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Coagulation and Filtration of Nanoparticles in Wastewater from Hsinchu Science-Based Industrial Park (HSIP)

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Abstract: The Hsinchu Science-based Industrial Park (HSIP) is a "high-tech" manufacturing base in Taiwan. Wastewater from the HSIP contains numerous nanoparticles, which are difficult to remove by conventional coagulation-sedimentation processes, and are the main foulants to ultrafiltration (UF) and reverse-osmosis (RO), membrane in filtration. This investigation observed that the coagulation rates of nanoparticles in wastewater could be significantly increased by raising the solution temperature to over 65°C, thus yielding large and compact aggregates. The proposed thermal treatment could considerably reduce the fouling potentials of UF and RO membranes, and thus represents a suitable pre-treatment for producing clean water from HSIP wastewater.

Keywords: HSIP, wastewater, nanoparticles, coagulation, thermal treatment

INTRODUCTION

To facilitate industrial development, the Taiwanese government has constructed 96 industrial parks island wide. The Hsinchu Science-based Industrial Park (HSIP), established in 1980, contains 350 companies, including

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representatives of the integrated circuit (IC), computers and peripherals, telecommunications, optoelectronics, biotechnology, and precision machinery industries.

The HSIP has not only significantly influenced the development of Taiwan's economy, but also has established an international reputation in the semiconductor and related information industries. The HSIP currently has a secondary biological wastewater treatment and a following physical-chemical treatment with a capacity of 86,000 m^3 d^{-1}. Wastewater from the IC and optoelectronics industries is significant, and accounts for 95 % of the total flow rate, and 73 % of BOD and COD. Most wastewater is pretreated by the company that produces it before being discharged into the sewer and, on average has BOD 44 mg l^{-1}, COD 133 mg l^{-1}, SS ranging from 14 to 163 mg l^{-1}, and fluoride concentration ranging from 2 to 8 mg l^{-1}. The fluoride-containing wastewater and chemical mechanical polishing (CMP) wastewater dominated the wastewater stream, in which nano-sized CaF_2 and silica represent the primary particulate phase (1, 2).

Owing to the lack of clean water supplies in Taiwan, the HSIP companies are legally required to recover and reuse over 85% of whatever wastewater they produce. A wastewater recycling program thus has been implemented in the park; however, nano-sized particles require extremely high doses of polyaluminum chloride (PACl) to achieve successful coagulation, producing a large volume of sludge. Furthermore, the removal efficiency achieved by the conventional coagulation-sedimentation process is too low to prevent fouling of subsequent UF-RO membrane modulus (shown later). This study demonstrated that the nano-particles in HSIP wastewater stream were self-aggregated at temperatures exceeding 64°C. The coagulation mechanisms were monitored using the small-angle light scattering technique.

MATERIAL AND METHODS

The Sample

The Wastewater Works of the HSIP comprise a bar screen, aerated grit chamber, equalization tank, contact aeration stage, and chemical coagulation-sedimentation basin. The particles in the wastewater stream were primarily removed by adding polyaluminum chloride (PACl, with 20,800 ppm as Al) and anionic polyelectrolyte flocculant (FA-40B, polyacrylamide, Sumimoto Chemical Co., Japan, $MW = 1.2 \times 10^7$ with a medium charge density) to a chemical coagulation basin followed by sedimentation.

The pH, turbidity, and zeta potential of the wastewater samples were measured with a pH meter (6010, JENCO), turbidity meter (HACH Model 2100 AN), and zetameter (Zetasizer 3000 HS, Malvern, UK). The results for the original wastewater sample were 7.0 ± 0.1, 85.5 ± 0.2, and -20.2 ± 0.9 mV, respectively. The chemical oxygen demand (COD) and soluble COD of the original wastewater sample were 78.3 ± 1.6 and 66.5 ± 2.8 mg l^{-1}, respectively, indicating that roughly 85% of the COD in the wastewater was soluble. The size of the wastewater sample particles was determined using two particle sizers covering the size ranges 0.1–2000 μm (Mastersizer 2000, Malvern, UK) and 2 nm-3 μm (Zetasizer 3000 HS, Type A, Malvern, UK), respectively. Finally, the floc size as determined using the Mastersizer 2000 was 43.3 μm.

