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Chemical and physical treatments of chemical mechanical polishing wastewater from semiconductor fabrication

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Abstract

Wastewater from chemical mechanical polishing (CMP) process of semiconductor fabrication was treated by physical methods. The CMP wastewater, as obtained from a large semiconductor manufacturer, was characterized by a high oxide particle content, high turbidity (NTU), and a chemical oxygen demand (COD) concentration up to 500 mg/l. Due to these characteristics, treatment of the CMP wastewater by either filtration or by traditional activated sludge method was inadequate. In the present work, physical methods consisting of chemical coagulation and reverse osmosis were employed to tackle the turbidity and COD problems. Experimental tests were conducted to assess the effectiveness of the treatment and to identify the optimum operating conditions. Test results clearly demonstrated the complementary advantages of the two methods. The treatment was capable of realizing over 99% oxide particle removal and lowering the wastewater COD to below 100 mg/l. The overall water quality of the final effluent was excellent and can be considered for reuse. Preliminary treatment of the RO retentate by ozonation was also attempted. The COD removal achieved in the ozonation was over 80% in an hour, rendering the treated RO retentate suitable for direct discharge.
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1. Introduction

Electronic industry has been a fast growing sector of economy in many countries around the world for the past several decades. The rapid growth of this industry is expected to continue in the foreseeable future. The electronic industry in fact consists of manufacturing of a range of products with which semiconductor is an important one. Semiconductor is used in computers and their peripherals, communication equipment, consumer electronic products, electronic control devices, and scientific and medical test equipment. The wide applications have established semiconductor as one of the key electronic products. Due to the increasing demand of this product in recent years, the semiconductor industry has been growing rapidly at a double-digit rate [1].

The semiconductor manufacturing involves many highly complex and delicate processes, including silicon growth, oxidation, doping, photolithography, etching, stripping, dicing, metallization, planarization, cleaning, etc. [2–5]. In fact, over two hundreds of high purity organic and inorganic compounds (proprietary or generic) are involved in the manufacturing processes. Moreover, large quantities of ultrapure water are utilized in various washing and cleaning steps of the semiconductor manufacturing processes. Consequently, different types of wastewater are generated. These semiconductor wastewaters commonly contain various solvents, acids, bases, salts, fine oxide particles and other organic and inorganic compounds [2–5]. Hence direct discharge of these wastewaters into a water body is strictly regulated by water quality control authorities.

Chemical mechanical polishing (CMP) represents an important operation of the semiconductor fabrication process [6,7]. This technology has been commonly adopted for integrated circuit (IC) devices at or below 0.2 μm. The CMP technology, however, has a major drawback in that it consumes a large amount of ultrapure water and produces approximately an equal amount of wastewater that is difficult to treat [8–11]. According to recent estimates, the CMP operation could account for as much as 40% of ultrapure water consumption in semiconductor fabrication by 2005 [10,11]. The ultrapure water is used in the cleaning step to remove the waste CMP slurry and small particulates from the wafer

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surface after a CMP operation is completed. The CMP slurry, most of the commercial ones being proprietary, consist of suspension of very fine SiO_2, Al_2O_3, or CeO_2 particles in the pH-controlled solution which also contains oxidizing agents (such as HNO_3, $Fe(NO_3)_3$, $CuSO_4$, H_2O_2, chlorates, etc.) and additives (such as NH_4OH, surfactants, organic acids, etc.) [6,7]. These organic and inorganic compounds eventually go to the wastewater after a wafer is cleaned by the ultrapure water.

