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Nanoparticles in wastewater from a science-based industrial park—Coagulation using polyaluminum chloride

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Abstract

The Hsinchu Science-based Industrial Park (HSIP) is the hi-tech manufacturing hub of Taiwan. Wastewater from the HSIP contains numerous nano-sized silicate particles whose size distributions peak at 2 and 90 nm. A 3–5 mg l^{-1} as Al dose of polyaluminum chloride (PACl) was used in the field to coagulate these particles, but the removal efficiency was low. Laboratory scale tests indicated that although PACl coagulation removed 52% of the turbidity and 48% of the chemical oxygen demand (COD) from water, its effect on nano-particle removal was minimal. About 58% of the soluble COD was associated with colloidal Si particles. A light scattering test and transmission electron microscopy (TEM) demonstrated that the nano-particles agglomerated in approximately linear aggregates of sizes 100–300 nm. Prolonged contact between residual PACl and the nano-particles generated large aggregates with sizes of up to 10 μm and a fractal dimension of 2.24–2.63. The results presented herein should be of interest in the processing of ''high-tech'' wastewater that contains nanosized silica particles.

Keywords: Nano-particles; Coagulation; Fractal dimension; Removal

1. Introduction

The Taiwanese government has constructed 96 industrial parks across the island to facilitate industrial development. The Hsinchu Science-based Industrial Park (HSIP), established in 1980, is home to 350 companies in, for example, the integrated circuit (IC), computer and peripheral, telecommunications, optoelectronics, biotechnology and precision machinery industries. The HSIP has not only substantially affected the development of Taiwan's economy, but has also gained an international reputation in the semiconductor and related information industries.

The HSIP currently has a secondary biological wastewater treatment works and a physical–chemical treatment plant with a capacity of 86,000 $m^3 d^{-1}$. Wastewater from the IC and optoelectronics industries represents 95% of the total flow rate, and 73% of the biochemical oxygen demand (BOD) and the chemical oxygen demand (COD). Fluoride-containing wastewater and chemical mechanical polishing (CMP) wastewater dominate the wastewater stream, in which nano-sized CaF_2 and silica constitute the primary particulate phase (Chuan et al., 2002; Yang et al., 2003; Chang et al., 2004). Individual plants in HSIP must treat their wastewater prior to discharge to the works.

The lack of clean water in Taiwan is such that HSIP companies are legally bound to recover and reuse over 85% of their wastewater. A wastewater recycling program has thus been implemented in the park; however, nano-sized particles require high doses of polyaluminum chloride (PACl) to ensure coagulation, which forms a large volume of sludge. Moreover, the efficiency of particle removal by conventional coagulation–sedimentation is too low to prevent the fouling of subsequent UF-RO membrane modules (Chang et al., 2006). Although the effluent COD range (30–70 mg l^{-1}) has been well below the National Standards (100 mg l^{-1}) over the last 5 years, the HSIP has been asked by the local community to reduce its COD

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emission further to reduce the organic burden on the water body to which the effluent is discharged.

This work shows that the soluble COD of the effluent is closely related to the amounts of nano-particles in the HSIP wastewater stream. Then, the coagulation characteristics of these nano-particles were examined using the PACl used in the field works.

2. Material and methods

2.1. Samples

The wastewater works of the HSIP have a bar screen, an aerated grit chamber, an equalization tank, a contact aeration unit and a chemical coagulation–sedimentation basin (Fig. 1). Most of the particles in the wastewater stream are removed by adding a concentrated mother liquor of PACl (with 20,800 ppm as Al) to the chemical coagulation basin followed by sedimentation. The PACl dose ranges from 3 to 5 mg l^{-1} as Al.