Coagulation and Membrane Test

Chemical coagulation tests using polyaluminum chloride (PACl) as coagulant were performed in standard jar testers. The 1,000-ppm PACl solution, with 11% available Al_2O_3, was slowly injected into the stirred water sample at 200 rpm for 60 s followed by 50 rpm for 8.5 min. The pH of the suspension was maintained at 7.0 by adding concentrated NaOH solution. The residual turbidities of supernatant of 2-hr settled coagulated samples were measured.

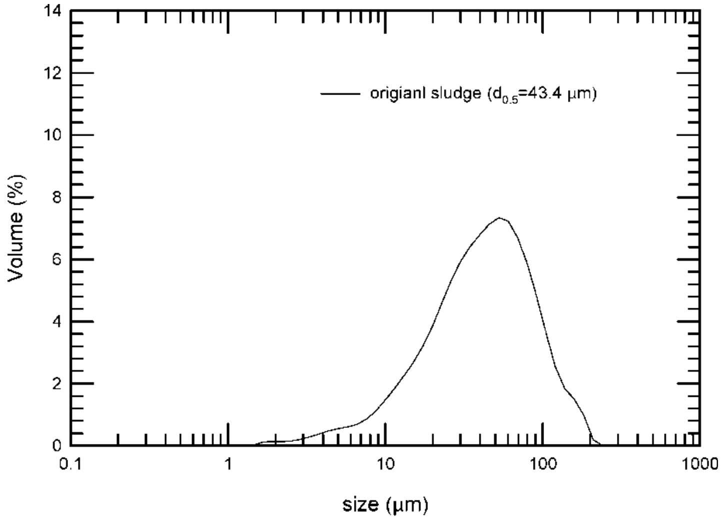
Thermal treatment of wastewater was performed by maintaining the sample in a 500 ml beaker at a specified temperature for 24 h. Part of the wastewater sample was first filtered using a 0.45 μm membrane and then heated to a prescribed temperature, and the size of the particles was continuously probed using the Zetasizer. The residual turbidities of supernatant of 2-hr settled treated samples were also measured.

The silt density index (SDI) of water samples was determined based on the decay in the time required to fill a 500-ml container using 30 psi of back pressure through a 0.45-μm cellulose acetate membrane (3). To demonstrate the fouling potential of the wastewater samples, a filtration apparatus with two filters, an ultrafiltration (UF) membrane (polyethersulfone membrane with MWCO = 14000 Da) followed by a reverse-osmosis (RO) membrane (polyamide membrane of MWCO = 200 Da), was set up and tested. The initially applied pressures of the UF and RO membranes were 2 kg cm^{-2} and 20 kg cm^{-2}, and the corresponding permeate recovery was 80% and 50%, respectively. Cleaning agents (citric acid and NaOH solutions) were adopted for membrane backwashing if the applied pressures increased to 3 and 28 kg cm^{-2}, respectively. The average times required for ten backwashing cycles were recorded and reported as the membrane cleaning frequencies. A long cleaning frequency denotes a low membrane fouling potential.

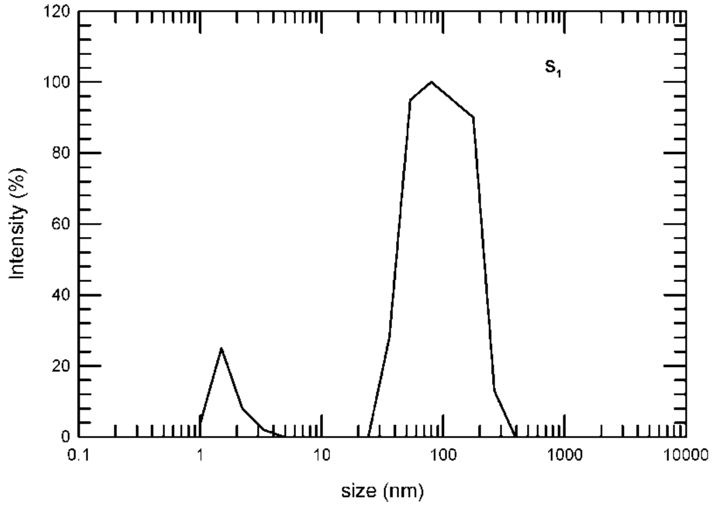
RESULTS

PACl Coagulation

Figures 1a and 1b illustrate the size distributions of particles in the wastewater stream detected for wastewater samples before and after filtering with a



(a)



(b)

Figure 1. Size distributions of particles in wastewater sample using (a) small-angle light scattering tester (Mastersizer 2000, Malvern, UK), (b) dynamic light scattering tester (Zetasizer HS, Malvern, UK).

