Development of a three-stage system for the treatment and reclamation of wastewater containing nano-scale particles

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Abstract
Reverse osmosis (RO) membrane technology cannot be applied for the direct purification of nano-scale particle-containing wastewater due to membrane fouling/clogging problems. In this study, a three-stage pre-treatment process was developed to remove nano-scale particles from wastewater prior to further water purification using RO. The proposed pre-treatment system involved chemical coagulation/flocculation followed by sand filtration (SF) and ultrafiltration (UF). Backgrinding (BG) wastewater, which contained high concentrations of inorganic nano-particles, was used to evaluate the feasibility of this three-stage process for nano-scale particle removal. The BG wastewater (collected from a semiconductor manufacturing plant) had turbidity and suspended solids concentrations of approximately 1403 NTU and 77.8 mg/L, respectively. Up to 98% of the turbidity and particles could be removed through chemical coagulation/flocculation when 2.2 mg/L of polyaluminum chloride was used as coagulant and 0.5 mg/L of polymer was used as flocculant. However, the SF system could not effectively remove the nano-scale particles from BG wastewater directly. More than 99% of the turbidity and particles could be removed with the application of a UF unit [spiral-wound (SW) or hollow-fiber (HF) membrane] after the coagulation/flocculation/SF processes. Results indicate that the three-stage system is appropriate for the pre-treatment of nano-particle-containing wastewater.
designed and operated in accordance with US Environmental Protection Agency (EPA) guidelines and usually provide effective organic carbon, suspended solid (SS), and nutrient removal rates\[32–35\]. However, the particle removal efficiency for sand filtration (SF) is not significant if the equivalent particle size is greater than 20 μm [23]. Thus, membrane processes are becoming increasingly popular for further particle removal to mitigate possible fouling of the succeeding RO unit. UF is usually used for microbial removal and is useful for the recovery of high molecular weight chemicals, which allows water recycling to be more economically feasible [36]. UF processes appear to be a more attractive option for wastewater treatment because they allow high fluxes at relatively low pressures [4].

Semiconductor manufacturing has become a representative and paramount industry in Taiwan [23,26,37,38]. Several environmental problems, including wastewater treatment challenges and high water demand, have resulted from the rapid development of the semiconductor industry [23,37]. Backgrinding (BG) is the final step in semiconductor manufacturing. BG wastewater contains inorganic particles and has a characteristic deep dark color, high turbidity, and low conductivity. The major contaminants of BG wastewater are nano-size particles, which is distinctly different from most industrial wastewaters [23,36]. Because a significant amount of BG wastewater is produced in the semiconductor industry, the development of effective and reliable wastewater reclamation technologies is required to recycle treated BG wastewater for reuse purposes. Thus, the removal of total solids (TS) and nano-size particles from BG wastewater has received the most attention from the perspective of water reuse and sustainable development. If TS and nano-size particles could be removed efficiently, then BG wastewater could be recycled and reused.

Currently, conventional treatment processes (e.g., SF and chemical coagulation/flocculation) have been applied for BG wastewater treatment. However, it is difficult to control the coagulant dosage when dealing with nano-size silica particles in wastewater. Dosage in the sweep flocculation range is therefore chosen to ensure effective solid-water separation [38]. When SF has been applied for water or wastewater treatment, it has shown promising results for treating organic carbon and ammonia nitrogen using adjusted hydraulic and organic loadings [39]. However, SF is not very effective for the removal of colloidal (particle size = 0.001 μm to 1 μm) and dissolved solids (particle size < 0.001 μm) [2,39]. Thus, an appropriate pre-treatment design is required for the application of RO systems for further reclamation of nano-particle-containing BG wastewater. Otherwise, effluent water quality cannot meet stringent water reuse standards [5].