The pH, turbidity and zeta potential of the wastewater samples collected at ports S_1–S_3 in Fig. 1 were measured using a pH meter (6010, JENCO), a turbidity meter (HACH Model 2100 AN), and a zetameter (Zetasizer 3000 HS, Malvern, UK). The pH, turbidity and zeta potential results of the sample S_1 were 7.0 ± 0.1, 85.5 ± 0.2 NTU and -20.2 ± 0.9 mV, respectively. The COD of the entire suspension and that after the 0.45 μm filtration (soluble COD) of S_1, measured using the standard methods of the Taiwan EPA (NIEA W517.50B), were 78.3 ± 1.6 and 66.5 ± 2.8 mg l^{-1}, respectively. Approximately 85% of the COD in the wastewater was in soluble form. The size of the particles determined using a Mastersizer 2000 (Malvern, UK) was 43.3 μm.

According to Table 1, the biological aeration unit does not effectively remove turbidity or SCOD. However, the chemical coagulation unit removed 52% of the turbidity and 48% of the COD. The effluent quality depends substantially on the performance of the final coagulation unit.

2.2. Coagulation tests

Chemical coagulation tests were performed in standard jar testers using PACl as a coagulant. The 1000 ppm PACl solution, with 11% available Al_2O_3, was slowly injected into the water sample S_1 which was stirred at 200 rpm for 60 s, and then at 50 rpm for 8.5 min. The residual turbidities and zeta potentials of the supernatant of 24 h settled coagulated samples were measured. Each experiment was repeated under identical conditions. Data reproducibility was within 2% in most cases.

Particle sizes were measured by dynamic light scattering in water samples filtered through a 0.45-μm filter, using an argon laser tube (Lexel 95 2W TEM Argon), a digital correlator BI-9000AT and a photomultiplier tube EMI 9863/350 (Brookhaven Instruments Co., USA). Images of nano-particles were obtained using a transmission electron microscope (TEM, JEM-2000EX) equipped with a side-entry double-tilt specimen holder and operated at 200 kV at a maximum magnification of 400,000×. The fractal dimension of the aggregates was determined by dynamic light scattering (using a Malvern 4800 autosizer with a 7032 correlator and an He–Ne light source with a maximum power of 100 mW). The scattered light was collected at angles between 15° and 90°, and the intensity I was plotted as a function of the wave vector, Q. The log–log plot of I against Q data collected in scattering tests was linear with a gradient of $-D$, which is called the mass fractal dimension of the aggregates. This Malvern sizer was also adopted to measure the size of the aggregates between 0.02 and 2000 μm. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AEA) was performed using an Elan-6000 spectrometer (Perkin Elmer Co., USA) to identify the elements the in supernatant of the water samples.

3. Results and discussion

3.1. Nano-particles

Figs. 2a and 2b plot the size distributions of particles in the filtered water samples S_1 and S_2. Two groups of nano-particles were observed, with mean sizes of approximately 90 and 2 nm. Comparing Figs. 2a and 2b reveals that the biological treatment stage of the HSIP (Fig. 1) is almost entirely ineffective in removing nano-particles. Similar

Table 1
The characteristics of sample S_1–S_3

	S_1	S_2	S_3
pH	7.0 ± 0.1	6.9 ± 0.1	7.5 ± 0.1
Turbidity (NTU)	85.5 ± 0.2	93.2 ± 0.3	41.2 ± 0.1
Turbidity after 24 h settling (NTU)	6.4 ± 0.3	5.29 ± 0.55	1.35 ± 0.1
Zeta potential (mV)	-20.2 ± 0.9	-18.8 ± 0.8	-17.6 ± 0.3
COD (mg l^{-1})	78.3 ± 1.6	63.7 ± 2.1	40.2 ± 0.8
SCOD (mg l^{-1})	66.5 ± 2.8	57.3 ± 2.1	34.0 ± 1.2
Floc size (μm)*	43.3	47.2	146

*Measured using Mastersizer 2000, Malvern, UK.