Due to its high solid content, the CMP wastewater is highly turbid with a milky color. Removal of the suspended oxide particles thus has received the most attention. Browne et al. [8] utilized ultrafiltration (UF) for removal of these fine suspended oxide particles. Golden et al. [11] investigated the effectiveness of chemical coagulation using a proprietary polymer coagulant followed by microfiltration. They found the combined process was effective in removing the fine suspended particles and some heavy metals, if present. Browne et al. [9] and Corlett [10] employed an online monitoring device to detect the fine particle concentration in the solution so that the cleaner CMP wastewater can be separated from the dirtier one and the former is recycled for non-critical uses. In the previous investigations, the researchers succeeded in eliminating the fine oxide particles from the CMP wastewater. However, the majority of the CMP wastewater from semiconductor fabrication contains more than just fine suspended oxide particles. They very often contain significant amounts of organic and inorganic pollutants as well, as manifested by their chemical oxygen demand (COD) concentration that can be as high as 500 mg/l. The processes employed in the previous investigations were not able to effectively remove the suspended oxide particles and the dissolved organic and inorganic pollutants as well. Hence the CMP wastewater recovered by these processes has only limited applications. To broaden the applications of recovered water, the CMP wastewater must be further treated to lower its other chemical pollutants and COD content as well.

The objective of this work is to utilize chemical coagulation and reverse osmosis for treating the CMP wastewater. Chemical coagulation using generic coagulant and coagulant aid was found very effective in a previous study [12] in rapidly removing the suspended particles in the industrial wastewater. The reverse osmosis (RO) method provided a convenient tool for tackling industrial wastewaters containing inorganic and refractory organic pollutants [13,14]. In the present study, the same generic coagulant and coagulant aid were adopted for removal of fine oxide particles from the CMP wastewater. A commercially available spiral wound RO unit was then employed to lower the CMP wastewater COD for further water quality enhancement.

2. Materials and methods

The CMP wastewater samples were obtained from a large semiconductor plant in northern Taiwan. The contents of this wastewater were very difficult to ascertain due to different types and amounts of CMP slurries (nearly all of them being proprietary) employed in the manufacturing process. The water quality of the CMP wastewater samples, such as the COD, BOD, surfactants (ABS), total solids (TS), suspended solids (SS), phosphorous, and pH and pH were measured by the standard methods [15]. The wastewater turbidity (in terms of NTU) was determined using a NDH-200 turbidimeter (Nippon Denshoku Industrial Co., Ltd., Tokyo, Japan). The same methods were adopted for measuring the water quality of CMP wastewater after chemical coagulation and reverse osmosis. A Malvern zeta potential analyzer (Model Zetasizer 3000HS, Malvern Instruments, Ltd., Worcester, UK) was used to determine the size distribution and zeta potential of the fine oxide particles in the CMP wastewater. A JOEL scanning electron microscope (SEM/EDS) (Model JSM-5610, JOEL Electronics, Inc., Tokyo, Japan) was employed for determining the particle elemental composition and registering the microscopic images.

Chemical coagulation was conducted using a jar test apparatus. The apparatus consisted of six 1-l glass jars sitting in a constant temperature bath for temperature control. Each jar was equipped with a stirrer that was allowed to vary between 0 and 300 rpm. Generic polyaluminum chloride (PAC) and polymer (coagulant aid) were employed in the coagulation tests. Both the PAC and polymer, as obtained from Fu Chang Chemical Co. (Taoyuan, Taiwan), were the type generally used in chemical coagulation treatment of industrial wastewater. One liter of the raw CMP wastewater was put in a jar. The stirrer was turned on and set at 100 rpm. A desired amount of PAC chosen between 50 and 400 mg/l was added to the CMP wastewater and the mixing was continued for 30 min. The stirrer speed was then slowed to 30 rpm and a proper amount of polymer was added. The amount of polymer was chosen within the range of PAC/polymer ratio between 30:1 and 300:1. After polymer addition, the mixing was continued for 15 min. The treated CMP wastewater was finally allowed to settle for 30 min. Supernatant samples were taken for water quality measurements.

The RO apparatus consisted of a microfilter and a RO unit. The polypropylene microfilter with an average pore size of 5 μm served to remove all unsettled particles. The RO module was a spiral-wound Filmtech TW30-1812-50 unit (Dow Chemical Co., Midland, Michigan). The module had polyamide membrane with a maximum operating pressure of 0.86 MPa and the operating pressure of the RO module was lower than most of the commercial RO units. In a typical test run, the CMP wastewater after chemical coagulation was placed in the wastewater reservoir that was maintained at a constant temperature. The wastewater was fed to the microfilter by a feed pump first and then to the Filmtech RO unit operating at a desired pressure. The permeate and retentate flow rates of the RO unit were registered. A test run took less than 30 min to reach a steady state. After that permeate and retentate samples were taken periodically for

water quality measurements. A RO test run usually lasted less than an hour.

