KINETICS OF DECOMPOSITION OF POLYETHYLENE GLYCOL IN ELECTROPLATING SOLUTION BY OZONATION WITH UV RADIATION

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ABSTRACT: The kinetics of the ozonation of polyethylene glycol (PEG) with ultraviolet (UV) radiation in the acid-based electroplating solution of the printed wiring board industry is studied. The substrate prescription of a typical electroplating solution is with pH of 0.18–0.42, [$CuSO_4 \cdot 5H_2O$] of 200 g/L, [H_2SO_4] of 60 g/L, and [Cl^-] of 0.03 g/L. Certainly, the discarded electroplating solution is hard to treat with the common chemical and biological processes because of its acidic and metallic compositions. In addition, it contains valuable substances suitable for recovery and reutilization. One of the most important processes for reviving it is to remove the aged organic additives such as PEG. A two-step reaction mechanism in terms of ozone A and total organic carbon is proposed to express the reaction kinetics of PEG ozonation with UV radiation with intensity [I_{uv}]. The initial concentration of PEG is 30 mg/L, according to the recipe of a typical electroplating solution, which is equivalent to total organic carbon of 16.3 mg/L. The reaction rate r expressions of the concentrations of the liquid phase ozone C_{ALb}, PEG C_{BLb}, and intermediates C_{ILb} are r_A ($=dC_{ALb}/dt$) $= -(k_{Am} + k_I[I_{uv}])C_{ALb} - (k_{R1} + k_{RI1}[I_{uv}])C_{ALb}C_{BLb} - (k_{R2} + k_{RI2}[I_{uv}])C_{ALb}C_{ILb}$, r_B ($=dC_{BLb}/dt$) $= -(k_{R1} + k_{RI1}[I_{uv}])C_{ALb}C_{BLb}$, r_{int} ($=dC_{ILb}/dt$) $= (k_{R1} + k_{RI1}[I_{uv}])C_{ALb}C_{BLb} - (k_{R2} + k_{RI2}[I_{uv}])C_{ALb}C_{ILb}$, with $k_{Am} = 0.0036\ s^{-1}$, $k_I = 4.654 \times 10^{-5} s^{-1}/(Wm^{-2})$, $k_{R1} = 13.525\ M^{-1}s^{-1}$, $k_{R2} = 0.751\ M^{-1}s^{-1}$, $k_{RI1} = 0.683\ M^{-1}s^{-1}/(Wm^{-2})$, and $k_{RI2} = 0.042\ M^{-1}s^{-1}/(Wm^{-2})$. These reaction kinetic expressions are useful and referable for the proper design of an ozonation system with UV radiation for the treatment of PEG in the printed wiring board electroplating solution.

INTRODUCTION

Wasted electroplating solution is one of the major wastewater sources in the printed wiring board (PWB) industry. The substrates (the major chemical species) of the recipe solution are inorganics such as sulfuric acid, copper sulfate, and hydrochloric acid, and the minor substances are organics such as polyethylene glycol (PEG), which is a brightening and stabilization agent (Fang 1996). Consequently, the characteristics of wasted electroplating solution include high acidity (pH = 0.18 to 0.42) and ionic strength. All of the above features make the solution hard to treat with conventional treatment processes (Suzuki 1976; Andreozzi et al. 1996a). The current major method used to treat the waste electroplating solution of PWB is chemical coagulation, which produces hazardous chemical sludge because of its high heavy metal content, such as copper. In Taiwan, the yield of the waste electroplating solution of PWB is approximately 106,000 m^3/day, resulting in about 21,000 ton waste sludge/year with 78% by weight moisture (*Waste* 1997). Furthermore, in view of the resource recycling, the waste electroplating solution of PWB has great reclamation and recycling potentials with high copper concentration and electric conductivity. However, the qualities of the organics of the electroplating solution are low and unreliable for the process after electroplating and electrophoresis. For this reason, removing the spent organic additives in order to add new additives is one of the key steps for the reutilization process.

