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Treatment of wastewater containing nano-scale silica particles by dead-end microfiltration: evaluation of pretreatment methods

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Abstract

Chemical mechanical polishing (CMP) is the process to planarize wafer in the IC manufacturing. In the process, a large amount of ultra pure water is used to clean the surface of the wafer, which generates large quantity of wastewater containing high concentration of nano-scale silica particles. The wastewater is generally treated with the traditional coagulation/sedimentation process, producing large quantity of sludge. In this study, a microfiltration (MF) process coupled with chemical pretreatment was investigated to separate the nano-scale particles from the CMP wastewater to reclaim the water. Wastewater was filtered through a polytetrafluoroethylene membrane of pore size 0.5 μm at a low vacuum pressure (0.65 kg/cm^2). The permeate flux was monitored and the degree of irreversible fouling of the membrane was estimated. The SEM images of the fouled membrane and the cake layer were used to diagnose the mechanism of membrane fouling. Several coagulants and flocculants were tested for their potential use prior to microfiltration. Polyaluminum chloride (PACl) plus cationic polyacrylamide (PAA) were selected for pretreatment, and their effects on permeate flux and fouling of the membrane were examined. The results indicated that PACl improved silica removal substantially. The addition of trace amount of PAA effectively increased the size of the flocs, and subsequently enhanced the permeate flux. The performance of the dead-end MF operation depended strongly on the turbidity of the influent. The addition of oxidant, i.e. Chlorine, after the flocculation reduced the irreversible fouling and promoted flux recovery of the membrane.

Keywords: CMP wastewater; Coagulation; MF; Fouling; Silica removal

1. Introduction

Chemical mechanical polishing (CMP) process is commonly practiced in the IC manufacturing, in which colloidal silica is used to planarize the oxide wafer surface. During the process, a large amount of ultra-pure water is used to clean the surface of the wafer, which generates large quantity of CMP wastewater containing high concentration of nano-scale particles. There are

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two kinds of fine particles, SiO_2 from the oxide CMP process and Al_2O_3 from the metal CMP process. Both particles are within nano-scale. As more IC fabs are being built in Taiwan, the treatment and reuse of CMP wastewater has become increasingly necessary. Until recently, the majority of the chip-making fabs rely on the conventional coagulation-flocculation process to treat the CMP wastewater. To meet the discharge limit, wastewater treatment units normally apply high dosage of coagulants to enlarge the nano-scale particles in 100 times to improve settling. This not only boosts the cost for chemical use but also produces large amount of sludge. An alternative is to separate the particles from the wastewater by using microfiltration (MF).

Many researchers have discovered that with a MF process the required coagulant dosage can be reduced substantially, which subsequently reduced sludge production [1,2]. Most of the studies on MF process have focused on maintaining the permeate level under the regulation limit. Studies on enhancing the performance of MF operation by mitigating membrane fouling with pretreatment are scarce.

The performance of MF in water and wastewater treatments can be significantly enhanced by the addition of inorganic coagulants [3]. It is a common practice to add flocculants to the feed to improve flux. In order to produce strong large flocs, polymeric coagulants/flocculants have been tested on wastewater containing high concentration of silica [1,4]. Due to the high negative charge of the silica surface (around –50 mV) [5], aluminum salts have been considered a prominent coagulant for silica removal [6,7]. In this study, we focused only on oxide CMP wastewater which contains mainly SiO_2 abrasives. The aim of this paper is to discuss the performance of MF operations in terms of particles size distribution, membrane flux and backwash efficiency as well as the degree of irreversible fouling and fouling mechanisms subject to different pretreatments.

2. Materials and methods

In this study, the oxide CMP wastewater samples were obtained from a semiconductor fab in the Hsinchu Science-based Industrial Park (HSIP) in Taiwan. A laboratory scale batch setup was designed to simulate the operation, as shown in Fig. 1. The coagulated feed water stored in a 3-L beaker was pumped through the MF by a vacuum pump and the permeate flux was continuously recorded by using a balance connected to a computer. At backwash, the 3-way valve was opened and the backpulse pressure was provided by the pump to drop down the cake.