3. Results and discussion

3.1. Characteristics of CMP slurry and wastewater

Table 1 lists the water qualities of a brand name CMP slurry and the CMP wastewater samples obtained for the present study during the experimental period. Both the CMP slurry and the CMP wastewater had a milky color that was apparently due to the fine suspended oxide particles. The CMP slurry and the wastewater had high total solids (TS) contents of 124,100 and 4500 mg/l, respectively, but the SS concentrations of both samples were negligible, being less than 0.2 mg/l. This was due to the fact that the size of the fine suspended oxide particles was less than the pore size (0.45 μm) of the standard filter paper used for the SS measurements while the TS concentration was measured by drying the sample in a crucible which retained all the fine oxide particles. The lower TS content of the CMP wastewater, as compared to the original CMP slurry, clearly reflected the fact that the waste CMP slurry was significantly diluted during wafer cleaning. It is further noted that the COD concentration of the CMP wastewater was much higher than the original slurry. This was attributable to mixing of the CMP wastewater with other process wastewater streams that contained rganic compounds, but little total solids. Hence COD removal from the CMP wastewater is as important as the removal of fine suspended oxide particles if the CMP wastewater is to be upgraded to a level for general reuse purpose.

Fig. 1a displays the elemental composition determined by the JOEL SEM/EDS. From the composition, the fine oxide particles were identified as silicon dioxide (silica, SiO_2) which is the most popular type of oxides employed in the CMP slurry [6,7]. Small amount of potassium was attributable to potassium hydroxide (KOH) added in the original slurry for pH control. Fig. 1b shows the size distribution of fine oxide particles in the CMP wastewater, as measured by the Malvern zeta potential meter. The oxide particle sizes fall within the narrow range between 50 and 200 nm with a great major of particle size around 100 nm which was more

than 10 times smaller than the pore size of the filter paper for the SS measurement. This accounts for the very low SS and high TS, as mentioned above.

All silica particles in the original CMP slurry were spherical in shape and kept in suspension in the aqueous solution by pH adjustment [6,7]. After the CMP operation, the wastewater pH was lower than the original slurry. In a lower pH environment, silica can form aggregate or agglomerate [16]. The aggregate and agglomerate were formed by chemical or physical attachment of silica particles. The aggregated formation of silica particles was shown in Fig. 2 that was the SEM microscopic image of dry CMP wastewater sample. The microscopic image clearly demonstrates the fibrous formation of the aggregate. The aggregate or agglomerate could also be formed in the original CMP slurry. They are not desirable and have to be removed by filtration before the CMP slurry is used [5].

3.2. Chemical coagulation

In the chemical coagulation process, the suspended particles are first aggregated by destabilization of the particle charge. The aggregated particles then form large, dense and rapid-settling flocs. The conventional inorganic coagulants, such as aluminum sulfate, ferrous or ferric chloride, ferric sulfate, etc., perform both functions in a single action [17]. On the other hand, PAC and polymer (a synthetic polyelectrolyte) do the work in a two-step process. In the coagulation step using PAC, aggregates are formed from destabilized suspended particles while in the ensuing flocculation step using polymer, large flocs are formed leading to rapid floc settling. These separate coagulation and flocculation actions may account for the much better performance of the PAC/polymer combination over the conventional coagulants.

