Treatment of Semiconductor Wastewater by Natural Coagulants: Corn, Sago and Rice Flour Using Response Surface Methodology

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Abstract

Wastewater from a semiconductor manufacturer generally contains a strong dark color due to the presence of refractory photoresist solvents. A study has been conducted to compare the treatment efficiencies of various natural coagulants (rice, corn and sago flour) on semiconductor wastewater. A three level factorial design has been chosen as an experimental design to study the interaction between two influencing factors; i.e. retention time and dosage of the coagulant to analyze the results. The parameters studied are chemical oxygen demand (COD) and turbidity. Results indicate the dosage of the coagulant has a higher influence in COD and turbidity reduction. The regressions for COD and turbidity reduction by corn flour are 57.78% and 77.86%, by sago flour are 84.48% and 78.74%, by rice flour are 73.44% and 83.22%, respectively.

1. Introduction

The electronic industry is known for its rapid growth of economy and is expected to continue expanding rapidly in many other countries around the world [1]. The semiconductor that is manufactured is used in computers and their peripherals, communication equipment, consumer electronic products, electronic control devices, scientific and medical test equipment [2]. Semiconductor manufacturing consist a large number of complex and highly delicate processes which includes silicon growth, oxidation, doping, photolithography, etching, stripping, dicing, metallization, planarization, cleaning, etc [3]. In the manufacturing process, a large quantity of ultrapure water is consumed as much as 40% [13] during the washing and cleaning steps and to rinse their crystal chips. This later on creates a large amount of wastewater. The wastewater contents are contributed from various sources and different types of processes during the manufacturing of the semiconductor i.e. spent solvents and liquids containing metals in the plating process of metallization; wafer cleaning; etc. Semiconductor wastewater commonly contain organic solvents, acids, bases, salts, heavy metals, fine suspended oxide particles, and other organic compounds. The wastewater generated was strongly dark colored because of the presence of refractory photoresists, solvents, dyes and salts. In addition, the wastewater has a high chemical oxygen demand (COD) concentration and turbidity, frequently exceeding 50 000 mg/l and 2000 NTU respectively. Many studies have been conducted on semiconductor wastewater. Electrocoagulation was used to remove silica nano-particles [3] and fluoride [5]. A combination treatment consisted of air stripping, Fenton oxidation and sequencing batch reactor (SBR) was utilized primarily to recover isopropyl alcohol (IPA); to destroy the recalcitrant organic chemicals with an additional aim to enhance their biodegradability and to further lower the wastewater COD to the discharge standard respectively [6]. Another approach to treat the wastewater was by anaerobic biodegradability and methanogenic toxicity of key constituents in copper chemical mechanical planarization effluents of the semiconductor industry [3]. Series of chemical and physical treatments chemical mechanical polishing wastewater was also adopted [2]. Pretreatment of coagulation and flocculation was also carried out to remove silica and metals in order to prevent fouling of reverse osmosis membranes [7]. The main problem of the semiconductor wastewater is

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that it consist the suspension of very fine SiO_2 particles along with other oxidizing agents. Therefore the objective of this research is to study the efficiency and compare different natural starches to act as coagulants to remove the chemical oxygen demand (COD) and turbidity using the application of Response Surface Methodology (RSM).

2. Materials and Methods

The chemical mechanical-planarization (CMP) wastewater samples were obtained during peak hours of operation from a large semiconductor plant located in Bayan Lepas, Penang, Malaysia. 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 wastewater COD was analyzed by adopting the HACH method and using a spectrophotometer DR21—(HACH). COD were analyzed before and after treatment.