The MF composite membrane (Gore Corp., USA) containing a thin active layer of polytetra-

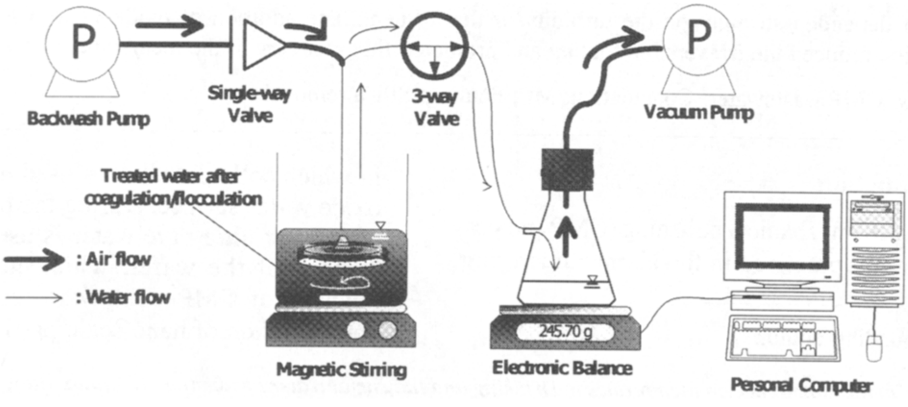

Fig. 1. Schematic of experimental set-up for dead-end membrane filtration.

fluoroethylene (PTFE) and a supporting layer of polypropylene (PP) was used for the filtration experiments. The membrane was in disc shape with an effective membrane area of 0.002 m^2 and nominal pore size of 0.5 μm. The filtration was operated at low vacuum pressure of 0.65 kg/cm^2. Turbidity was measured by a turbidity meter (WTW, Turb555, Germany), and total silica concentration was determined by an Inductively Coupled Plasma (ICP, Jobin-Yvon Corp., JY24, France) at wavelength of 212.4 nm. Dissolved silica concentration was determined by the molybdosilicate method (USEPA Method 4500) using a spectrophotometer at wavelength of 452 nm (HACH, DR/4000, USA). Two kinds of particle size distribution analyzer were used in this experiment. For raw water sample, a Mastersizer 2000 (Malvern corp., GB) was used, of which the detection range is between 20 nm and 2,000 μm. For treated wastewater, a Zetasizer nano ZS (Malvern Corp., GB) with lower detection range of 0.6 nm~6 μm was employed.

Jar tests were conducted to determine the optimal PACl (Showa Chemicals Corp., Japan) dosage as well as the operational pH for the pre-coagulation. After coagulation, the cationic polyacrylamide (PAA, Zimmite Corp, Taiwan) was applied additionally to evaluate its effect on membrane fouling. Oxidant, namely, sodium hypochlorous (NaOCl, Wako Pure Chemicals Inc., Japan) was added to test the effect of oxidation on membrane flux and fouling. The flocs after coagulation/ flocculation pretreatment were characterized via the floc-settling test. The mechanism of membrane fouling was investigated by examining the characteristics of the flocs and the particle size distributions prior to the membrane filtration.

3. Results and discussion

3.1. Characteristics of oxide CMP wastewater

Due to its caustic chemical content, the pH values of the oxide CMP wastewater were generally between 7.9 and 8.9. The turbidity of the test samples varied from 196.5 to 340.4 NTU depending on the types of the CMP process. The total silica concentrations varied from 489.0 to 934.2 m g/L as SiO_2, and their corresponding dissolved silica concentrations were between 41.8 and 70.2 mg/L as SiO_2. The sample wastewater contained particles of sizes ranging from 70 nm to 250 nm. After filtering through a membrane of pore size 0.1 μm at a low vacuum pressure (0.65 kg/cm^2), the silica particles landing on the membrane surface were observed by the SEM (TOPCON, ABT-55, Japan), as shown in Fig. 2. The SEM image of the fouled membrane showed that silica particles in the CMP wastewater led to serious scaling, and the cake layer was dense and nonporous in appearance. It implied that the nano silica particles polymerized on the MF membrane, suggesting the need for appropriate pre-treatment.

3.2. Particle size distribution of coagulated and flocculated samples

The decline of membrane flux after backwash indicated serious membrane fouling. Pretreatment of the sample by coagulation/flocculation could alleviate the fouling by enlarging the floc size.