The amounts of PAC and polymer and the initial wastewater pH have been reported to be the important factors influencing the turbidity reduction efficiency of chemical coagulation [12]. Fig. 3a and b demonstrate the effect of the amount of PAC on the turbidity (NTU) and COD reductions and the final wastewater pH. Note that the amount of polymer added was fixed at 1% of PAC according to our past experience [12]. Fig. 3b reveals that the final wastewater pH decreased steadily with an increase in the PAC concentration. As observed in the present experimental tests, good size flocs were firmed only between pH 5 and 7.5 and they rapidly settled out of the wastewater in the tests. Beyond that pH range, there was very little floc formation, resulting in no appreciable change to the milky wastewater color. The NTU reduction of the CMP wastewater followed closely the trend of floc formation and hence the PAC concentration between 100 and 180 mg/l was considered as a good operating range. Fig. 3b also shows slight increase in the wastewater COD with PAC. For PAC ≤100 mg/l, the PAC and polymer added were insufficient to effect good floc formation primarily because of high pH above 7.5, leading to poor NTU removal. This low dosage of PAC and polymer

Table 1
Water quality of the CMP slurry and wastewater

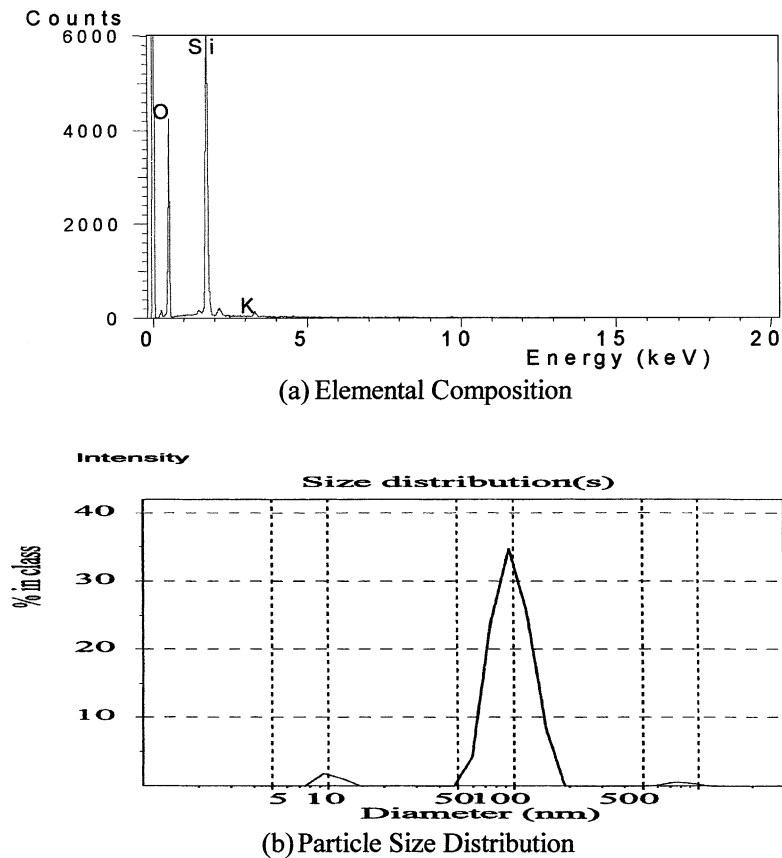|	CMP slurry	CMP wastewater
PH	10.2	9.3–9.7
TS (mg/l)	124100	4100–5300
SS (mg/l)	0.2	0–0.2
ABS (mg/l)	0.05	0.01–0.03
TP (mg/l)	7.5	1–2
Density (g/l)	0.97	∼1
COD (mg/l)	98	175–500
BOD/COD	–	0.11–0.15
Color	Milky	Milky

(a) Elemental Composition

(b) Particle Size Distribution

Fig. 1. The SEM/EDS spectraphotos of CMP oxide particles (a) and their particle size distribution (b).

did not contribute much additional wastewater COD either. For PAC $\geq$180 mg/l, floc formation was poor either due to low pH below 5, leading to poor NTU removal. But for this instance, the PAC and polymer in the aqueous solution were sufficient to adversely impact the wastewater COD. From the above results, 150 mg/l PAC was deemed as a good dosage for the CMP wastewater treatment.