In this laboratory-scale feasibility study, a three-stage pre-treatment process was developed to remove nano-scale particles from wastewater. The proposed three-stage pre-treatment system contained a chemical coagulation/flocculation system followed by SF and UF units. In this study, BG wastewater containing high concentrations of inorganic nano-particles was used to evaluate the effectiveness of this proposed process for the removal of nano-scale particles prior to the application of an RO unit for further water purification. Wastewater discharged from the BG process of a semiconductor factory was collected and tested in this study. This study had the following objectives: (1) investigate the characteristics of the tested wastewater discharged from the BG process of a semiconductor factory was collected and tested in this study. This study had the following objectives: (1) investigate the characteristics of the tested wastewater discharged from the BG process of a semiconductor factory was collected and tested in this study. This study had the following objectives: (1) investigate the characteristics of the tested wastewater discharged from the BG process of a semiconductor factory was collected and tested in this study. This study had the following objectives: (1) investigate the characteristics of the tested

<table>
<thead>
<tr>
<th>Item</th>
<th>UF module</th>
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<tbody>
<tr>
<td></td>
<td>Hollow-fiber membrane</td>
</tr>
<tr>
<td></td>
<td>(outside-in)</td>
</tr>
<tr>
<td>Membrane material</td>
<td>PVDF(^a)</td>
</tr>
<tr>
<td>Membrane area (m(^2))</td>
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<tr>
<td>Pore diameter (μm)</td>
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<tr>
<td>pH range</td>
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<td></td>
<td>Spiral-wound membrane</td>
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<tr>
<td>Membrane material</td>
<td>PS(^b)</td>
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<tr>
<td>Pore diameter (μm)</td>
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<tr>
<td>Fiber inner/outer diameter (mm)</td>
<td>–</td>
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<tr>
<td>pH range</td>
<td>2.5–11</td>
</tr>
</tbody>
</table>

\(^a\) PVDF = polyvinylidene difluoride.
\(^b\) PS = polysulfone.
BG wastewater; (2) perform jar tests to determine the optimal
dose and initial pH value of the selected coagulant/flocculant for
the coagulation/flocculation process; (3) evaluate the feasibility of
using SF for BG wastewater pre-treatment; (4) evaluate the effec-
tiveness of using UF system for water quality improvement after
pre-treatment by coagulation/flocculation or SF; and (5) design a pre-
treatment process to be used prior to the application of an RO unit for
the reclamation and reuse of nano-scale particle-containing wastewater.

2. Materials and methods

2.1. Characterization of BG wastewater

BG wastewater collected from the BG process of a semiconductor
factory in Taiwan was tested in this study. The BG wastewater samples
were collected monthly from the discharge pipe of the BG facility during
the one-year investigation period. Water samples were analyzed
for water quality-indicating parameters, including pH, conductivity,
turbidity, mean particle size (MPS), total organic carbon (TOC), COD,
TS, SS, total dissolved solids (TDS), sulfate (SO4$^{2-}$), silicate (SiO4$^{2-}$
as SiO2), zeta potential (ZP), ammonia nitrogen (NH3-N), and total hardness
(TH). Sample analyses were performed in accordance with the American
Public Health Association Standard Methods [40]. An ion chromatogra-
phy system ( Dionex, USA) was used for the analysis of inorganic nutri-
ts and anions [40]. The pH measurements were conducted using an
pH/Eh MP120 meter (Mettler-Toledo). TOC was determined using a
total carbon analyzer (Multi N/C 3000, Analytik Jena AG, Germany).
MPS and ZP analyses were performed using a laser particle size analyzer
(Malvern 4700, UK) following the methods developed by the US EPA
[41].

2.2. Treatment by sand filtration

In this study, a column experiment was conducted to evaluate the
effectiveness of SF in BG wastewater pre-treatment. Quartz sand was
used as the filling material (media) within glass columns. The column
had the following characteristics: bed depth = 180 mm, inside diam-
eter = 50 mm, filtration velocity = 0.6 m/h, and effective media
size = 0.4 to 0.8 mm. Fig. 1 shows a schematic diagram of the sand fil-
tration system. A peristaltic pump (Cole Parmer MasterFlex L/S®)
was used to deliver the wastewater into the column system. All tub-
ing materials that were in contact with the solution were made of Tef-
lon. Water samples from the column outlet were collected and
analyzed for water quality-indicating parameters described in the
previous section.