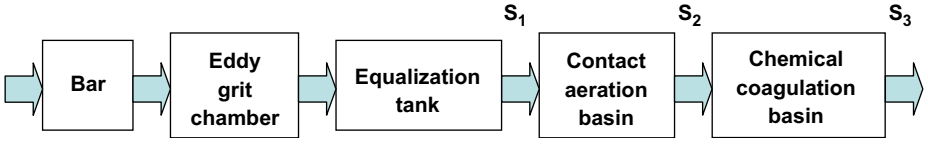

Fig. 1. The schematic of the treatment plant of HSIP.

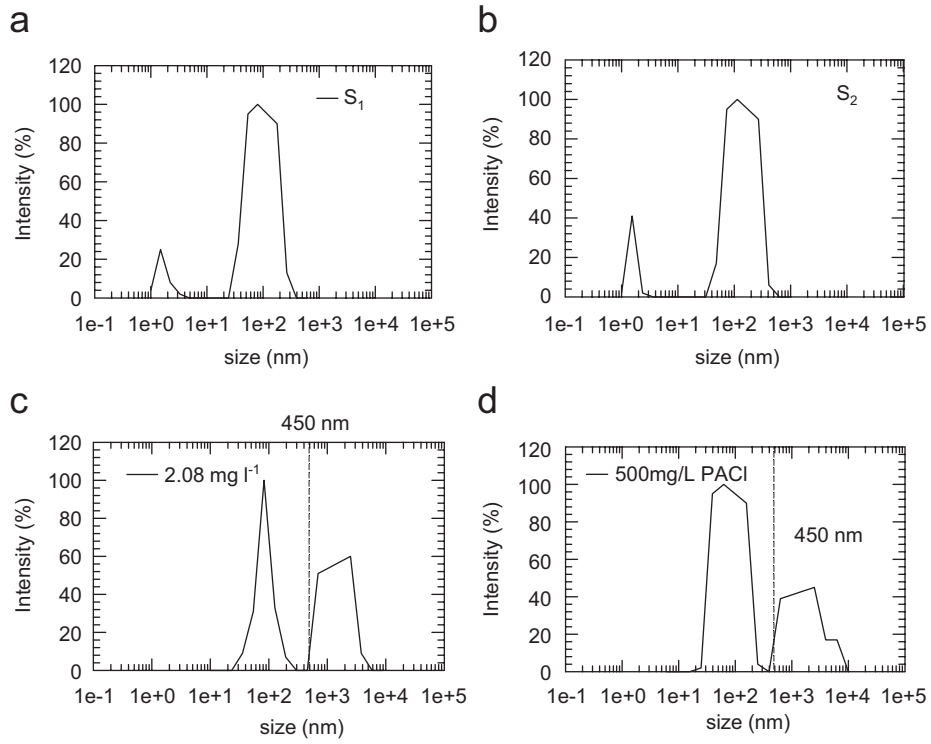

Fig. 2. Size distributions of particles in wastewater samples: (a) Sample S_1 filtered with 0.45-μm filter; (b) sample S_2 filtered with 0.45-μm filter; (c) effluent from sample S_1 coagulated with PACl dose of 2.08 mg l^{-1} followed by 0.45-μm filtration; (d) effluent from sample S_1 coagulated with PACl dose of 10.4 mg l^{-1} followed by 0.45-μm filtration.