The 100:1 ratio of PAC/polymer adopted in the chemical coagulation tests of Fig. 3a and b was based on our

Fig. 2. The SEM image of silica agglomerates in the CMP wastewater.

past experiences dealing with other industrial wastewaters [12]. However, for the present application, the PAC/polymer ratio still needs to be ascertained. In Fig. 4, the wastewater NTU as a function of polymer dosage between 0.5 and 5 mg/l for a fixed 150 mg/l PAC concentration was demon-
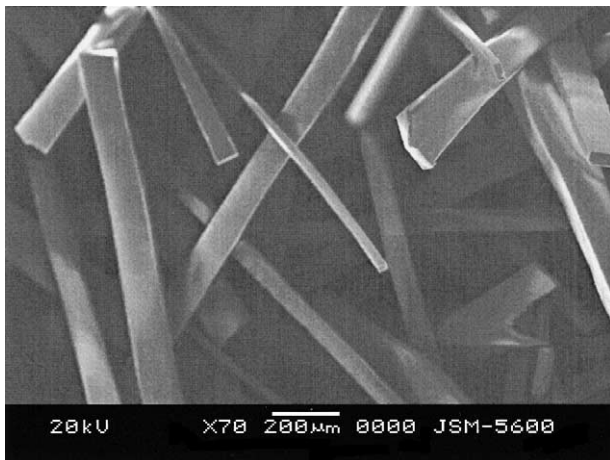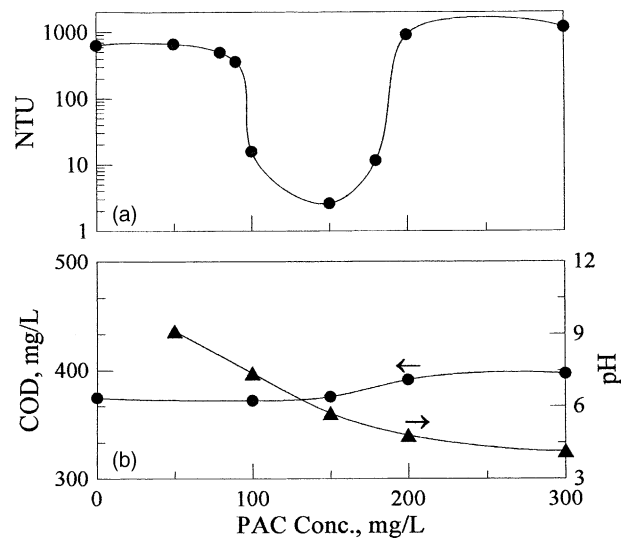

Fig. 3. The effect of PAC concentration on the NTU and COD reduction and the final wastewater pH with PAC/polymer ratio of 100:1, initial NTU 632, COD 374 mg/l and pH 9.34.
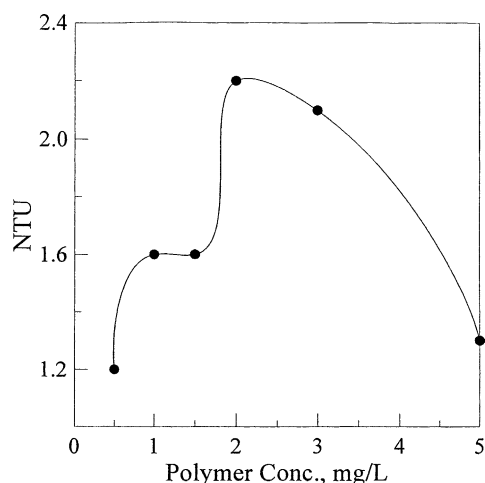
Fig. 4. The effect of polymer concentration on the NTU reduction with initial NTU 632, COD 374 mg/l and pH 9.34.
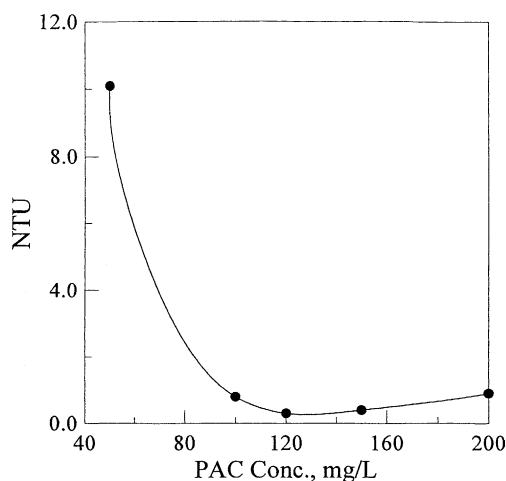