2.3. Treatment by coagulation/flocculation

The coagulation/flocculation experiments were performed in jar
tests, which had three main steps: coagulation, flocculation, and set-
ting. The jar tests were conducted in six 1-L polyvinylchloride bea-
kers, and each breaker contained 500 mL of BG wastewater. The
effectiveness of TS, SS, turbidity, and COD removal using the coagula-
tion/flocculation process was evaluated. During the jar tests, pH
values were controlled using HCl (1 N) and NaOH (1 N) at room tem-
perature. The coagulant used in this study was 10% polyaluminum
chloride (PAC) (Al2Cl6) (Komax Chemical Co., Korea). Cationic [poly-
acrylamide (CPAM) (CH2\-\-CH-)n] and anionic polymer [polyacryl-
amide (PAM) (CH2\-\-CH(CONH2)-)n] (Seimao Co., Taiwan) were used
as the flocculants, which had average molecular weights of 1600
and 600 Da, respectively. The coagulation processes were used 2.2
to 100 mg/L PAC to 1 L BG wastewater sample. The mixing speeds
and duration of the coagulation and flocculation processes were
200 rpm for 1 min and 30 rpm for 20 min, respectively. After rapid
mixing, the pH value was used HCl and NaOH to control in range 6
to 10. Different types (PAM and CPAM) and concentrations (0.5, 1.0,
1.5, 2.0 and 2.5 mg/L) of polymer were added and mixed by slow mix-
ing. The settling time was 20 min. Variations in the pH and turbidity
of the wastewater were monitored during the experiments. The

![Fig. 3. Schematic diagram showing the HF-UF (outside-in) membrane system.](image)

![Fig. 4. Photos of the SW-UF membrane and laboratory-scale system (A: SW-UF membrane module, B: SW membrane, C: electronic balance for permeate monitoring, and D: computer for date collection).](image)
time required for floc formation was monitored, and the size of the floc was measured.

2.4. Treatment using an UF membrane system

In this study, the effectiveness of the UF membrane system for BG wastewater pre-treatment was evaluated. The experiments were performed using two different types of UF membrane modules: a hollow-fiber (HF) outside-in membrane (Ecologix Technologies, USA) and a spiral-wound (SW) membrane (GE Osmonics, USA). Table 1 shows the key characteristics of the two different types of UF membrane systems. The photos in Fig. 2 show the HF-UF membrane and laboratory-scale system. The maximum wash and backwash pressures for the UF membrane were 0.8 and 1.6 kgf/cm², respectively. The operation time for the HF and SP membrane system was 90 and 55 min, respectively. Flux data were collected by the online computer system. The amount of permeate was determined by weighing collected permeate using an electronic balance (METTLER TOLEDO, PB3002, Switzerland) connected to the computer. A cycle of filtration pumping for 9 min followed by backwash pumping for 1 min was applied. Fig. 3 shows a schematic diagram of the HF-UF (outside-in) membrane system. The system contained a feed tank, HF-UF membrane module, and filtrate tank. In this study, the following wastewater flow direction was used: feed tank → valve A → HF-UF membrane module (outside-in) → pump A → pressure meter A → flow meter → filtrate tank. The following wastewater flow direction was used for the backwash process: filtrate tank → pump B → valve D → pressure meter B → HF-UF membrane module (inside-out). The air flow of the air scouring process was directed from the air pump to the HF-UF module.

Fig. 4 presents the photos showing the SW-UF membrane and laboratory-scale system. The system included four parts: A: SW-UF membrane module, B: SW membrane, C: electronic balance for permeate monitoring, and D: computer for data collection. Fig. 5 shows the schematic diagram of the SW-UF membrane system. The SW-UF membrane system contained a feed tank, SW-UF membrane module, and filtrate tank. The following flow direction was used for the filtration process: feed tank (influent) → pump A → pressure meter A → SW-UF membrane module → valve B → flow meter → filtrate tank. A peristaltic pump (Cole Parmer MasterFlex L/S®) was used to deliver the wastewater into the UF membrane module for each system. All tubing materials that were used in contact with solution were made of Teflon. Water samples from the system outlets were collected and analyzed for water quality-indicating parameters described in the previous section.

Table 2
Characteristics of the BG wastewater.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum value</th>
<th>Maximum value</th>
<th>Mean value a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
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<td>28</td>
<td>26</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
<td>8.1</td>
<td>7.9</td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>16</td>
<td>454</td>
<td>373</td>
</tr>
<tr>
<td>ZP (mV)</td>
<td>−28</td>
<td>−32</td>
<td>−30</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>0.2</td>
<td>0.35</td>
<td>0.25</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>1325</td>
<td>1457</td>
<td>1403</td>
</tr>
<tr>
<td>MPS² (nm)</td>
<td>304</td>
<td>1680</td>
<td>1466</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>0.9</td>
<td>3.9</td>
<td>2.4</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>1.3</td>
<td>4.0</td>
<td>2.5</td>
</tr>
<tr>
<td>TS (mg/L)</td>
<td>662</td>
<td>2848</td>
<td>1366</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>61.4</td>
<td>92.4</td>
<td>77.8</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>405</td>
<td>684</td>
<td>546</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>129</td>
<td>199</td>
<td>158</td>
</tr>
<tr>
<td>SiO₂ (mg/L)</td>
<td>3.2</td>
<td>7.6</td>
<td>6.1</td>
</tr>
<tr>
<td>TH (mg as CaCO₃/L)</td>
<td>165</td>
<td>195</td>
<td>179</td>
</tr>
</tbody>
</table>