Chemical coagulation was conducted using a jar test apparatus (SCIENTIFIC-JELP). The apparatus consisted of six 500 ml glass jars. Each jar was equipped with a stirrer that was allowed to vary between 10 and 300 rpm. Natural polymer of starches: corn flour, sago flour and rice flour were employed as coagulants in the coagulation tests. Five hundred milliliters of the raw wastewater was put in the beaker. The pH was adjusted to pH 12 as pretreatment [7]. A desired amount of coagulant was added based on the design of experiment of response surface methodology (RSM). The dosage added to the wastewater was fixed at 3 different concentrations viz. 0.02 g/l, 3.01 g/l and 6.0 g/l whereas the retention time is 0 min, 30 min and 60 min. After coagulant addition, the initial rapid mixing stage took place for 5 min at 100 rpm [6]. The following slow mixing stage was set at a speed of 10 rpm for 15 minutes. The treated wastewater was finally allowed to settle according to their respective retention times in the RSM design of experiment. Supernatant samples were withdrawn from the beaker with a micropippete (Eppendorf) at the top liquid level at the beaker. The samples were then analyzed for COD and turbidity.

Design of Experiment

Response surface methodology may be summarized as a collection of statistical tools and techniques for constructing and exploring an approximate functional relationship between a response variable and a set of design variables [12]. A Three Level Factorial design in the software of response surface methodology was applied in the jar test coagulation study. For this design approach, the interactions among the experimental factors and some confounding relations are taken into account by using the proper defining relations. In the present study the variables selected were retention time (minutes) and dosage of coagulants (g/l) while the responses observed were COD (mg/l) and turbidity (NTU). Suppose we code the levels in standardized units so that the values taken by each of the three variables X_1, X_2 and X_3 are -1, 0, +1, and suppose also that the second degree quadratic polynomial fitted by the method of least squares is:

$$Y = B_0 + \sum_{i=1}^{k} B_i X_i + \sum_{i=j=i}^{k} B_{ij} X_i X_j \tag{1}$$

where, Y = predicted response, it can be observed that in the present study, three variables are involved and hence k takes the value 3. Thus, by substituting the value 3 for k, Eq. (1) becomes:

$$Y = B_0 + B_1 X_1 + B_2 X_2 + B_{12} X_1 X_2 + B_{11} X_1^2 + B_{22} X_2^2 \tag{2}$$

where, Y is predicted response X_1 and X_2 are input variables (viz., retention time and dosage); B_0 is a constant; B_1 and B_2 are linear coefficients; B_{12} and B_{23} are cross product coefficients; B_{11} and B_{22} are quadratic coefficients. The low, middle and high levels of each variable, namely retention time and dosage, that were coded as -1, 0, +1 respectively are given in Table 1 and shown the actual design of experiments is given in Table 2. By solving Eq. (2), it was found that

Table 1. The levels of variables chosen for trials

Retention Time (min) (X_1)	Dosage (g/l) (X_2)
0 (-1)	0.02 (-1)
30 (0)	3.01 (0)
60 (+1)	6.00 (+1)

Table 2 The Three Level Factorial design for the three independent variables

Std	Run	Retention Time (minutes)	Dosage (g/l)	COD (mg/l)
2	1	30.00	0.02	
1	2	60.00	0.00	
6	3	30.00	60.00	
12	4	0.00	30.00	
13	5	30.00	30.00	
3	6	60.00	60.00	
4	7	60.00	0.00	
9	8	30.00	60.00	
7	9	0.00	0.00	
8	10	30.00	30.00	
10	11	60.00	30.00	
11	12	60.00	30.00	
5	13	0.00	30.00	

a total of 13 runs were necessary in order to optimize the COD and turbidity removal that involved two independent variables, viz., retention time and dosage, wherein each variable has its own effect on the response, viz., COD and turbidity. The design experiments were carried out using the Design Expert (Courtesy: Stat-Ease Inc., Statistics Made Easy, Minneapolis, MN, USA. Version 6.0.10, 2003).

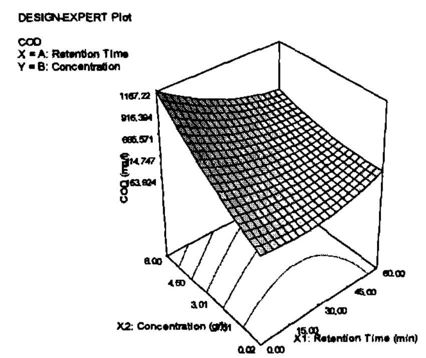
3. Results and Discussion

The characteristics of main pollution parameters for a 24-hour operation for 14 consecutive days of semiconductor manufactured wastewater are presented in Table 3.