Fig. 5. NTU reduction as a function of the PAC concentration when the final wastewater pH being adjusted to 7 with PAC/polymer ratio of 100:1, initial NTU 632, COD 374 mg/l and pH 9.34.

strated. The figure indicates that all polymer concentrations yielded very good NTU results because that at NTU <3, the CMP wastewater contained very little suspended silica particles. Hence the PAC/polymer ratio does not appear to be an important factor in the present case. A low 300:1 ratio of PAC/polymer (i.e. a 0.5 mg/l polymer dosage for fixed 150 mg/l PAC) appears to be a good choice, although the real saving of the amount of polymer in practical application is insignificant.

The final wastewater pHs demonstrated in Fig. 3b were those reflected naturally by the CMP wastewater after PAC and polymer additions. This pH was seen to play a crucial role in the flocculation processes. A point worth of further exploration is that whether artificial adjustment of the final wastewater pH to 7 after PAC/polymer addition will be beneficial to the flocculation process and thus the NTU reduction. To address this issue, test runs similar to Fig. 3a were performed, but in the present cases, the final wastewater pHs of all test runs were all adjusted to 7. Fig. 5 shows the wastewater NTU as a function of the PAC concentration, noting that the PAC was added each experimental test before final wastewater pH adjustment. This figure reveals that the beneficial effect of final wastewater pH adjustment was enormous. Good floc formation and rapid floc settling were observed for PAC concentration exceeding 100 mg/l. Even in the case of recommended PAC dosage (i.e. 150 mg/l), the NTU was further improved from the original 2.7 to below 0.5. In view of these results, 100 mg/l PAC and 1 mg/l polymer with final wastewater pH adjustment to 7 was adopted as the standard operating conditions for other chemical coagulation runs in the present work and was recommended for practical purposes.

3.3. Reverse osmosis

The transmembrane pressure has been known to play a crucial role in the RO system [15,16]. In Fig. 6, the pressure

effect on the flux of CMP wastewater after chemical coagulation is demonstrated. Also shown in this figure is the flux of deionized (DI) water versus the transmembrane pressure. Both permeate fluxes increase steadily with an increase in the transmembrane pressure. Such a beneficial pressure effect on the permeate flux is in line with the trend reported in the literature [13,14]. The permeate flux of the CMP wastewater is seen to be 10–20% lower than the DI water, due apparently to the dissolved organic and inorganic compounds in the CMP wastewater.

Fig. 7 shows the effect of transmembrane pressure on the permeate COD and the COD rejection coefficient (R_{COD}), the latter being defined as [13,14]:

$$R_{COD} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad (1)$$

in which C_p is the permeate COD and C_f the feed COD. This figure reveals that the COD rejections of the RO process were excellent for all transmembrane pressures. The perme-
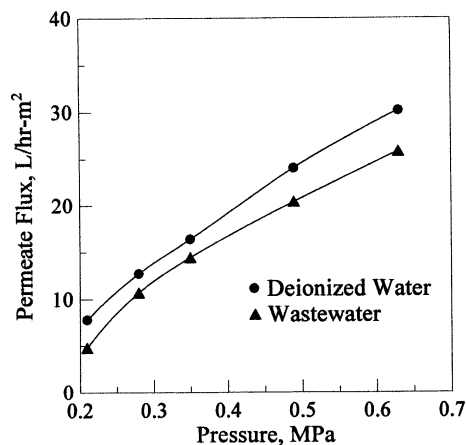