* Mean value = mean value of 12 samples.
3. Results and discussion

3.1. Characterization of BG wastewater

The BG wastewater collected from a semiconductor factory had low conductivity (mean value = 373 μS/cm), TOC (mean value = 2.4 mg/L), COD (mean value = 2.5 mg/L), ZP (mean value = −30 mV), and MPS (mean value = 1466 nm) values (Table 2). However, the BG wastewater also had high SS (mean value = 77.8 mg/L), TS (mean value = 1366 mg/L), and turbidity (mean value = 1403 NTU) values. These results reveal that the main components of the wastewater were inorganic chemicals and very small particles. Therefore, nano-size particles would be a major concern for future water purification processes using RO membrane system. Conventional water filtration methods (e.g., sand filtration and microfiltration) would not be an effective option for BG wastewater treatment. Results from Table 2 show that sulfate, TH, and silicate (as SiO2) concentrations were between 129 and 199, between 165 and 195, and between 3.2 and 7.6 mg/L, respectively. These results confirm that the BG wastewater had a high concentration of fine particles and low levels of organics and ions.

Figs. 6 and 7 show the variations in particle size (percentage of mean intensity) and ZP distribution of the BG wastewater at different pH values. Variations in pH and ZP of the water samples caused changes in the particle size distribution, and higher pH values corresponded to the lower ZP and MPS values. Higher MPS and ZP values were observed when the pH was 2. This finding indicates that the scattered particle distribution caused a decrease in MPS and increased the repulsion force between particles at high pH. However, a lower pH caused a higher MPS and decreased the repulsion force, which resulted in the appearance of a larger particle size [42]. ZP measurements can be applied to evaluate the surface charge of the membrane and play an important role in the selection of an appropriate membrane for water treatment. Results from this study indicate that a membrane with a negative ZP should be considered for BG wastewater treatment. The results presented in Fig. 7 show that the ZP was close to zero mV when the pH value was 2. ZP decreased to −59 mV when the pH value went up to 12. These results indicate that the particles in BG wastewater were negatively charged when the pH was in the range of 2 to 12, and ZP ranged from −24 to −28 mV when the pH was between 7 and 8. Therefore, because the pH value of BG wastewater varied from 7.8 to 8.1 (Table 2), the particle surfaces were negatively charged.

3.2. Pre-treatment by sand filtration

In this study, SF was used as a pre-treatment process for the removal of solids and turbidity. Table 3 presents the turbidity, solid, and conductivity measurements before and after the SF process. The turbidity value and SS concentration dropped to 920 NTU and 80 mg/L, respectively, after the SF treatment. The calculated percentages of turbidity and SS removal were only 9.5 and 13.4%, respectively. No significant changes in MPS, TDS, or conductivity were observed (Table 3). SF is usually effective in the removal of solids with particle diameters greater than 20 μm [23,43], and thus, SF is not effective for the treatment of BG wastewater containing nano-size particles. If the particle size can be increased by the coagulation/flocculation process, then SF should be able to remove the resulting flocs.

Table 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BG wastewater before treatment</th>
<th>After treatment</th>
<th>Removal (%) a</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.1</td>
<td>7.6</td>
<td>– b</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>1440</td>
<td>920</td>
<td>36.1</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>92.4</td>
<td>80</td>
<td>13.4</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>684</td>
<td>487</td>
<td>–</td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>454</td>
<td>281</td>
<td>–</td>
</tr>
<tr>
<td>MPS (nm)</td>
<td>1680</td>
<td>1648</td>
<td>–</td>
</tr>
</tbody>
</table>

a Removal (%) = ([influent value − effluent value] × 100/[influent value]).

b – = not available.

Fig. 7. Variations in the zeta potential distribution of BG wastewater at different pH values.

Fig. 8. Effect of PAC dose on turbidity removal efficiency and the variation in conductivity at a pH value of 7.2.