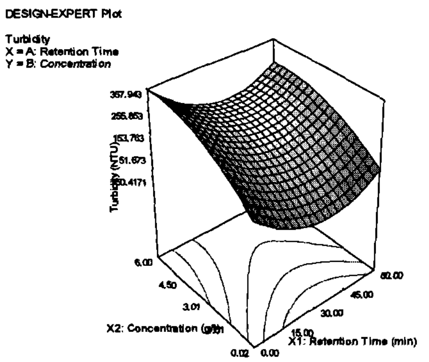
Table 3 Characteristics of Semiconductor Wastewater

Day	pH	Temp (°C)	TS (mg/L)	COD (mg/L)	TSS (mg/L)	Turbidity (NTU)
1	4.26	29.7	0.237	708	96	2183
2	5.39	29.5	0.204	1542	136	2093
3	4.84	29.3	0.067	1194	44	2098
4	5.12	29.1	0.138	1552	56	4245
5	5.15	28.8	0.148	1387	68	2605
6	5.96	28.6	0.071	1097	40	1941
7	4.81	28.5	0.014	824	36	1996
8	5.42	29.5	0.127	1147	8	2203
9	4.85	29.6	0.163	1418	48	2136
10	5.76	30.4	0.027	1382	24	1093
11	4.93	28.5	0.08	961	76	1701
12	5.15	28.5	0.088	1132	188	2386
13	5.02	28.3	0.133	857	120	2191
14	4.94	29.4	0.113	724	92	1928

The pH value of the semiconductor wastewater displayed fluctuated values between pH 4 to 6. In addition, samples that were analyzed displayed high concentrations of COD and turbidity beyond the standard limits set by the Environmental Quality Act 1974, Malaysia. Though the results of TSS analyzed were slightly more than 100 mg/l, it was observed that the semiconductor wastewater consist of high concentrations of very fine silica oxide particles which suspends constantly with time.



(a)



(b)

Figure 1. The effect of corn flour addition and pH control on the removal of (a) COD, and (b) turbidity from semiconductor wastewater

The results of corn flour coagulation are presented in Fig. 1. In Fig. 1a, COD removal as a function of corn dosage is shown with pH control, while in Fig. 1b is shown the corresponding turbidity reduction. In pH-controlled experimental runs the pH value was adjusted at 12, by the addition of appropriate amount of NaOH pellets. The addition of corn flour resulted in an almost 91.77% success with a dosage of 0.02 g/l and a retention of 60 minutes. However, a lower percentage of COD removal was achieved at 10.42% if added the highest dosage value, 6.0 g/l and no retention time is give at all. Furthermore, as shown in Fig. 1b, the turbidity removal was 99.2% during the addition of tapioca flour at 0.02 g/l with a retention time of 60 min. However, when a higher dosage of 6.0 g/l was added, turbidity removal was successfully achieved at 93.9%.

Table 4 Analysis of Variance (ANOVA) of (a) COD and (b) turbidity removal for corn flour

Source	COD		
	Sum of Squares	***Mean Square***	***F Value***
Model	7.947E+005	1.589E+005	4.28
Residual	2.597E+005	37100.29	
Cor Total	1.054E+006		
R^2	57.78		

(a)

Source	Turbidity		
	Sum of Squares	***Mean Square***	***F Value***
Model	1.332E+005	26641.73	9.44
Residual	19758.78	2822.68	
Cor Total	1.530E+005		
R^2	77.86		