Fig. 6. The pressure effect on the permeate fluxes of deionized water and CMP wastewater.
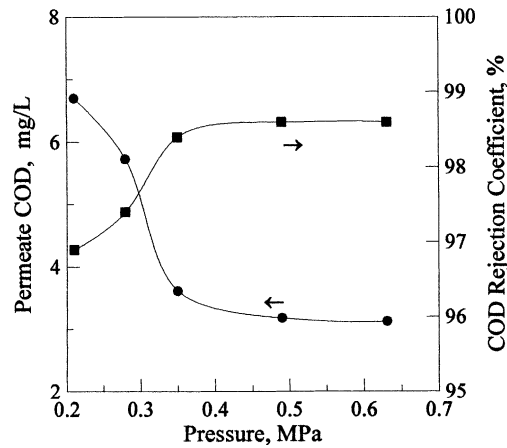
Fig. 7. Effect of the transmembrane pressure on the permeate COD and the COD rejection coefficient with 221 mg/l initial wastewater COD.

Fig. 9. Effect of the initial wastewater pH on the permeate flux and the permeate recovery with 221 mg/l initial wastewater COD.

ate COD varied from 6.7 mg/l (96.9% rejection) at 0.21 MPa to 3.1 mg/l (98.6% rejection) at 0.63 MPa. The COD rejection tends to level off to a steady value of 98.6% in Fig. 7 beyond 0.49 MPa. In addition to the excellent COD removal, the permeate NTU was found to be only about 0.2. This permeate water quality was as good as the input water for the ultrapure water process of the semiconductor manufacturer. Hence the permeate can be readily recycled for reuse.

Pertaining to Fig. 7, the effect of transmembrane pressure on the retentate COD and the retentate COD increase is demonstrated in Fig. 8. The retentate COD is seen to increase rapidly from 239 mg/dm^3 (8.1% over the feed COD of 221 mg/l) at 0.21 MPa to 437 mg/l (97.7%) at 0.63 MPa. The increase in the retentate COD accounts for the decrease in the permeate COD shown in Fig. 7.

In the chemical coagulation of the CMP wastewater, the final wastewater pH was adjusted to 7 for optimum NTU results. It would be of practical interest to know whether such a final wastewater pH adjustment has any influence on the RO performances. To address this issue, RO test runs
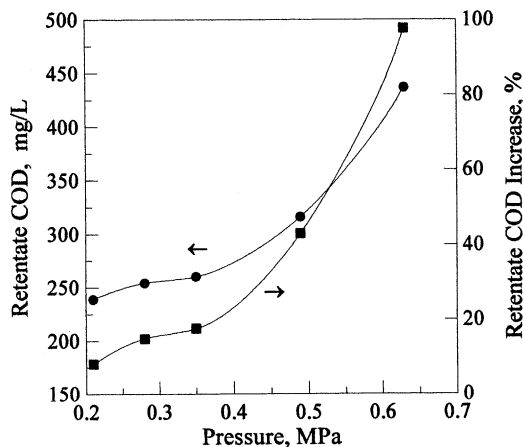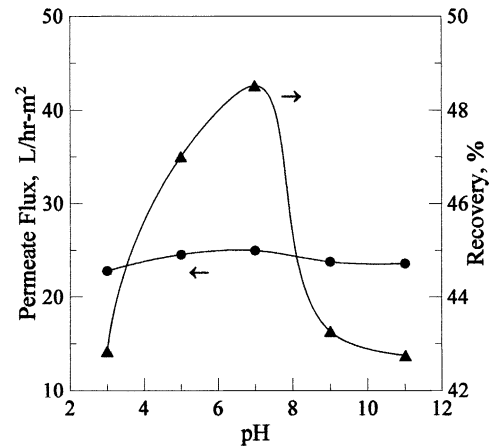
were conducted for various pHs of the CMP wastewater. Such an initial pH effect on the permeate flux is displayed in Fig. 9. Also shown in this figure is the recovery (R) that is defined as:

$$R = \frac{(\text{flux})_p}{(\text{flux})_f} \qquad (2)$$

where (flux)$_p$ is the permeate flux and (flux)$_f$ the feed flux. The initial pH effect on the permeate flux is seen to be relatively small with only a slightly better permeate flux at pH 7. However, there appears to be a maximum permeate recovery at pH 7. Hence the final wastewater pH adjustment is beneficial not only to the NTU reduction in the chemical coagulation stage, but also to the permeate recovery in the RO stage.