Ozonation is an effective way to reduce the chemical oxidation demand and total organic carbons (TOCs) by oxidizing the stream solutions with ozone (Hewes and Davison 1971). Ozonation takes place via two different reaction pathways (Gurol and Singer 1982). Ozone can directly react with pollutants, ''direct ozonation'' by means of O_3 molecules. It can also indirectly react with pollutants, ''radical ozonation,'' by means of the highly oxidative free radicals such as hydroxyl radicals, which are produced by the ozone decomposition in the aqueous solution (Sotelo et al. 1987). The radical ozonation is nonselective and vigorous. The ozonation process in the acid condition mainly takes place through the direct oxidation reaction, which is selective (Beltrán and Alvarez 1996; Hautaniemi et al. 1998). Ozonation combined with ultraviolet (UV) radiation is deemed as a more effective process to remove organics as compared to the pure ozonation. UV radiation is commonly employed to enhance the ozone decomposition, yielding more free radicals and resulting in a higher ozonation rate (Prengle 1983; Chang et al. 1996). The decomposition rate expressions of ozone in the presence of UV radiation reported by Ikemizu et al. (1987) and Ku et al. (1996) were $-d[O_3]/dt = k_{aI}[O_3]^{1.5} + k_{bI}[O_3] + k_{II}[I_{uv}][O_3]$ and $k_{aK}[O_3]^{1.5} + k_{IK}[I_{uv}]^{0.9}[O_3]^{1.5}$, respectively, where the reaction rate constants were some functions of [OH^-]. The catalytic effect of the UV radiation of ozone decomposition was found significant in the acid region (Huang and Chen 1993). However, all their results were proposed for the aqueous solution and are not applicable to the electroplating solution of PWB examined in this study.

As reported by Suzuki (1976), the PEG chain is cleft randomly by the ozone in water. Compounds with a terminal hydroxyl group and esters are formed as the major products of ozonation. The electrophilic attack of ozone on the ester bond takes place. Andreozzi et al. (1996a) studied the ozonation of

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PEG 2000 in aqueous solution using the simple PEG-like structure substances such as ethylene glycol (EG), diethyleneglycol (DEG), and triethylene glycol (TEG). It was found that the direct ozonation mechanism at the acid condition is applicable for explaining that the relatively small amount of EG, glycolic aldehyde, and glycolic acid derivative appear as the intermediates of the DEG oxidation process. However, at the basic condition, the marked occurrence of EG, glycolic aldehyde, and glycolic acid derivatives is likely the consequence of the low selectivity of the radical ozonation mechanism. Note that they described the reaction kinetics of ozone A and PEG-like substances B as $-dC_A/dt = -dC_B/dt = k_B C_A C_B^n$, where C = concentration, k_B = reaction rate constant, and n = reaction order. The values of n for DEG, TEG, tetra-EG, and PEG 2000 are close to unit, whereas those of k_B for DEG, TEG, tetra-EG, and PEG 2000 are 0.348, 0.468, 0.416, and 5.182 $M^{-1}s^{-1}$, respectively. All their results are useful for the PEG ozonation in water or aqueous solution but do not refer to the electroplating solution. Recently, Li et al. (2000) investigated the kinetics of the ozonation of PEG in the PWB electroplating solution. However, the study did not consider the effect of UV radiation.

The objective of this study is to model and investigate the reaction kinetics of ozone photolysis and PEG decomposition by the combined ozonation with UV radiation in the electroplating solution of the PWB industry. Batch and semibatch ozonation experiments with UV radiation are proceeded under different reaction conditions. The dissolved liquid C_{ALb} and off-gas C_{AGe} ozone concentrations are measured for the samples drawn out from the reactor at specified time intervals. TOC is chosen as a mineralization index of PEG. PEG decomposition accompanies TOC variation and ozone consumption. The reaction rate expressions of ozone (dC_{ALb}/dt), PEG (dC_{BLb}/dt), and intermediate organic species (dC_{ILb}/dt) can then be obtained. These results can provide useful information about removing the PEG from the electroplating solution of PWB by ozonation with UV radiation for the reutilization process.

EXPERIMENTAL

Chemicals

The substrate recipe of the electroplating solution is $[CuSO_4 \cdot 5H_2O]$ = 200 g/L, $[H_2SO_4]$ = 60 g/L, and $[Cl^-]$ = 0.03 g/L. The concentration of PEG as the sole organic target is 30 mg/L according to the electroplating prescription. PEG with the chemical formula $HO(C_2H_4O)_nH$, which is used as a brightening and stabilization agent in the electroplating process, has an average molecular weight equal to 6,000, ranging from 5,000 to 7,000. All the chemicals employed are purchased in reagent grade from Merck (Darmstadt, Germany) and used without any further purification. All electroplating solutions are prepared with deionized water without other buffers. The pH value of the electroplating solution is about 0.25. The variation of pH during the experiments is found to be very slight because of the high acid concentration of the solution.