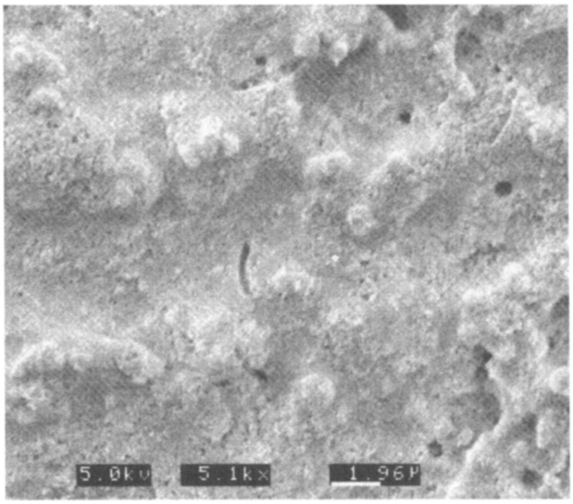

Fig. 2. SEM image of silica particles on the membrane surface (5.0 kv, 5.1 k).

Previous study on coagulation of CMP wastewater in our lab has found that the optimal dosage of PACl was 30 mg/L as Al at pH 6. Particle size distributions of raw, coagulated and flocculated CMP wastewater are shown in Fig. 3. After coagulation, the average particle size of the oxide CMP wastewater was enlarged significantly from 0.2 μm to 100 μm. The particles were further enlarged to 297 μm by the addition of PAA possibly by promoting the adsorption of particles and the subsequent bridging of particle-polymer-particle.

3.3. Microfiltration test

Microfiltration test was conducted by direct filtration of two sample wastewaters pretreated by PACl coagulation and PACl coagulation plus PAA flocculation. The flux and the accumulated permeate of the microfiltrations are shown in Fig. 4. The flux decreased rapidly during the early stage of the filtration followed by a much slower decline. At the end of the filtration run, the average fluxes were 0.40 and 0.98 $m^3/m^2/h$ for respective

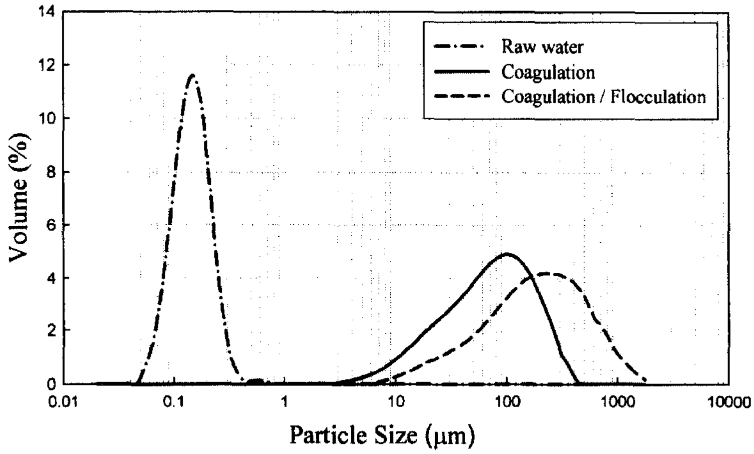

Fig. 3. Particle size distributions for raw, coagulated, coagulated/flocculated CMP wastewaters.