0.45-μm filter paper. Three groups of particles were detected, with mean sizes 43.4 μm (Fig. 1a), 89.6 and 1.8 nm (Fig. 1b). Figures 2a–c illustrate microscopic photographs of particles in the HSIP wastewater stream. Large particles with size 30 μm (Fig. 2a), 1–4 μm (Fig. 2b), and two groups of particles of around 2–5 nm and 30–300 nm (Fig. 2c) are observed.

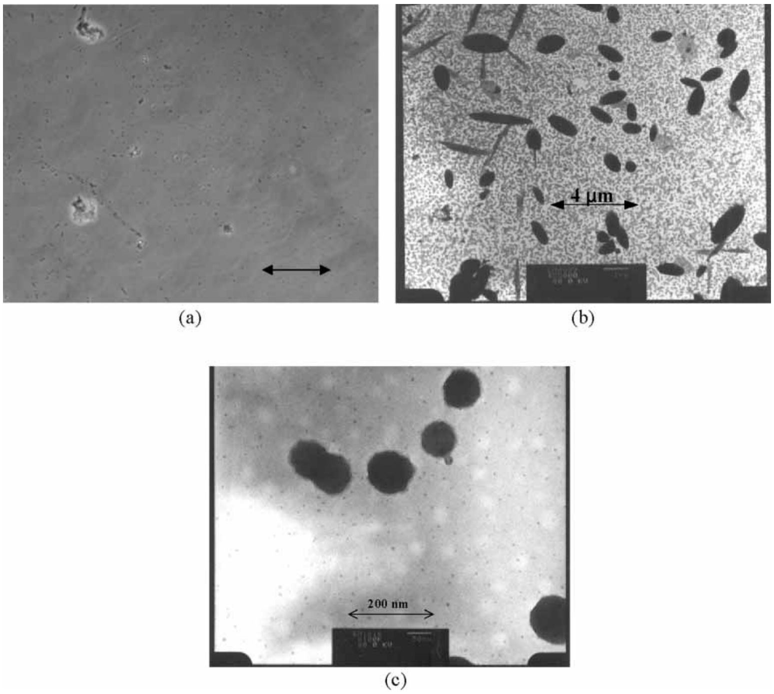


Figure 2. Particles in HSIP wastewater stream. (a) Phase contrast image (200X) of water sample with bar referring to 50 μm. (b) TEM image (5,000X) of particles in water sample filtered using 0.45-μm membrane. Bar refers to 4 μm length (c) TEM image (100,000X) of particles in water sample filtered using 0.45-mm membrane. Bar refers to 200 nm length.

Following 24 h settling, large particles could be completely removed from the supernatant, while submicron sized particles remained unsettled, resulting in a stable suspension that requires further treatment to destabilize the particles.

Table 1 shows the attributes of the water samples, before or after conditioning. Table 1 shows that a dose of PACl of 2.08 mg l^{-1} as Al could remove 44% of SCOD, while an increased dose did not increase the removal of SCOD from water. The PACl coagulation and following sedimentation could effectively remove supernatant turbidity from 6.4 to 0.76, 0.55 and 0.39 at PACl doses of 2.08, 6.24, and 10.4 mg l^{-1} as Al, respectively, resulting in a 88–94% reduction. The corresponding reduction in SDI of 24-h settled supernatant was from 64.7 for the original wastewater sample to around 26.3–27.7 for the coagulated samples, regardless of the PACl dose. Therefore, the effluent from the coagulation-sedimentation process still has high membrane fouling potential. The UF membrane could produce satisfactory effluents with SDI ranging from 2.4 to 3.0 given a PACl dose not exceeding 6.24 mg l^{-1} as Al. However, at 10.4 mg l^{-1} as Al, the SDI of