Instrumentation

The airtight reactor, 17.2-cm inside diameter, is made of Pyrex glass with an effective volume of 8 L and is equipped with a water jacket to maintain a constant solution temperature of 25°C in all experiments. The design of the reactor is based on the criteria of the shape factor of a standard six-blade turbine (McCabe et al. 1993). The gas diffuser, cylindrical shape with pore size of 10 μm, is located at the bottom of the reactor. Two quartz tubes of 4.4-cm outside diameter, symmetrically installed inside the reactor, are used to house the UV lamps. The low-pressure mercury lamps, with various output powers emitted principally at 254 nm, supply the UV radiation. The radiation intensity ($[I_{uv}]$, Wm^{-2}) is measured by a Spectroline (Spectronics Corp., New York) model DRC-100X digital radiometer with a DIX-254 radiation sensor (Ku et al. 1996). About 3.705 L of solution is used in each experiment, and the total sampling volume is within 5% of the solution. The stirred speed is as high as 800 rpm to ensure the complete mixing of liquid and gas phases, according to previous tests (Li et al. 2000). The generation of ozone is controlled by the power input of a Sumitomo (Sumitomo Co., Tokyo, Japan) model SG-01A ozone generator at constant gas pressure (1 kg force/cm^2, or 9.8 N/cm^2). The ozone generator used employs two steel plate electrodes and a ceramic dielectric. The discharge gap is 0.8 mm with air cooling. As specified by the supplier, the power needed is 0.4 kW at 30 gO_3/h, 100 gO_3/Nm^3, and 0.3 Nm^3O_2/h. Ozone-containing gas generated by pure oxygen is introduced into the reactor with a gas flow rate of 1.78 L/min at 273 K. The fed C_{AGi0} and discharged C_{AGe} gas ozone concentrations are measured by the Seki (Seki Electronics, Tokyo, Japan) model SOZ-6002 UV photometric analyzer, which is calibrated by the KI (potassium iodine) titration method (Rankness et al. 1996). The Orbisphere (Orbisphere Lab., Neuchâtel, Switzerland) model 3600 liquid ozone monitor with a sensor of membrane-containing cathode, which is calibrated by the indigo method (Bader and Hoigné 1981) as previously described (Li et al. 2000), is used to analyze the dissolved ozone concentration C_{ALb} in the electroplating solution. A circulation pump is used to transport the liquid from the reactor to the sensor of the monitor with a flow rate of 0.18 L/min and to reflow it back during the ozonation. Samples are drawn out from the reactor at desired intervals in the course of the experiments. The residual dissolved ozone in the sample is removed by stripping with nitrogen. The TOC concentration of the sample is analyzed by an OIC (O. I. Corp., Tex.) model 700 TOC analyzer. The instrument uses the UV-persulfate technique to convert the organic carbon for the subsequent analysis by an infrared carbon dioxide analyzer calibrated with the potassium hydrogen phthalate standard. All fittings, tubing, and bottles are made of stainless steel, Teflon, or glass. The experimental apparatus employed in this work is shown in Fig. 1.

Experimental Procedures

Before starting the ozonation experiments, the ozone-containing gas is bypassed to the photometric analyzer to assure the stability and ozone concentration. Four different light intensities ($[I_{uv}]$ = 20.5, 31.1, 47.0, and 57.6 Wm^{-2}) are employed to test the UV radiation effect on the ozonation. A part of the gas stream at the present flow rate is directed into the reactor when reaching the set conditions.

Both semibatch and batch experiments are performed to study the ozone decomposition with UV radiation and carried out until reaching the steady-state $C_{ALb,ss}$ and zero concentrations of dissolved ozone for the semibatch and batch cases, respectively. The batch experiment of PEG ozonation is conducted by the stopped-flow-like method (Kuo and Huang 1995), with PEG-containing liquid being injected into the reactor prefilled with the electroplating solution of known dissolved ozone concentration C_{ALb}. The liquid phase experiment is operated at a high agitation speed of 800 rpm to eliminate the mass transfer influence.