Fig. 9. Effect of PAC dose on the variation in the MPS at a pH value of 7.2 and initial turbidity of 1440 NTU.
3.3. Pre-treatment by coagulation/flocculation

3.3.1. Effect of coagulant addition on turbidity removal

Jar tests were performed to evaluate the effectiveness of coagulation and flocculation processes on particle removal from BG wastewater. The results can also be applied for the selection of the membrane used for further BG wastewater treatment. Fig. 8 presents the effect of coagulant dose on turbidity removal efficiency and the variation in conductivity values at a pH value of 7.2 and an initial turbidity of 1440 NTU. Fig. 9 shows the effect of PAC dose on the variation in MPS at a pH value of 7.2 and an initial turbidity of 1440 NTU. Greater than 89% turbidity removal was observed, and the conductivity remained below 48 μS/cm when 2.2 to 5 mg/L of PAC was added as the coagulant. A decrease in turbidity removal efficiency and an increase in conductivity were observed with increased PAC dose. When an overdose of coagulate was used, extra ions likely caused an increase in conductivity. Torres [44] reported that pH and flocculant/coagulant dosage play important roles in the removal of conductivity (as a measure of dissolved salts). Song [45] reported that an increased PAC dose resulted in increased turbidity, which is caused by the restabilization of the suspension by excess coagulant [46,47]. Thus, pH and coagulant dosage are two major factors that significantly affect the efficiency of the coagulation process [48]. Moreover, coagulation rate and coagulant type are also important parameters in coagulation processes [48].

When PAC is used as the coagulant, polymerization occurs between Al ions and AlCl3 [29]. The major parameters that affect this polymerization process include pH, temperature, Al salt concentration, and reaction time [28,29]. Moreover, Al salt dissociates in water to form Al ions that then react with water to form Al(H2O)63+ [28,29]. When PAC is used as the coagulant at high pH conditions, compounds that are less complex and have high valences are formed, which causes the coagulation efficiency to decrease. This is also true when an anionic polymer is used [49]. Thus, coagulant type, pH, and Al content are major factors that affect the coagulation efficiency, and a significant addition of the appropriate cationic polymer would enhance the bridging activity [49].

The results of this study indicate that the MPS was affected by the PAC dose (Fig. 9). A lower PAC dose (2.2 mg/L) caused an increase in particle size (4.9 × 104 nm) and a greater turbidity removal efficiency.

3.3.2. Effect of flocculant addition on turbidity removal

In this jar test, 2.2 mg/L of PAC was added to the BG wastewater, and the solution was mixed for one min. Different doses of flocculant were then added to the beakers, and 30 min of mixing was applied.

This greater efficiency would minimize fouling in the subsequent membrane UF process. Increased PAC doses also caused a decrease in MPS, especially when the PAC dose was greater than 30 mg/L. The decrease in MPS corresponded with decreased turbidity removal efficiency (Fig. 8). This decrease in efficiency was due to the adsorption of extra coagulants (with high ionic strength) onto flocs, which caused a decrease in the electric potential resulting charge neutralization [50]. This process causes a reversal of the electric potential and restabilization, which prevents the formation of larger-sized particles [29,51]. Lin [29] found that when PAC was used as the coagulant, larger Al(OH)3 colloids were formed, and a significant production of crystalline structures was not observed. This was due to the fact that coagulation of negatively charged particles by charge neutralization would effectively enhance the settling and dewatering characteristics of flocs [29].

Table 4
Effects of different doses of cationic polymer on turbidity removal from BG wastewater with the addition of 2.2 mg/L of PAC (initial pH = 7.7; turbidity = 1457 NTU; TDS = 684 mg/L; conductivity = 454 μS/cm; zeta potential = −32 mV; MPS = 1680 nm).