Table 1. Characteristics of water samples

	Original	2.08 mg l^{-1} as Al	6.24 mg l^{-1} as Al	10.4 mg l^{-1} as Al	Thermal treatment
COD (mg l^{-1})	78.3 ± 1.6	77 ± 3.1	75 ± 2.7	72 ± 2.6	75 ± 1.7
SCOD (mg l^{-1})	66.5 ± 2.8	37 ± 2.9	39 ± 2.2	37 ± 3.8	9.9 ± 2.6
Residual turbidity (NTU)[a]	6.4 ± 0.3	0.76 ± 0.2	0.55 ± 0.1	0.39 ± 0.2	0.08 ± 0.02
SDI of supernatant after 24 h settling (−)	64.7 ± 4.9	26.9 ± 3.1	27.7 ± 2.6	26.3 ± 2.9	8.5 ± 0.2
Cleaning frequency for UF membrane (h)	2.6	2.3	2.0	2.8	>100
SDI of effluent after UF (−)	3.0 ± 0.3	2.7 ± 0.4	2.4 ± 0.4	3.9 ± 0.8	1.7 ± 0.3
Cleaning frequency for RO membrane (h)	1.4	3.9	4.2	4.5	>100

[a]Measured with sample at 1 cm below water surface after 24 h settling.

effluent from UF membrane increased, indicating the presence of excess fine particles or other pollutants to water not rejected by UF owing to certain restabilization mechanisms.

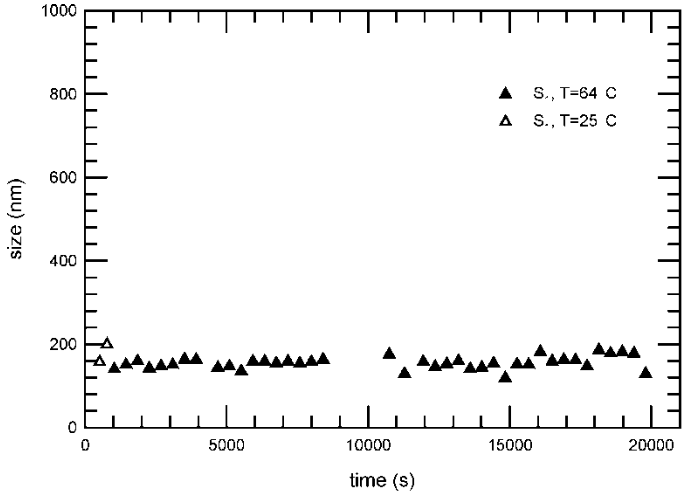
The average cleaning frequencies for UF and RO membranes were 2.6 h and 1.4 h for the original wastewater. That is, consistent with the high SDI (64.7) for original wastewater, the membranes were easily fouled when treated with original wastewater. The application of PACl coagulation could prolong the time required for backwashing the RO membrane (3.9–4.5 h), but did not significantly improve the UF membrane fouling. Therefore, the efficiency of PACl coagulation did not significantly influence UF membrane fouling, but did significance influence the cleaning frequency required for the following RO membrane. The dosed coagulants must intersect with certain micro pollutants from the original wastewater passing through the UF membrane to achieve RO fouling.

Thermal Treatment

The dynamic light scattering tests revealed that at a solution temperature of 64°C particle morphology (or size of floc) did not change significantly, with mean particle size ranging from 150 to 180 nm (Fig. 3a). However, at 65°C, particle agglomeration gradually occurred. In Fig. 3b, the solution temperature reached 65°C and then stabilized at $t > 2388$ s, while floc size increased correspondingly. The mean particle size increased with time. For instance, at $t = 17500$ s (4.86 h), the mean size of aggregates reached 650–800 nm, roughly 4–5 times the original size. Figure 4 illustrates the microscopic photograph of aggregate for the wastewater sample heated at 65°C for 24 h. Aggregates sized 200–300 μm were formed, about 1300–1600 times the original mean size. These aggregates had a compact structure, were easily settled, and their shape remained stable, with reducing temperature.

The existence of a threshold temperature for coagulation suggests a high energy barrier for the coagulation reaction between sub-micron particles. Since the interior structure of the thermally induced aggregates of particles was compact (Fig. 4), the mechanism corresponding to the noted agglomeration should be controlled by the rate of surface reaction. This hypothesis corresponds to the relatively slow coagulation rate compared to PACl coagulation, then hydrodynamic induced, diffusional processes controls those coagulation processes.