RESULTS AND DISCUSSION

The results of the kinetic study include two parts: (1) O_3/UV decomposition in the substrates of the electroplating solution; and (2) PEG ozonation with UV radiation. Ozone photolysis in the electroplating solution is studied under various ozone dosages and light intensities. The temporal variations of dissolved and off-gas ozone concentrations are monitored to

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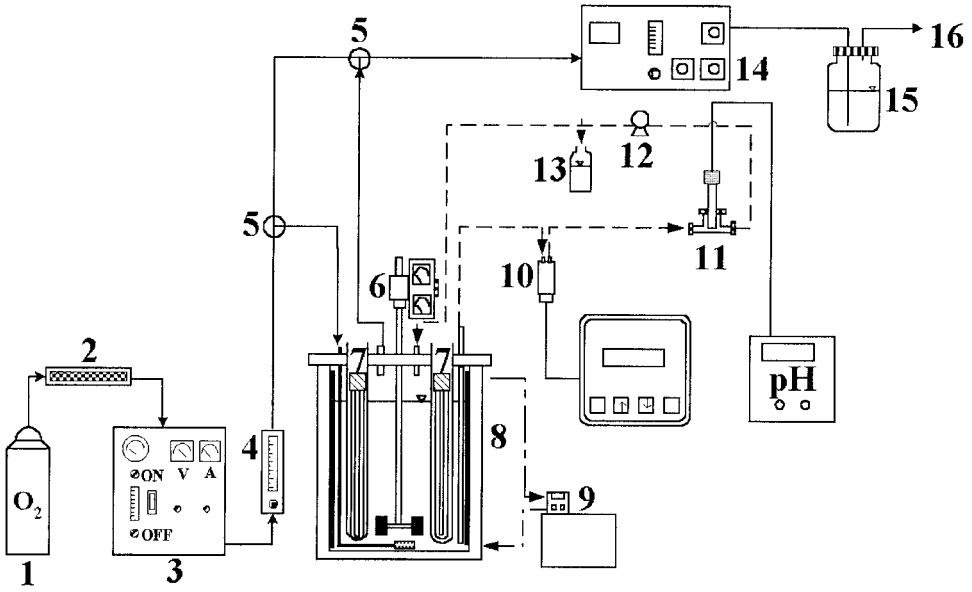

FIG. 1. Experimental Apparatus Sketch—Components: 1. Oxygen Cylinder, 2. Drying Tube, 3. Ozone Generator, 4. Flow Meter, 5. Three-Way Valve, 6. Stirrer, 7. UV Lamp, 8. Reactor, 9. Thermostat, 10. Liquid Ozone Sensor, 11. pH Sensor, 12. Circulation Pump, 13. Sample Port, 14. Gaseous Ozone Detector, 15. KI Solution, 16. Vent to Hood

provide the data for determining the kinetics parameters. PEG ozonation is carried out with different UV radiation intensities. The temporal concentrations of TOC and dissolved ozone are analyzed for model acquirement.

Ozone Self-Decomposition with UV Radiation in Electroplating Solution

Although there have been numerous studies about ozone decomposition in aqueous solution, such information in the electroplating solution is still scarce. It is well known that UV radiation enhances the ozone decomposition. However, its role in the electroplating solution remains indeterminate. For this reason, the kinetic expression of O_3/UV decomposition reaction is first established in the present experiments. The general reaction rate expression of ozone decomposition was proposed by Chang et al. (1996)

$$-d[O_3]/dt = k_{Am}[O_3]^m + k_{Bn}[O_3]^n + k_{Iu}[O_3]^u \quad (1)$$

where k_{Am}, k_{Bn}, and k_{Iu} represent the acidic, basic, and radiation decomposition reaction rate constants, respectively. In the expression, k_{Am}, k_{Bn}, and k_{Iu} are dependent slightly on $[OH^-]$, strongly on $[OH^-]$, and on $[OH^-]$ and $[I_{uv}]$, respectively. The rate equation can be reduced to $-d[O_3]/dt = k_{Am}[O_3]^m + k_{Iu}[O_3]^u$ by neglecting the basic term for the strong acid condition of the electroplating solution. Further noting that the variation of acidity is slight in the strong acidic electroplating solution, one then has the ozone decomposition rate equation with UV radiation in the electroplating solution

$$-r_A = -\frac{dC_{ALb}}{dt} = -r_{Ad} - r_{Au} = k_{Am}C_{ALb}^m + k_I[I_{uv}]^i C_{ALb}^u \quad (2)$$

where C_{ALb} = concentration of ozone A in bulk liquid; $[I_{uv}]$ = light intensity of UV radiation; and k_I = rate constant of radiation decomposition expressed excluding the term $[I_{uv}]$. For the case without UV radiation, (2) reduces to $-r_A = k_{Am}C_{ALb}^m$. The values of k_{Am} and m were determined by Li et al. (2000) as 0.0036 s^{-1} and 1, respectively. The k_{Am} value is >0.00032 s^{-1} obtained by Sotelo et al. (1987) for the water system at the same pH because of the high ionic strength of the electroplating solution employed by Li et al. (2000).