<table>
<thead>
<tr>
<th>Polymer (+) (mg/L)</th>
<th>Turbidity (NTU)</th>
<th>TDS (mg/L)</th>
<th>pH</th>
<th>Conductivity (μS/cm)</th>
<th>MPS (nm)</th>
<th>ZP (mV)</th>
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</thead>
<tbody>
<tr>
<td>0.5</td>
<td>37.3</td>
<td>14</td>
<td>5.3</td>
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<td>17,800</td>
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<tr>
<td>1.0</td>
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<td>5.1</td>
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<tr>
<td>1.5</td>
<td>54.0</td>
<td>9</td>
<td>5.1</td>
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<td>21.1</td>
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<tr>
<td>2.0</td>
<td>51.3</td>
<td>10</td>
<td>5.1</td>
<td>19</td>
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<td>6.7</td>
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<tr>
<td>2.5</td>
<td>51.9</td>
<td>8</td>
<td>5.1</td>
<td>21</td>
<td>1320</td>
<td>18</td>
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Table 5
Effects of different doses of anionic polymer on turbidity removal from BG wastewater with the addition of 2.2 mg/L of PAC (initial pH = 7.7; turbidity = 1457 NTU; TDS = 684 mg/L; conductivity = 454 μS/cm; zeta potential = −32 mV; MPS = 1680 nm).

<table>
<thead>
<tr>
<th>Polymer (−) (mg/L)</th>
<th>Turbidity (NTU)</th>
<th>TDS (mg/L)</th>
<th>pH</th>
<th>Conductivity (μS/cm)</th>
<th>MPS (nm)</th>
<th>ZP (mV)</th>
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<tr>
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<td>10</td>
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<td>7240</td>
<td>2.26</td>
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Table 6
Residual metal concentrations in BG wastewater after coagulation/flocculation and UF treatment.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Treatment unit</th>
<th>After coagulation (mg/L)</th>
<th>UF (mg/L)</th>
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<tbody>
<tr>
<td>Cd</td>
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<td>0.001</td>
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<td>Cu</td>
<td>0.016</td>
<td>0.013</td>
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<tr>
<td>Mn</td>
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<td>0.003</td>
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</tr>
<tr>
<td>Pb</td>
<td>0.013</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
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<tr>
<td>Fe</td>
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</tr>
<tr>
<td>Al</td>
<td>0.560</td>
<td>0.190</td>
<td></td>
</tr>
</tbody>
</table>
served with increased anionic polymer addition, which was due to
suspensions [55]. An increase in turbidity removal ef
[54]. Moreover, polymeric
ticles had a negative charge; thus, the impulsion forces between the
lant. This lower ef
[53]. Thus, the doses of coagulant and
cblems are preferable because of the resulting high sedimentation ve-
cles [53]. Thus, the doses of coagulant and flocculant should be applic-
table for the treatment of BG wastewater.

Table 4 shows the effects of different doses of cationic polymer on
turbidity removal in BG wastewater with the addition of 2.2 mg/L of
PAC (initial pH = 8.1; turbidity = 1457 NTU; TDS = 684 mg/L; con-
ductivity = 454 μS/cm; ZP = −32 mV; and MPS = 1680 nm). Signifi-
cant decreases in turbidity (from 1457 to 37.3 NTU), TDS (from 684
to 14 mg/L), conductivity (from 454 to 28 μS/cm), and ZP (from
−32 to 4.55 mV) were observed with the addition of 0.5 mg/L of cationic
polymer and 2.2 mg/L of PAC (Table 4). An increase in the MPS (from
1680 to 17,800 nm) was also observed. Through flocculation, the
settling velocity of small particles bound within flocs can effect-
tively increase by several orders of magnitude [52]. Large and dense
flocs are preferable because of the resulting high sedimentation ve-
clos [53]. Thus, the doses of coagulant and flocculant should be applic-
table for the treatment of BG wastewater.

Table 5 shows the effects of different anionic polymer doses on
turbidity removal in BG wastewater with the addition of 2.2 mg/L of
PAC (initial pH = 8.1; turbidity = 1457 NTU; TDS = 684 mg/L; con-
ductivity = 454 μS/cm; ZP = −32 mV; and MPS = 1680 nm). Com-
pared to the cationic polymer, the observed turbidity removal ef-
ciciency was lower when an anionic polymer was used as the floccu-
lant. This lower efficiency could have been due to the fact that BG par-
ticles had a negative charge; thus, the impulsion forces between the
particles and polymer would have inhibited the formation of flocs
[54]. Moreover, polymeric flocculants can destabilize fine-particle
suspensions [55]. An increase in turbidity removal efficiency was ob-
served with increased anionic polymer addition, which was due to
the charge neutralization effect when more anionic polymer was
added [56]. Particles with negative charges would facilitate floccula-
tion when cationic flocculant was added [57]. When cationic polymer
was used, floc strength was higher due to the strong polymer chains
bonds that resulted from the formation of bridging between particles
[58]. Coagulation of negatively charged particles by charge neutrali-
zaation would effectively enhance the settling and dewatering charac-
teristics of flocs. Removal of larger-sized flocs would reduce membrane
fouling. Thus, to minimize the polymer dosage and extend the mem-
brane life, a cationic polymer should be used as the flocculant during
the flocculation process.