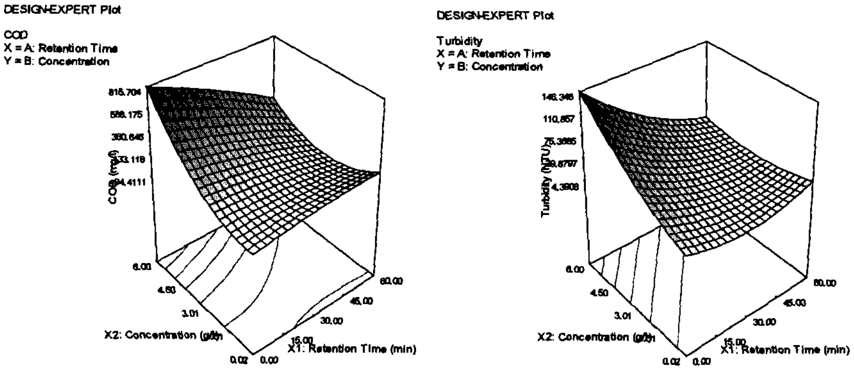
(b)

The analysis of variance table for corn flour displays the total and error sum of square is shown in Table 2. The coefficient of determination (R^2) for the values of COD and turbidity respectively are 57.78 and 77.86. From the ANOVA table, the values of F for the COD and turbidity for tapioca flour are 4.28 and 9.44. This implies that the Model F-value for both COD and turbidity removal are significant. The Prob>F for COD and turbidity are 0.0419 and

0.0051, respectively. In the case of COD removal, the variable X_2 is a significant model term. However, in the case of turbidity removal, the variables X_2 and X_1^2 are significant model terms. The model descriptions for COD and turbidity of sago flour are shown below. This indicates that the 2nd order equation that were used was significant.

$$Y_{COD}=204.96-4.59X_1+113.48X_2+0.12X_1^2+7.81X_2^2-2.07X_1X_2 \quad (3)$$

$$Y_{TURB}=119.98-9.93X_1+85.21X_2+0.14X_1^2-7.62X_2^2-0.09X_1X_2 \quad (4)$$



(a) (b)

Figure 2 The effect of sago flour addition and pH control on the removal of (a) COD, and (b) turbidity from semiconductor wastewater

The results of sago flour coagulation are presented in Fig. 2. In Fig. 2a, COD removal as a function of sago dosage is shown with pH control, while in Fig. 2b is shown the corresponding turbidity reduction. In pH-controlled experimental runs the pH value was adjusted at 12, by the addition of appropriate amount of NaOH pellets. The addition of sago flour resulted in an almost 96.92% success with a dosage of 0.02 g/l and a retention of 30 minutes. However, the percentage of COD decreased as much as 29.37% if the dosage value of 6.0 g/l was added and analyzed at t=0. Furthermore, as shown in Fig. 2b, the turbidity removal was 99.59% during the addition of sago flour at 0.02 g/l with a retention time of 60 min. When a higher dosage of 6.0 g/l was added and t=0, turbidity removal was successfully achieved at 93.32%.

Table 5 Analysis of Variance (ANOVA) of (a) COD and (b) turbidity removal for sago flour

Source	COD		
	Sum of Squares	*Mean Square*	*F Value*
Model	6.896E+005	1.379E+005	14.06
Residual	68666.22	9809.46	
Cor Total	7.583E+005		
R^2	84.48		

(a)

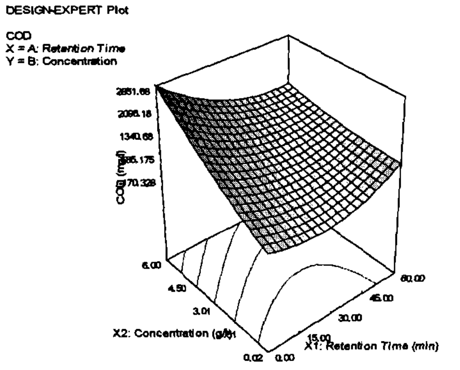
Source	Turbidity		
	Sum of Squares	*Mean Square*	*F Value*
Model	18019.41	3603.88	9.89
Residual	2550.51	364.36	
Cor Total	20569.92		
R^2	78.74		

(b)