Consider the combined absorption and decomposition of ozone in a semibatch stirred gas-liquid reactor. The mass balance equations describing the steady-state condition *ss* in the reactor for the consumption of ozone by the O_3/UV decomposition reactions are as following:

$$Q_G(C_{AGi0} - C_{AGe,ss})/V_L = -r_A \quad (3)$$

$$Q_G(C_{AGi0} - C_{AGe,ss})/V_L - k_{Am}C_{ALb,ss} = -r_{Au} = k_I[I_{uv}]^i C_{ALb,ss}^u \quad (4)$$

where Q_G = gas flow rate; V_L = liquid volume in reactor; C_{AGi0} and $C_{AGe,ss}$ = ozone concentrations of inlet and steady-state outlet gases; and $C_{ALb,ss}$ = ozone concentration of bulk liquid at steady state.

The value of u can be obtained from the slope of the plot of $\log(-r_{Au})$ versus $\log(C_{ALb,ss})$ under a fixed UV radiation intensity. Table 1 gives the values of $C_{AGe,ss}$ and $C_{ALb,ss}$ at various C_{AGi0} and $[I_{uv}]$ for the semibatch system of the electroplating solution substrate, with pH = 0.18 to 0.42, Q_G = 1.78 L/min at 273 K, and V_L = 3.705 L. Employing the data of Table 1 with UV radiation intensity equal to 57.6 Wm^{-2}, one may perform a linear regression by plotting $\log(-r_{Au})$ against $\log(C_{ALb,ss})$, as shown in Fig. 2. From the slope (=1.019) of the straight line obtained by the least-squares calculation procedure, the reaction order of ozone in the photolysis reaction may be regarded as first order (u = 1). It indicates that both ozone self-decomposition and photolysis reaction rates are proportional to ozone concentration. Consequently, the slope of $\log(-r_{Au}/C_{ALb,ss})$ versus $\log([I_{uv}])$ may be used to find the value of i. As shown in Fig. 3, the slope representing the order

TABLE 1. Steady-State Concentrations of Ozone in Exit Gas $C_{AGe,ss}$ and Bulk Liquid $C_{ALb,ss}$ at Various Inlet Gaseous Ozone Concentrations C_{AGi0} and UV Radiation Intensities $[I_{uv}]$—Q_G = 1.78 L/min at 273 K, V_L = 3.705 L, T = 298 K

C_{AGi0} (mg/NL)	$[I_{uv}]$ (W/m^2)	$C_{AGe,ss}$ (mg/NL)	$C_{ALb,ss}$ (mg/L)
25.0	57.6	21.10	5.00
23.0	57.6	19.37	4.62
20.0	57.6	16.94	3.95
15.0	57.6	13.20	2.30
10.0	57.6	8.68	1.70
5.0	57.6	4.30	0.91
20.0	47.0	17.06	4.03
20.0	31.1	17.28	4.12
20.0	20.5	17.69	4.15
8.0	20.5	7.00	1.79

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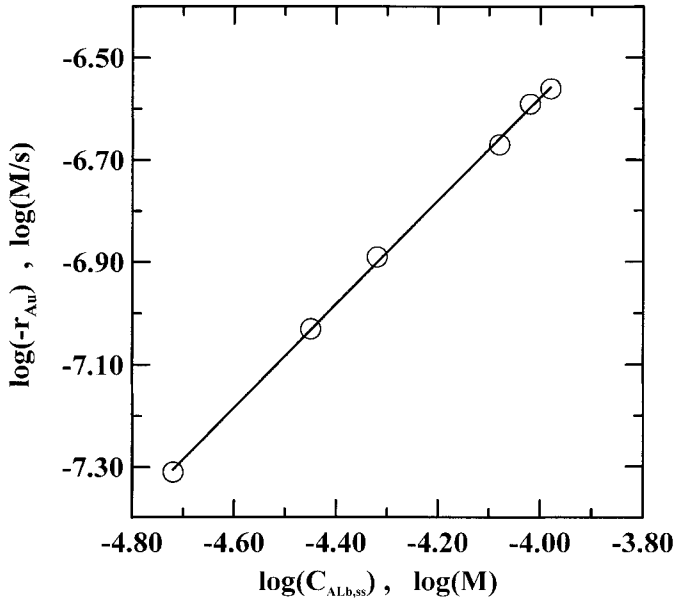