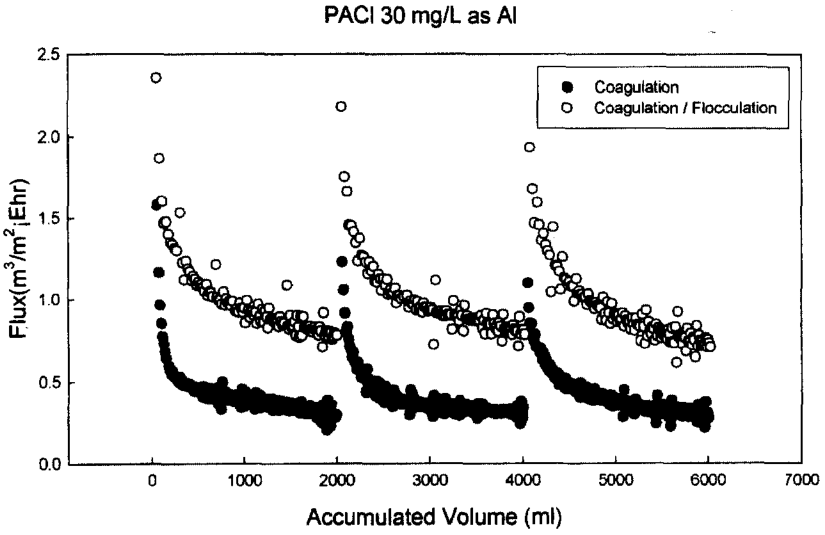

Fig. 4. Permeate flux and accumulative permeate volumes for coagulated and flocculated CMP wastewaters by MF membrane filtration after extensive period.

pre-treatment process. The permeate flux nearly doubled by adding a trace amount of cationic PAA, of which the average flux after backwash was kept stable. However, the initial flux dropped sequentially after each backwash for both treatments. The decline in flux of the next run is probably due to the reduction of effective pore diameter by the adsorption of particles smaller than the pores of the membrane on the pore. These small particles are difficult to remove from the membrane during the backwash.

3.4. Evaluation of irreversible fouling

Pure water fluxes of the fresh and backwashed MF membranes were determined to evaluate the degree of irreversible fouling of raw wastewater, coagulated wastewater, and coagulated/flocculated wastewater. In dead-end operation, the flux is given by

$$J_0 = \frac{\Delta P}{\mu(R_m)} \tag{1}$$

and

$$J'_0 = \frac{\Delta P}{\mu(R_m + R_i)} \tag{2}$$

where J_0 is the pure water flux before microfiltration (m^3/m^2/s), J'_0 is the pure water flux after microfiltration (m^3/m^2/s), ΔP is the pressure drop across the membrane (N/m^2), μ is the absolute viscosity of water at 20°C (kg/m s), R_m is the membrane resistance (m^{-1}), and R_i is the irreversible resistance of membrane (m^{-1}).

Table 1 lists the pure water flux recovery and membrane resistance of membrane filtrations of raw wastewater, coagulated wastewater, and coagulated/flocculated wastewater. Irreversible fouling was indicated by the difference in pure water flux between fresh and backwashed membrane. It shows that without pretreatment the recovered average flux was much smaller than those with pretreatment. The high content of fine particles, as shown in Fig. 3, in the raw wastewater was the main cause for the high irreversible resistance of the membrane, as high as 35.4×10^7 m^{-1}, and the poor recovery of the pure water flux. Precoagulation by PACl improved the particle size and reduced the potential for membrane fouling as evidenced by the significantly reduced irreversible resistance of the membrane, 3.80×10^7 m^{-1}. Addition of trace amount of cationic PAA reduced the irreversible resistance of the membrane further to 2.60×10^7 m^{-1} and the recovery of pure water flux was also dramatically improved from 27.0% to 84.3%.

3.5. Effect of coagulation on membrane fouling

It is believed that the characteristics of the particles play an important role in fouling behavior. Fouling characteristics have been described by the modified fouling index (MFI) [8]. By substitution and integration, the equation of membrane flux

Table 1
Recovery of pure water flux and membrane resistance for raw wastewater, coagulated wastewater, and coagulated/flocculated wastewater by membrane filtration

Influent sample	Raw sample	Coagulated sample (PACl 30 mg/L)	Coagulated and flocculated sample (PACl 30 mg/L + PAA (+) 0.1 mg/L)
Recovery of pure water flux, %	27.0	79.8	84.3
Membrane resistance R_m, 10^7 m^{-1}	13.1	14.9	13.7
Membrane resistance plus irreversible resistance (R_m+ R_i), 10^7 m^{-1}	48.5	18.7	16.3
Irreversible resistance R_i, 10^7 m^{-1}	35.4	3.80	2.60

can be rearranged into a linearized parabolic rate law equation,

$$\frac{t}{V}=\frac{\mu R_m}{A\Delta P}+\frac{\mu J}{2A^2\Delta P}V \tag{3}$$

where A is the effective membrane area, t is the filtration time, V is the permeate volume, and J is the fouling potential. The fouling mechanism in the filtration process can be predicted from the plot of t/V vs. V. By the MFI value, Boerlage et al. [9] has proposed three stages of fouling during filtration process: deep-bed filtration, cake filtration without compaction and cake filtration with cake compaction. The first stage is the blocking of membrane pores that leads to rapid decline in flux, the second stage is the cake filtration without compression, and the third stage is the cake filtration with compression.