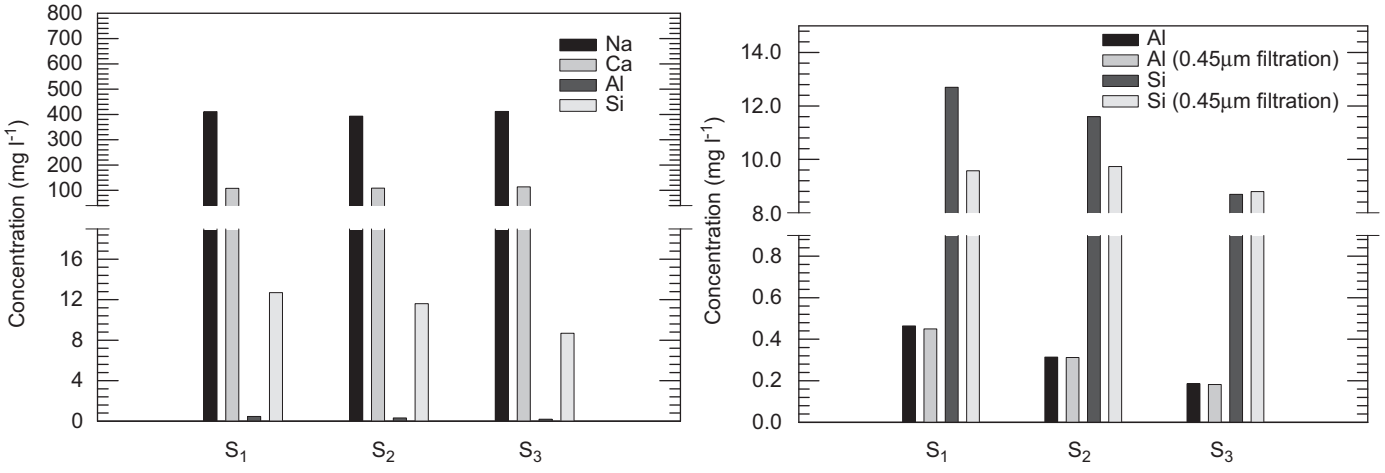

Fig. 3. Concentrations of certain chemical elements in water samples.

particle size distributions of the 24 and 48 h settling samples were noted (data not shown), indicating that the nano-particles in the water samples were not settleable in the test.

The metal elements in the filtered water samples detected by ICP-AES included Na, Ca, Si and Al (Fig. 3), of which Na and Ca were the products of neutralization and the removal of fluoride in the wastewater pre-treatment units in individual plants. The CMP wastewater streams contained mainly Si and Al particles. The 0.45 μm filtration removed only 15% of the Si from the water. Additionally, the solubility of silica in water is low. Therefore, most of the Si in the investigated filtered water samples was in colloidal (<0.45 μm) form.

According to Fig. 3, the concentrations of Na and Ca did not drop after contact aeration or chemical coagulation (Fig. 1). The biological unit removed 9% of Si, mostly from the suspended particles fraction (>0.45 μm). The chemical coagulation unit effectively removed most of the suspended particles, but the removal rate of the colloidal fraction was limited. Although 3–5 mg l^{-1} as Al of PACl was directly added to the chemical coagulation unit (Fig. 1), only

approximately 9% of the colloidal Si-particles were removed. The presented wastewater treatment process exhibits a very low efficiency of removal of nano-particles.

3.2. PACl coagulation

Fig. 4 plots the zeta potential and residual turbidities of coagulated water samples following settling for 24 h. The PACl dose did not considerably affect the zeta potential. Accordingly, charge neutralization is not the dominant mechanism by which particles are destabilized in the system of interest. The residual turbidity of the supernatant of the original S_1 was 6.42 NTU. Adding a PACl dose to an Al concentration of 2.08 mg l^{-1} significantly reduced the residual turbidity to 0.78 NTU, yielding a turbidity removal ratio of 87%. Further increasing the PACl dose incrementally reduced residual turbidity.

Fig. 2 also plots the size distributions of nano-particles in the wastewater sample S_1, following coagulation, sedimentation and 0.45 μm filtration. With a PACl dose of 2.08 mg l^{-1} as Al, particles of sizes 1–5 nm were effectively coagulated and removed. Adding more PACl did not greatly alter the size distribution, but yielded aggregates with sizes of up to 10 μm (Fig. 2d). Since the samples referred to in Figs. 2c and 2d were those after 0.45 μm filtration, aggregates of size >0.45 μm were formed by the self-agglomeration of residual particles in the effluent. This phenomenon does not occur in raw water samples, and so was caused by the action of residual PACl in the filtered effluent.