3.3.3. Effect of the initial pH value on turbidity removal

Fig. 10 presents the turbidity removal percentage with different
polymer dosages (a: cationic polymer addition; b: anionic polymer
addition) and initial pH values. These results show that the variation
in polymer dosage caused varied turbidity removal efficiencies under
different pH values. A higher turbidity removal efficiency was ob-
served when the pH was neutral and a lower dosage of polymer
was used. The turbidity removal efficiency dropped from 40 to 50%
when the pH value was 10 (Fig. 10). Gohary and Tawfik [49] reported
that a higher flocculation efficiency can be obtained if the initial pH is
less than 8. Thus, pH should be appropriately controlled to enhance
the flocculation efficiency. These results suggest that pH adjustments
would not be necessary prior to the coagulation/flocculation process
because BG wastewater has a neutral pH when it is discharged from
the factory. Moreover, a lower polymer dosage would be sufficient
for the enhancement of the flocculation process [59,60]. The

Table 7
Turbidity, TDS, COD, and NH3-N removal efficiencies after treatment using the three-stage system.

<table>
<thead>
<tr>
<th>Item</th>
<th>unit</th>
<th>BG wastewater</th>
<th>Coagulation/flocculation effluent</th>
<th>SW</th>
<th>SF</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductivity</td>
<td>μS/cm</td>
<td>8.1</td>
<td>6.2</td>
<td>6.4</td>
<td>7.6</td>
<td>7.3</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>1457</td>
<td>23.0</td>
<td>98.4</td>
<td>99.1</td>
<td>100.0</td>
</tr>
<tr>
<td>SS</td>
<td>mg/L</td>
<td>92.4</td>
<td>&lt;1</td>
<td>98.9</td>
<td>98.9</td>
<td>99.1</td>
</tr>
<tr>
<td>MPS</td>
<td>nm</td>
<td>1680</td>
<td>17,800</td>
<td>6780</td>
<td>940</td>
<td>985</td>
</tr>
<tr>
<td>TDS</td>
<td>mg/L</td>
<td>684</td>
<td>158</td>
<td>76.9</td>
<td>77.5</td>
<td>78.2</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>4.0</td>
<td>0.2</td>
<td>42.9</td>
<td>0.2</td>
<td>42.9</td>
</tr>
<tr>
<td>NH3-N</td>
<td>mg/L</td>
<td>0.35</td>
<td>0.2</td>
<td>42.9</td>
<td>0.2</td>
<td>42.9</td>
</tr>
</tbody>
</table>

[removal efficiency (%) = (influent value − effluent value) × 100/influent value].

a % = total removal efficiency by coagulation.
b % = total removal efficiency by SF.
c % = total removal efficiency by SW-UF.
d % = total removal efficiency by HF-UF.
e − = not available.

\[\text{turbidity}=\text{removal efficiency} \times 100/\text{influent value}].

\[\text{a} = \text{total removal efficiency by coagulation}.
\[\text{b} = \text{total removal efficiency by SF}.
\[\text{c} = \text{total removal efficiency by SW-UF}.
\[\text{d} = \text{total removal efficiency by HF-UF}.
\[\text{e} = \text{not available.}.

![Fig. 11. Variation in membrane fluxes versus time for two different tests with the application of HF-UF membranes.](image1)

![Fig. 12. Variation in membrane fluxes versus time for two different tests with the application of SW-UF membranes.](image2)
flocculation process caused the adsorption of flocs onto the organic polymer through the bridging mechanism [61].

Table 6 shows the residual metal concentrations in BG wastewater after the coagulation and subsequent UF processes (with 0.5 mg/L of cationic polymer and 2.2 mg/L of PAC). Although the polymer and PAC contained Cd, Mn, and Cr, the residual metal concentrations were low. Except for a higher concentration of Al (0.56 mg/L), the other metals had concentrations lower than 0.031 mg/L. A significant drop in metal concentrations was observed after the UF treatment (Table 6). Therefore, the adverse effects of coagulant and polymer addition on the RO membrane would be insignificant.