Fig. 5 shows the difference in the plot of t/V vs. V by pretreatment. Abrupt reduction in permeate flux resulted from the rapid accumulation of ultra-fine particles of the raw water within membrane. Therefore, the three stages of filtration couldn't be differentiated. The filtration was mainly cake filtration with compaction. For the membrane filtrations underwent coagulation and coagulation/flocculation, a reflection point was found around the accumulated permeate (filtrate) volume of 700 ml. Prior to this point, the fouling was mostly contributed by pore blocking. When the flux approached a quasi-steady value, after collecting 700 ml of permeate, the fouling mechanism was switched to cake filtration without compression.

Addition of trace amount of cationic PAA after coagulation increased the size of floc substantially, which mitigated the fouling potential, as indicated by its relatively small MFI. Hence, the accumulated permeate volume was more than that of coagulation only, in a much shorter filtration time. When cake filtration without compression was the dominant fouling mechanism, the fouling phenomenon could be interpreted by the slope of the curve. As shown in Fig. 5, the t/V increased linearly with the total filtration volume, V, in the second stage. The greater slope indicated the greater membrane fouling without the flocculation of cationic PAA. Consequently, the coagulation/flocculation pre-treatment could lessen the degree of membrane fouling.

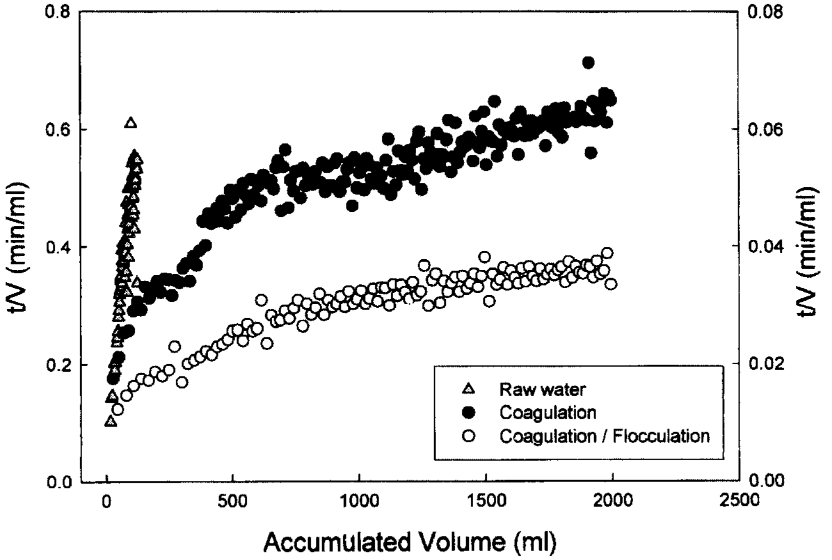

Fig. 5. Plot of t/V vs. V for raw, coagulated, and coagulated/flocculated CMP wastewater treatments by MF membrane filtration.

3.6. Effect of oxidant on recovery of pure water flux

Sodium perchlorine (NaOCl) was applied after the flocculation to test its effect on irreversible fouling. The effect of chlorine oxidation on membrane flux is shown in Fig. 6. The permeate flux of coagulation/flocculation/oxidation was about the same as that of coagulation only. This leads to the hypothesis that NaOCl can destroy the bridging between flocs, resulting in reduced floc size. The irreversible fouling and the recovery of pure water flux of the membrane were also evaluated. As shown in Table 3, after backwash, the pure water flux recovery of the membrane was promoted to 92.7% and the irreversible fouling was reduced to 1.20×10^{-7} m. Although NaOCl addition reduced the permeate flux, it improved the irreversible fouling substantially. It implied that the addition of NaOCl broke not only the bridging between flocs but also the bonding of the organic matters causing irreversible fouling.