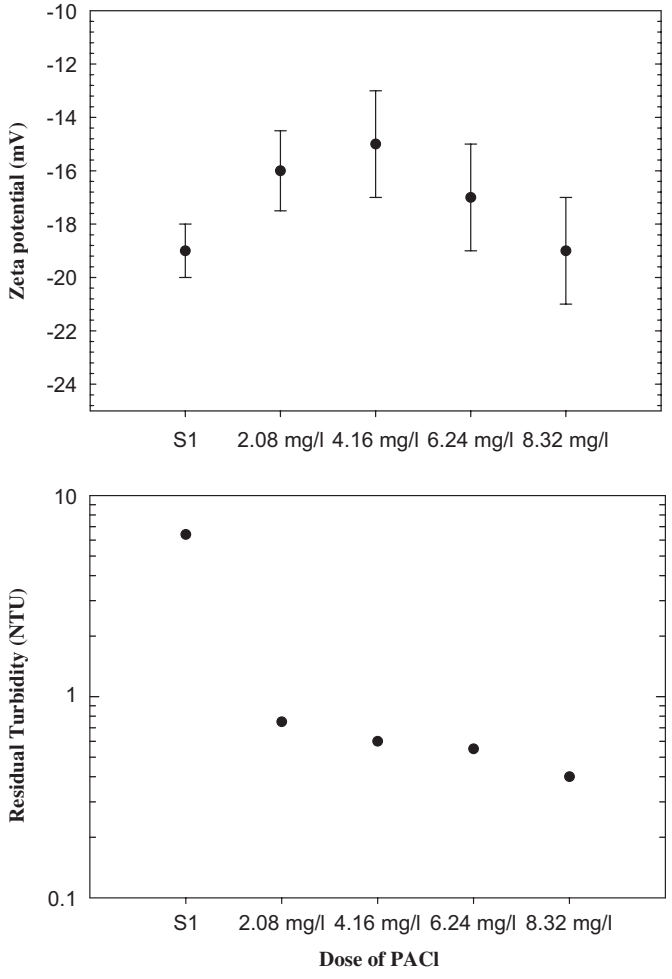

Fig. 4. Zeta potentials and residual turbidities of supernatant of water samples S_1.

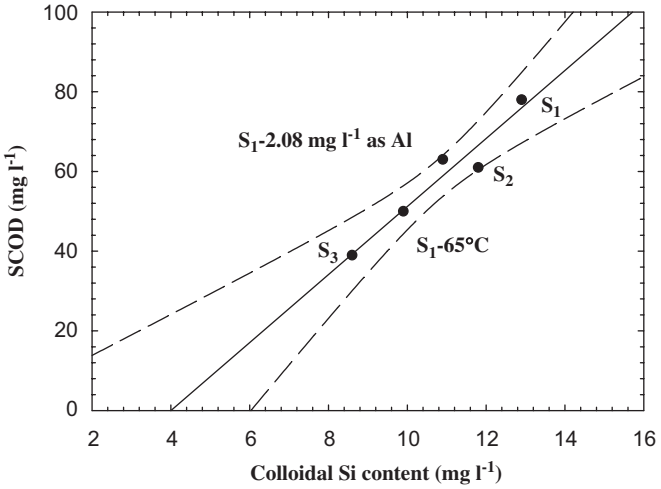

Fig. 5. Soluble chemical oxygen demand (SCOD) versus Si content in 0.45-μm filtered water samples. Solid line: correlation line; dashed curves: curved for 95% confidence intervals. S_1−2.08 mg l^{-1} as Al denotes the sample S_1 after coagulation at 2.08 mg l^{-1} as Al and subsequent sedimentation.

Fig. 5 plots the soluble COD and the colloidal Si content in the water samples S_1–S_3, and the corresponding data following coagulation. For comparison, another sample underwent thermal treatment at 65 °C (Chang et al., 2006). SCOD was linearly correlated with Si content according to SCOD = 8.54 Si −34.2 (in mg l^{-1}), with $r^2 = 0.94$. This result reveals that the substances in the filtered wastewater samples from HSIP in the COD test were strongly associated with the included Si nano-particles. The linear correlation can be extrapolated to the SCOD = 0 mg l^{-1} axis at Si = 4 mg l^{-1}, indicating that only approximately 58% of the colloidal Si particles effectively adsorbed SCOD, while the remaining 42% could not. However, SCOD in the effluent from HSIP can be further reduced, as requested by the local community, only by the effective removal of Si nanoparticles in the coagulation–sedimentation unit. Further work must be undertaken to verify the correlation between the concentrations of colloidal Si particles and the SCOD.

