiO2 (mg/L)</th>
<th>TS (mg/L)</th>
<th>TCOD (mg/L)</th>
<th>SCOD (mg/L)</th>
<th>SDI5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water</td>
<td>7.24</td>
<td>2900</td>
<td>7.1</td>
<td>34.0</td>
<td>1980</td>
<td>92.2</td>
<td>73.5</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>60/0/0</td>
<td>7</td>
<td>2950</td>
<td>0.2</td>
<td>22.0</td>
<td>1088</td>
<td>74.8</td>
<td>56.4</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>60/0.5/0</td>
<td>2950</td>
<td>0.2</td>
<td>772</td>
<td>63.7</td>
<td>47.5</td>
<td>17.5</td>
<td></td>
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</tr>
<tr>
<td>60/0.5/90</td>
<td>2930</td>
<td>0.3</td>
<td>820</td>
<td>44.2</td>
<td>31.5</td>
<td>15.1</td>
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<tr>
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<td>0.3</td>
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<td></td>
</tr>
</tbody>
</table>

Figure 8 Comparisons of coagulation at the conditions of PACl 60 mg/L Al2O3, PAA 0.5 mg/L and waste flocs 90 mg/L.

Conclusion

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References