3.7. Relationship between membrane flux and floc characteristics/particle size

The density, settling velocity, size and fractal dimension of the flocs can be measured with simple floc-settling test [10]. As shown in Table 2, membrane flux could not be explained by the characteristics of the flocs. The coagulation and membrane flux were most efficient at operational pHs of 6 and 7 which did not comply to the particle size, settling velocity and density of the flocs. Although the relationship between particles size of the influent and fouling potential of the membrane is well documented, the influence of settling velocity and density of the floc on membrane flux remained unclear. The quantity of smaller particles, especially those close to the pore size of the membrane, should be the major contributor to the decline of the membrane flux. Hence, the ratio of smaller particles in the suspension could be an index to predict membrane flux as well as membrane fouling.

Table 2
Characteristics of flocs, turbidity of supernatant after settling, and flux-related parameters for membrane filtration at different pH conditions

pH	4	5	6	7	8	9
Average diameter, mm	1.38	1.69	1.01	0.97	0.84	1.01
Settling velocity, mm/s	4.73	6.62	3.45	4.43	2.24	12.93
Effective density, kg/m^3	9.69	10.41	13.33	19.58	11.32	71.90
Fractal dimension, D_f	1.77	1.56	1.38	1.43	1.94	1.34
Turbidity of supernatant after settling, NTU	67.5	49.3	2.0	2.5	93.3	160.9
Recovery of pure water flux, %	76.6	77.6	87.3	84.8	83.8	37.7
$\bar{J}/J_o$, $\times10^{-2}$	0.75	0.96	2.11	1.68	1.16	0.31

Table 3
Recovery of pure water flux and irreversible fouling of three pretreatment conditions

Condition	Recovery of pure water flux (%)	Irreversible fouling ($R_i\times10^{-7}$ m^{-1})
Coagulation	81.8	3.6
Coagulation/flocculation	86.7	2.5
Coagulation/flocculation/oxidation	92.7	1.2

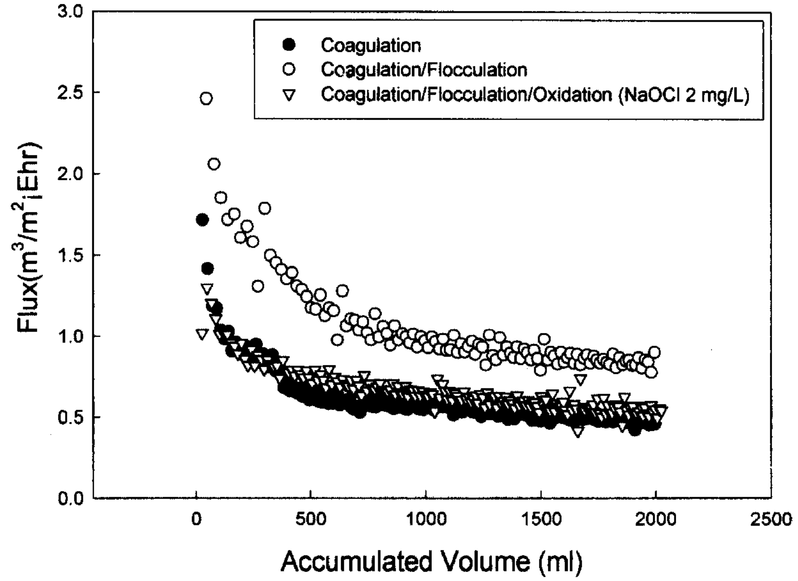

Fig. 6. Membrane flux vs. accumulative volume for CMP wastewaters treatment by MF membrane filtration with three different pretreatments.