3.3. Particle Aggregates

Fig. 6 presents the I–Q plots of the original and coagulated S_1 samples. The gradient of the I–Q curve was close to −1 over the size range 140–300 nm, indicating that the aggregates have a dimensionality of about unity, a linear structure.

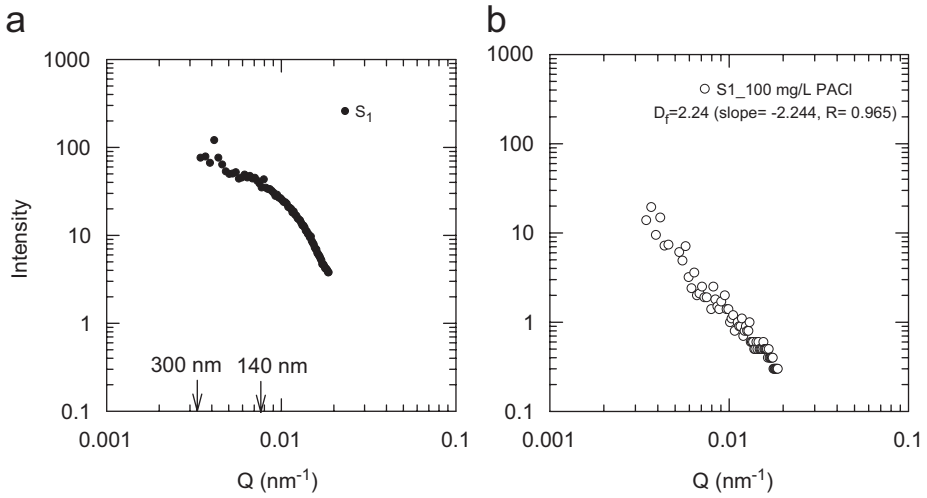

Fig. 6. The I–Q plots for water samples after 0.45-μm filtration: (a) original S_1, corresponding to Fig. 2a; (b) coagulated S_1, corresponding to Fig. 2c.