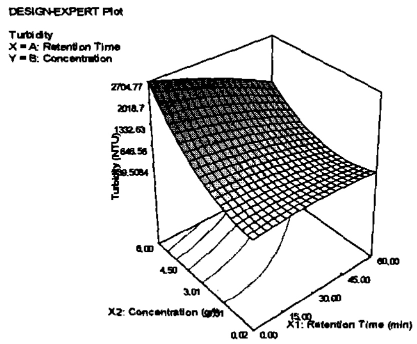
The analysis of variance table for sago flour displays the total and error sum of square is shown in Table 3. The coefficient of determination (R^2) for the values of COD and turbidity respectively are 84.48 and 78.74. From the ANOVA table, the values of F for the COD and turbidity for sago flour are 14.06 and 9.89. The Model F-value of 14.06 for COD removal and 9.89 implies the model is significant. The Prob>F for COD and turbidity are 0.0016 and 0.0045, respectively. In the case of COD removal, all variables, X_1, X_2, X_2^2 and X_1X_2 are significant model terms. However, in the case of turbidity removal, all variables, X_1, X_2 and X_1X_2 are significant models terms. The model descriptions for COD and turbidity of sago flour are shown below. This indicates that the 2nd order equation that was used was significant.

$$Y_{COD}=7.77+3.29X_1-12.23X_2-0.03X_1^2+24.48X_2^2-2.06X_1X_2 \quad (5)$$

$$Y_{TURB}=22.21-1.23X_1+10.85X_2+0.02X_1^2+1.64X_2^2-0.37X_1X_2 \quad (6)$$



(a)



(b)

Figure 3 The effect of rice flour addition and pH control on the removal of (a) COD, and (b) turbidity from semiconductor wastewater

The results after adding rice flour as a coagulant with pH adjustment for COD removal are presented in Fig. 3a and the corresponding turbidity removal is shown in Fig. 3b. COD and turbidity removal acted as a function of rice flour dosage are shown in this figure. The pH values were adjusted to pH 12 as pretreatment with the appropriate amount of NaOH pellets before adding rice flour as a coagulant. Results in Fig. 3a displayed that by adding a dosage of 6.0 g/l with no retention time further increased the COD value up to 65.5% from its original value while Fig. 3b showed the turbidity value increased 22.0% from its original value. However, with a smaller dosage of 0.02 g/l and a retention time of 30 minutes, the results indicated a 94.13% and 97.15% successful COD and turbidity removal, respectively.

Table 6 Analysis of Variance (ANOVA) of (a) COD and (b) turbidity removal for rice flour

Source	COD		
	Sum of Squares	***Mean Square***	***F Value***
Model	6.791E+006	1.358E+006	7.63
Residual	1.245E+006	1.779E+005	
Cor Total	8.036E+006		
R^2	73.44		

(a)

Source	Turbidity		
	Sum of Squares	***Mean Square***	***F Value***
Model	7.012E+006	1.402E+006	12.90
Residual	7.610E+005	1.087E+005	
Cor Total	7.773E+006		
R^2	83.22		

(b)

The analysis of variance table for rice flour displays the total and error sum of square is shown in Table 2. The coefficient of determination (R^2) for the values of COD and turbidity are 73.44 and 83.22, respectively. From the ANOVA table, the values of F for the COD and turbidity removal using rice flour are 7.63 and 12.90 which implies that the Model F-value is significant. The Prob>F for COD and turbidity are 0.0094 and 0.0020, respectively. In the case of COD removal, the variable X_2 and the interaction of variables X_1X_2 are significant model terms. However, in the case of turbidity removal, all variables, X_1, X_2, X_2^2 and X_1X_2 are significant model terms. The model descriptions for COD and turbidity of sago flour are shown below. This indicates that the 2nd order equation that was used was significant.