FIG. 2. $\log(-r_{Au})$ versus $\log(C_{ALb,ss})$ for Ozone Decomposition with UV Radiation Intensity of 57.6 W/m^2 in Electroplating Solution Substrate in Semibatch System (Slope Represents Reaction Order u of Ozone; Line: $Y = 1.019X - 2.500$, $r^2 = 0.999$; ○ = Experimental Data)

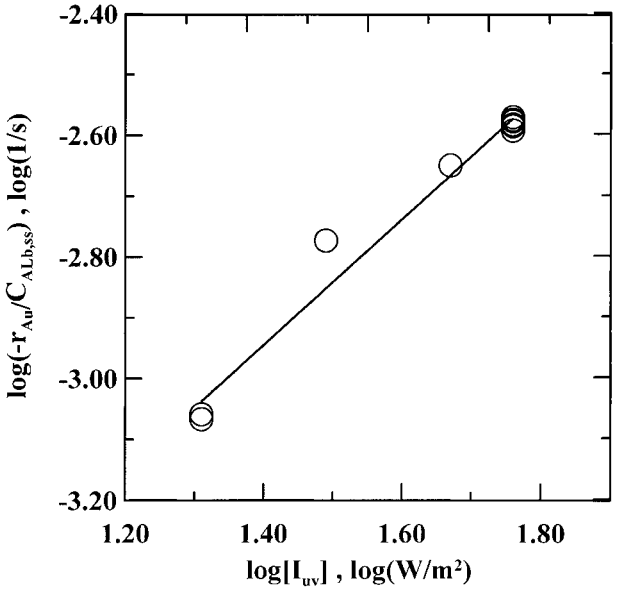

FIG. 3. $\log(-r_{Au}/C_{ALb,ss})$ versus $\log([I_{uv}])$ for Ozone Decomposition with UV Radiation in Electroplating Solution Substrate in Semibatch System (Slope Represents Reaction Order i of UV Radiation; Line: $Y = 1.038X - 4.399$, $r^2 = 0.977$; ○ = Experimental Data)

of UV radiation is 1.038. Thus, one may employ the first reaction order to describe UV radiation ($i = 1$) and get the ozone photolysis reaction equation as $-r_{Au} = k_I[I_{uv}]C_{ALb}$. It illustrates that the ozone photolysis reaction rate depends on both ozone concentration and UV radiation intensity with the first reaction order of each. Then the ozone photolysis reaction rate constant k_I is fitted to be 4.654×10^{-5} m^{2}W^{-1}s^{-1} with r^2 of 0.991 by plotting $-r_{Au}$ against $[I_{uv}]C_{ALb,ss}$ (Fig. 4). This gives

$$-r_A = k_A C_{ALb} \tag{5}$$

with $k_A = k_{Am} + k_I[I_{uv}] = (0.0036 + 4.654 \times 10^{-5}[I_{uv}])$ s^{-1}.

The decomposition rate of ozone increases about 25–75% owing to the UV radiation (20.5–57.6 W/m^2) in the present experiments. The UV radiation initiates the photolysis of dissolved ozone to generate hydrogen peroxide and an oxygen molecule. The hydrogen peroxide can then be decomposed into hydroxyl radicals by being exposed to UV radiation. This thus enhances the ozone decomposition rate. According to the above pathway, Peyton and Glaze (1988) gave the following decomposition reactions of O_3 with UV radiation:

$$O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2$$

$$H_2O_2 + h\nu \rightarrow 2OH\cdot$$

$$pH_2O_2 \rightleftarrows HO_2^- + H^+$$

$$O_3 + HO_2^- \rightarrow \cdot O_3^- + HO_2\cdot$$

The value of the reaction rate constant k_I of this study is lower than the k_{II} of Ikemizu et al. (1987). At the same pH