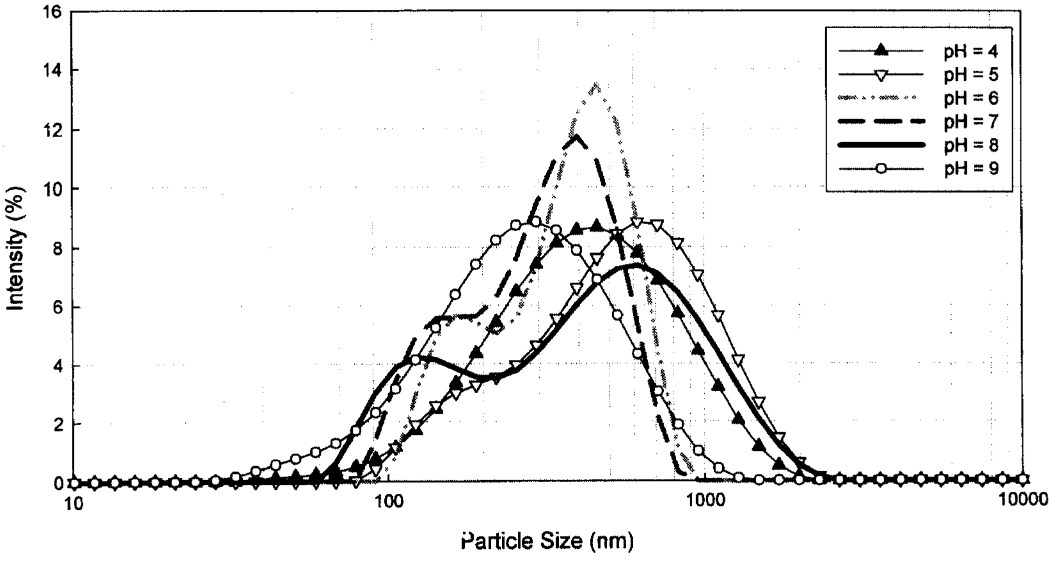

Fig. 7. Particle size distribution of supernatants after coagulation and quiescent settling at different pH conditions.

Fig. 7 shows the particle size distributions of supernatants after coagulation and quiescent settling at different pHs. Two types of particle size distributions were observed, one with two modes, those of pH 6, 7, and 8, and one with single-peak distribution. Of those with single mode distribution, largest particles occurred at pH 5, coinciding to the higher recovery in pure water flux >26%, as shown in Table 2. Of those with double-peak distributions, the distribution of particles gradually

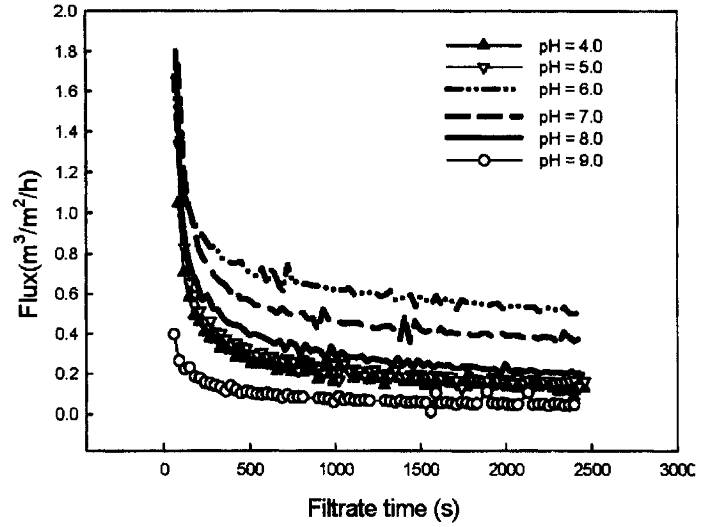

Fig. 8. Permeate flux of mixing liquid after coagulation at different pH conditions.

shifted toward larger sizes from pH 6 to pH 8. When compared to the membrane flux, as shown in Fig. 8, larger particles promoted membrane flux and lessened the membrane fouling. It is, therefore, concluded that particle size distribution plays a significant role on membrane flux.

4. Conclusion

Membrane fouling is a serious problem for treating CMP wastewater with microfiltration. Pre-coagulation by PACl improves particle size and retards the decline of membrane flux. Addition of trace amount of cationic PAA after coagulation can enlarge the size of the flocs, improve the membrane flux, and promote the pure water flux recovery after backwash. The major fouling mechanism of microfiltration is cake filtration without compression when the wastewater is pretreated by coagulation and coagulation/flocculation. Addition of oxidant after flocculation promotes the pure water flux recovery of the membrane. The characteristics of flocs , e.g. density, settling velocity and fractal dimension, is not closely related to membrane flux. Particle size distribution and the number of small particles in the water are responsible for the reduction of pure water flux recovery.

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