The retentate was shown to have a high COD concentration over 400 mg/l in Fig. 8 at the transmembrane pressure larger than 0.6 MPa. This retentate needs to be properly treated for final discharge. Due to the low biodegradability of the original CMP wastewater, as shown in Table 1, biological treatment of the retentate would not be appropriate. Preliminary ozonation treatment of the retentate was attempted. One liter of retentate was placed in a pyrex column reactor (5 cm i.d., 70 cm long) and the ozone gas from a Mitsubishi ozone generator was bubbled through the retentate. The retentate COD was periodically measured during the ozonation treatment and the test results were demonstrated in Fig. 10 which shows the COD removal as a function of the treatment time for four initial pHs. The retentate COD removal by ozonation is seen to improve with an increase in the initial wastewater pH with the best COD removal at pH 11. This was due to hydroxyl (OH$^\bullet$) oxidation under strong alkaline conditions in contrast to molecular oxidation under weak alkaline or acidic conditions. Over 80% COD removal achieved in an hour with pH 11 renders the remaining wastewater COD below 100 mg/l which is the current discharge standard of industrial wastewater in Taiwan.
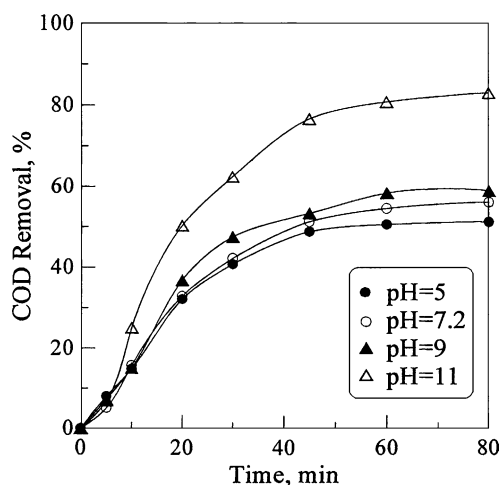

Fig. 8. Effect of the transmembrane pressure on the retentate COD and the retentate COD increase with 221 mg/l initial wastewater COD.

Fig. 10. COD removal achieved by ozonation of the RO retentate with 466 mg/l initial retentate COD and 219 mg/min ozone mass flow rate.

4. Conclusions

Treatment of CMP wastewater from semiconductor manufacturer by chemical coagulation and reverse osmosis was attempted. While chemical coagulation was employed for removal of fine oxide particles, reverse osmosis targeted the COD reduction. Based on the results of experimental tests, the following conclusions can be drawn:

(1) The CMP wastewater was found to have a high total solids content over 4000 mg/l. The SS concentration was very low because of fine oxide particle size with an average diameter of 100 nm. The oxide particle was identified to be silicon dioxide (silica) and the silica particles formed agglomerate at lower wastewater pH from the original slurry. The wastewater was found to have a COD concentration up to 500 mg/l.
(2) In the chemical coagulation, commercial grade PAC and polymer were found to be highly efficient in removing the silica particles and reducing the wastewater turbidity. The optimum dosages of PAC and polymer were 100 and 1 mg/l, respectively. It is also recommended that the final wastewater pH be adjusted to neutral for rapid floc settling.
(3) The RO process was able to reject the wastewater COD by over 95% and the wastewater COD rejection increases with an increase in the transmembrane pressure.
(4) The water quality of the CMP wastewater after chemical coagulation and RO treatment is of the same level of input water for the ultrapure water process of the semiconductor manufacturer and hence the permeate from the RO process can be readily recycled for reuse.

(5) Preliminary treatment the RO retentate, which had a COD concentration over 400 mg/l, by ozonation was able to achieve over 80% COD reduction and enable the wastewater to meet the direct discharge standard (<100 mg/l).

Acknowledgements

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