$$YCOD=122.07-26.95X_1+354.75X_2+0.61X_1^2+16.69X_2^2-6.33X_1X_2 \quad (7)$$

$$Y_{TURB}=181.86+8.26X_1+17.92X_2-0.13X_1^2+67.09X_2^2-4.59X_1X_2 \quad (8)$$

4. Conclusion

The application of coagulation treatment using natural coagulants on semiconductor wastewater was examined in this study. The semiconductor wastewater were characterized by a high concentration of fine oxide suspended particles with a turbidity of 2000 NTU and chemical oxygen demand (COD) value higher than 1000 mg/l. By adjusting the pH to a very alkali state as pretreatment stage, the suspended silica particles easily dissolved and settled along with the coagulants added. The Response Surface Methodology involving an experimental design and regression analysis was effective in finding the optimum point of the two independent variables and in assessing their effects on the response considered. Research has been undertaken to evaluate the performance of natural starches of corn flour, sago flour and rice flour to act as coagulants. The COD value for every coagulant that was used was highly influenced by the dosage (X_2) of the coagulant compared to retention time (X_1). In all three cases, the main variable was the dosage of the coagulant (X_2). The study shows that natural characteristics of starch can be an efficient coagulant for semiconductor waste but would need further study in modifying it to be efficient to the maximum.

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References

[1] Lai, C.L.; Lin, S.H. 2004. Treatment of chemical mechanical polishing wastewater by electrocoagulation: system performances and sludge settling characteristics, Chemosphere 54: 235-242

[2] Lin, S.H.; Yang, C. R. 2004. Chemical and physical treatments of chemical mechanical polishing wastewater from semiconductor fabrication, Journal of Hazardous Materials B108: 103-109

[3] Hollingsworth, J.; Sierra-Alvarez, R.; Zhou, M.; Ogden, K.L.; Field, J.A. 2005. Anaerobic biodegradability and methanogenic toxicity of key constituents in copper chemical mechanical planarization effluents of the semiconductor industry, Chemosphere 59: 1219-1228

[4] Wu, M.; Sun, D.; Tay, J.H. 2004. Process-to-process recycling of high-purity water from semiconductor wafer backgrinding wastes, Resources Conservation and Recycling 41: 119-132

[5] Hu, C. Y., Lo, S. L., Kuan, W. H. and Lee, Y. D. (2005). Removal of fluoride from semiconductor wastewater by electrocoagulation-flotation. *Water Research*. **39**: 895 – 901.

[6] Lin, S.H.; Kiang, C.D. 2003. Combined physical, chemical and biological treatments of wastewater containing organics from a semiconductor plant, Journal of Hazardous Materials B97: 159-171

[7] APHA, 1992. Standard methods for the examination of water and wastewater, 17th ed., American Public Health Association, Washington, DC

[8] Lai, C.L.; Lin, S.H. 2003. Electrocoagulation of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication, Chemical Engineering Journal 95: 205-211

[9] Nik Norulaini, N.A.; Fatehah, M.O.; Teng, T.T.; Norli, I.; Sabrina, K. 2005. Induction of silica settling in wafer washing using pH adjustment, Seminar Kebangsaan Ke 4: Pengurusan Persekitaran 2005, Universiti Kebangsaan Malaysia, 279-288

[10] Park, S. -J., Yoon, T. -I., Bae, J. -H., Seo, H. -J. and Park, H. -J. (2001). Biological treatment of wastewater containing dimethyl sulphoxide from the semi-conductor industry. *Process Biochemistry*. **36**: 579 – 589.

[11] Sheikholeslami, R. and Bright, J. (2002). Silica and metals removal by pretreatment to prevent fouling of reverse osmosis membranes. *Desalination*. **143**: 255 – 267.

[12] Tanyildizi, M.S.; Őzer, D.; Elibol, M. 2005. Optimization of α-amylose production by *Bacillus sp.* using response surface methodology, Process Biochemistry 40: 2291-2296.

[13] Den, W. and Huang, C. (2005). Electrocoagulation for removal of silica nano-particles from chemical-mechanical-planarization wastewater. *Colloids and Surfaces A: Physicochemical Engineering Aspects*. **254**: 81 – 89