### 3.4. Treatment using the developed three-stage systems

The results from the pre-treatment study indicate that effective turbidity and particle removal can be obtained using coagulation/flocculation processes. Thus, coagulation/flocculation was applied as the first stage of BG wastewater pre-treatment followed by a second stage of SF and third stage using UF. In this study, the three-stage system was applied for BG wastewater pre-treatment prior to RO membrane purification for further water purification. Table 7 presents the removal efficiencies for turbidity, TDS, COD, and NH$_3$-N after processing using the three-stage pre-treatment system. These results show that approximately 98% of turbidity and 99% of SS were removed after the coagulation/flocculation process. The turbidity removal efficiency reached 99 and nearly 100% after treatment by SF and UF, respectively. Thus, the three-stage pre-treatment system could effectively remove nano-scale particles from BG wastewater and improve the water quality to minimize membrane fouling in the succeeding RO unit. However, increases in conductivity, MPS, and TDS were observed after the coagulation/flocculation process due to the addition of coagulant and flocculant in the first treatment stage. No significant declines in conductivity, MPS, TDS, COD, or NH$_3$-N were observed in the effluents of the three-stage system. This finding indicates that SF and UF were not capable of dissolved solid removal [5,62,63]. The MPS increased to 17,800 nm after the coagulation/flocculation process and then decreased to 6780 nm after the SF treatment. The MPS in UF effluents decreased to 940 and 985 nm after the SW-UF and HF-UF treatments, respectively, indicating that SF and UF were able to remove micro-scale particles. Thus, SF and UF units are appropriate pre-treatment alternatives for removing micro-scale particles and preventing fouling of RO membranes. Thus, the RO unit for dissolved solid removal can be installed after the three-stage system. In Taiwan, the suggested water reuse standards developed by industrial park for SS, TDS, turbidity, and conductivity are $<$5 mg L$^{-1}$, $<$500 mg L$^{-1}$, $<$2 NTU, $<$300 μS cm$^{-1}$, respectively. Thus, the treated water after RO unit is required to meet the suggested water reuse standards for industrial use.

In this study, two different pilot-scale operational processes were evaluated. In the first process, BG wastewater was treated by coagulation/flocculation followed by SF and UF. In the second process, only UF was applied. Fig. 11 shows the membrane flux for the two different tests with the application of HF-UF. In the first test, the pressure was controlled at 0.41 kg/cm$^2$ in the SF and UF units. The operational mode used pumping for 9 min and backwashing for 1 min. The results from this test show that solids were retained on the surfaces of sand filters and the UF membrane, and then inorganic fouling occurred. The measured fluxes for the first and second processes were 16 and 14 L/m$^2$ h, respectively, which indicate that a higher flux can be obtained with the coagulation/flocculation and SF pre-treatment. Fig. 12 presents the membrane flux for two different tests with the application of SW-UF. The measured fluxes for the first and second tests were 90 and 80 L/m$^2$ h, respectively. The results show that the coagulation/flocculation processes would ensure a high membrane permeate flux [64]. Furthermore, the permeate flux could be used to evaluate surface fouling and clogging problems. Song [65] reported a flux decrease of greater than 5% after the application of MF or UF membrane processes for solid/water separation. In this study, flux decreases of approximately 8% and 11% were observed when HF-UF and SW-UF membranes, respectively, were used compared to systems with pre-treatment (coagulation/flocculation followed by SF). This finding indicates that a higher flux would be obtained when a pre-treatment system is applied.

### 4. Conclusions

In this laboratory study, a three-stage pre-treatment system was developed to remove nano-scale particles from wastewater. The three-stage pre-treatment system involved chemical coagulation/flocculation followed by SF and UF processes. Conclusions of this study include the following:

- Significant amounts of turbidity and particles (up to 98%) could be removed through chemical coagulation/flocculation processes. However, the SF system alone could not effectively remove nano-scale particles from BG wastewater.
- More than 95% of turbidity and particles could be removed with the application of the UF unit [spiral wound (SW) UF membrane or hollow-fiber (HF) UF membrane] after the coagulation/flocculation/UF processes.
- In the UF system, a higher flux could be obtained when the pre-treatment system (coagulation/flocculation followed by SF) was applied.
- The results of this study indicate that the three-stage pre-treatment system is appropriate for the treatment of nano-particle-containing wastewater prior to the use of an RO membrane for further water purification.
- The results from this study will be helpful in designing a scaled-up system for practical applications.

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### References