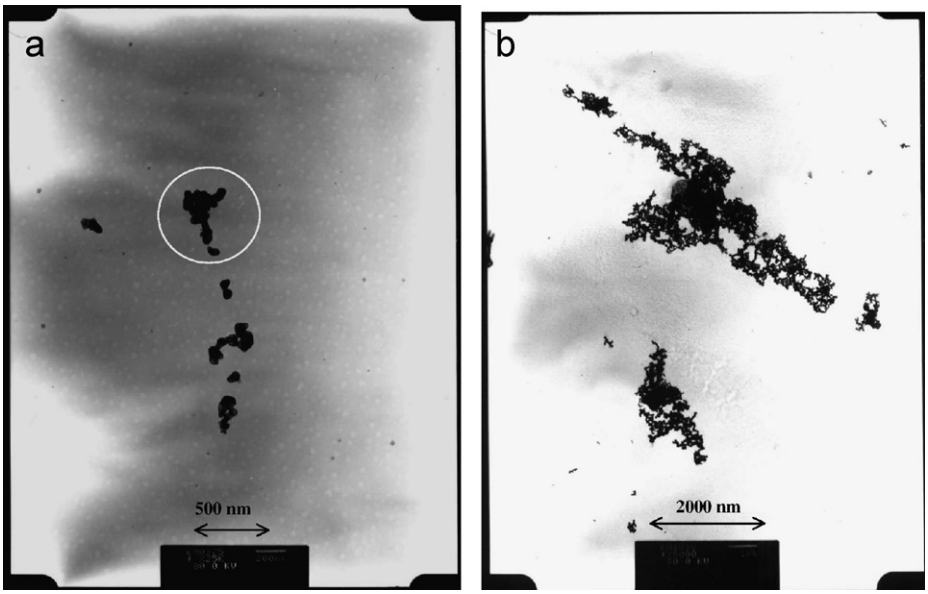

Fig. 7. TEM images of particles in water samples: (a) aggregates in sample S_1 after 0.45-μm filtration. 25000 × magnification; (b) aggregates in sample S_1 after coagulation of PACl dose of 2.08 mg l^{-1} as Al followed by 0.45-μm filtration. 10,000 × magnification.

Following aggregation, the I–Q data exhibits a linear correlation over the range 30–300 nm. For example, as Fig. 6b indicates, linear regression of the I–Q data for a PACl dose of 2.08 mg l^{-1} as Al yields a gradient of -2.24 ± 0.06 with $r^2 = 0.97$. The fractal dimensions of the coagulated samples thus estimated are 2.24 ± 0.06, 2.30 ± 0.07, 2.56 ± 0.05, 2.63 ± 0.04 and 2.49 ± 0.07, for PACl doses as Al of 2.08, 4.16, 6.24, 8.48 and 10.6 mg l^{-1}, respectively. Restated, the self-agglomeration of fine particles in the 0.45 μm filtered water samples generated aggregates whose fractal dimensionality increased with PACl dose.

Figs. 7a and b show the TEM images of the aggregates in the original and the coagulated water samples (2.08 mg l^{-1} as Al). In the original water sample (Fig. 7a), linear aggregates of size 100–300 nm, as determined by the light scattering test (Fig. 6a), are observed. Numerous particles of size < 10 nm were dispersed in the sample. Adding a coagulant caused particle agglomeration to form a large, fractal-like structure.

The nano-particles in the wastewater of HSIP coagulated to a limited extent (Fig. 7a). These particles with a size of 100–300 nm could not be effectively removed from the sedimentation basin. The interception efficiency of a normal sand filter is also doubtful. However, the noted self-agglomeration of residual fine particles in filtered water samples reveals that retaining the effluent from the coagulation–sedimentation basin for 24 h in a calm hydrodynamic environment, and then rapidly filtering it through sand, may represent a cost-effective way to effectively remove particles in the effluent from HSIP, thereby reducing the associated SCOD (Fig. 5).

4. Conclusions

Hsinchu Science-based Industrial Park (HSIP) is a "high-tech" hub for Taiwan's economy. It is home to the integrated circuit (IC), computer and peripheral, telecommunications, optoelectronics, biotechnology and precision machinery industries. The wastewater of HSIP contains numerous nanosized silicate particles whose size distributions peak at 2 and 90 nm, which are not effectively removed by the existing works, which use a secondary biological stage and a coagulation–sedimentation unit with PACl as a coagulant. Laboratory scale tests revealed that about 58% of the soluble COD was associated with the colloidal Si particles. The effective removal of Si nano-particles is critical to fulfilling the demands of the local community to reduce further COD emission from HSIP.

Although not significantly affecting the zeta potential, the PACl dose did reduce the residual turbidity of the supernatant from 6.42 NTU to under 1 NTU with a PACl dose of 2.08 mg l^{-1} as Al. A further increase in the PACl dose caused an incremental drop in residual turbidity. A light scattering test and transmission electron microscopy (TEM) imaging demonstrated that the nano-particles agglomerated to generate linear aggregates of size 100–300 nm. With a PACl dose of 2.08 mg l^{-1} as Al, the particles of size 1–5 nm were effectively coagulated. Adding more PACl did not greatly change the size distribution of particles. Prolonged contact between residual PACl and nano-particles formed large aggregates of size up to 10 μm and a fractal dimension of 2.24–2.63, facilitating COD removal from the wastewater. The results presented herein should be of interest in processing "high-tech" wastewater that contains nanosized silica particles.

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