The thermally treated water contained large aggregates that were easily settled and separated from water. The 24–h settling supernatant had turbidity 0.08 ± 0.02 NTU, zeta potential -14.7 ± 1.2 mV, COD of 75 ± 1.7 mg l^{-1}, and SCOD 9.9 ± 2.6 mg l^{-1}. The corresponding reduction in SDI of 24-h settled supernatant was from 64.7 for the original wastewater sample to 8.5 for the thermally treated sample, representing around 30% of that of the PACl coagulated sample. The cleaning frequency of UF membrane exceeded



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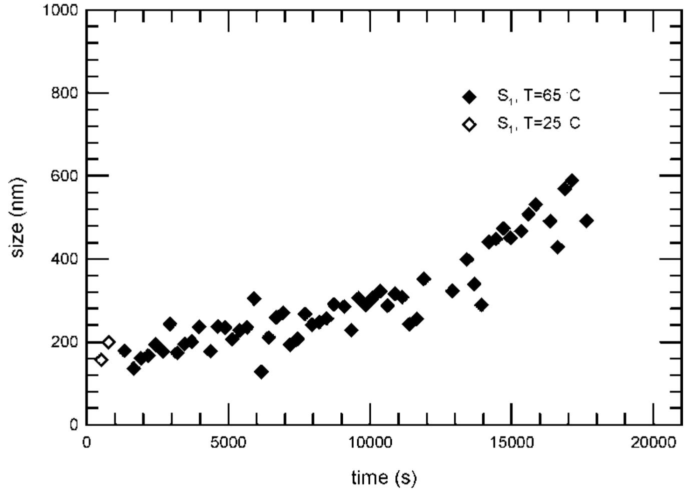

(b)

Figure 3. Mean floc size versus time plot. (a) Temperature increases from 25°C ($t = 0 - 800$ s) to 64°C ($t > 2345$ s). (b) Temperature increases from 25°C ($t = 0–800$ s) to 65°C at ($t > 2388$ s).

100 h. Moreover, the effluent of UF membrane has an SDI of 1.7, yielding a cleaning frequency exceeding 100 h for RO membrane. Thermal treatment at 65°C could satisfactorily condition wastewater from HSIP to a state of low fouling potential for the UF and RO membranes.

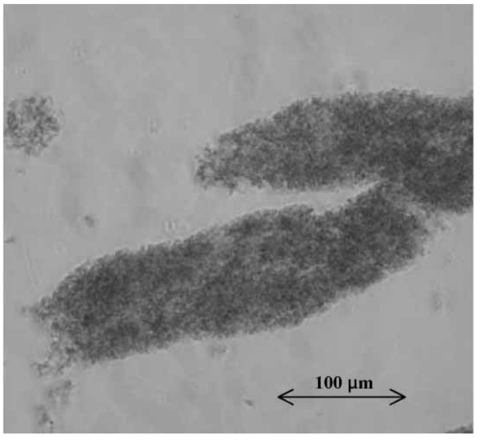

Figure 4. Microscopic photograph of aggregates after 24-h thermal treatment at 65°C (100X).

CONCLUSIONS

This study examined the efficiency of adopting polyaluminum chloride (PACl) coagulation or thermal treatment at 65°C for removing nanoparticles from wastewater of the Hsinchu Science-based Industrial Park (HSIP). The PACl coagulation and sedimentation could remove 44% of soluble chemical oxygen demand (SCOD), 88–94% of turbidity, and reduce the silt density index (SDI) from 64.7 to approximately 27. However, the effluent subsequently yielded still had high potential to foul the ultrafiltration (UF) and reverse-osmosis (RO) membrane in filtration. To maintain the suspension at a temperature exceeding 65°C stimulated particle agglomeration to produce large and dense aggregates. This thermal treatment could remove 85% of SCOD, 98.5% of turbidity, and reduce SDI to 8.5. This treated water stream had low fouling potential to UF and RO membranes, and thus could be used as the source for reclaiming water for HSIP.

REFERENCES

1. Chuan, T.C., Huang, C.J., and Liu, J.C. (2002) Treatment of semiconductor wastewater by dissolved air flotation. *J. Environ. Eng., ASCE*, 128: 974–980.
2. Yang, G.C.C., Yang, T.Y., and Tsai, S.H. (2003) Crossflow electro-microfiltration of oxide-CMP wastewater. *Water Res.*, 37: 785–792.
3. ASTM D4189-82, *Standard Test Method for Slit Density Index (SDI) of water.*