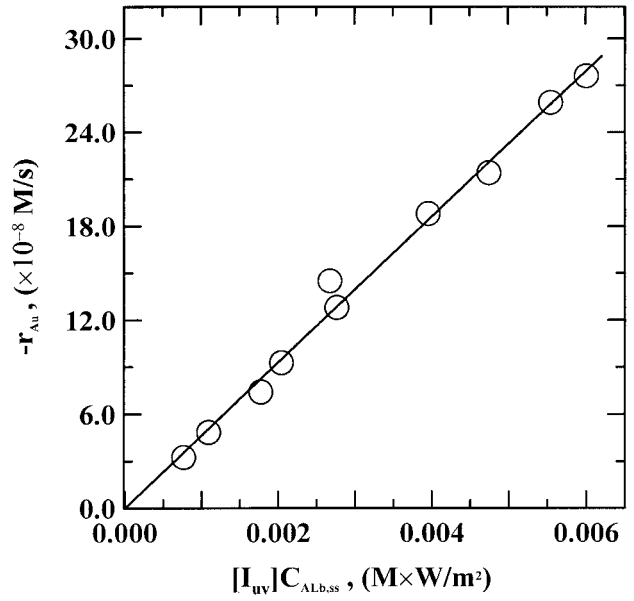

FIG. 4. $-r_{Au}$ versus $[I_{uv}]C_{ALb,ss}$ for Ozone Decomposition with UV Radiation in Semibatch System (Slope Represents Reaction Rate Constant k_I of Ozone Photolysis Reaction; Line: $Y = 4.654 \times 10^{-5}X$, $r^2 = 0.991$; ○ = Experimental Data)

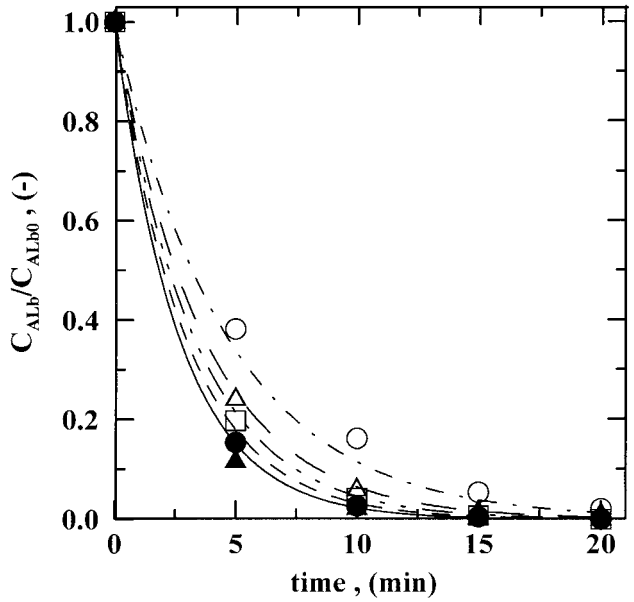

FIG. 5. (C_{ALb}/C_{ALb0}) versus Time for Ozone Decomposition with UV Radiation in Electroplating Solution Substrate in Batch System ($R^2 = 0.988$; Symbols, Lines: Experiments, Prediction; ○ and —·—, △ and — —, □ and —··—, ● and --------, ▲ and ——: $[I_{uv}] = 0.0$, 20.5, 31.1, 47.0, 57.6 Wm^{-2})

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value of 0.25, the values are 4.654×10^{-5} (k_I) and 4.802×10^{-4} $m^2W^{-1}s^{-1}$ (k_{II}), respectively. Noting that the solution of chemicals such as metallic ions may absorb UV light (Leifer 1988), one may regard the low k_I as attributed to the high molar absorptivity of the medium of the electroplating solution.

To further verify the kinetic expression of (5), batch experiments of O_3/UV photolysis are performed. The concentrations of dissolved ozone are measured at different reaction times. One may have (6) for the batch system

$$C_{ALb} = C_{ALb0}e^{-k_A t} \tag{6}$$

where k_A described in (5) is a function of UV random intensity. The comparison of experimental data and predicted values is shown in Fig. 5. It is seen that the kinetic model is attuned to the experimental data with $R^2 > 0.98$.

PEG Ozonation with UV Radiation in Electroplating Solution

PEG ozonation with a distinct UV radiation intensity in the batch system is carried out to study the kinetics. UV radiation is combined with ozone to create the synergistic effect on the mineralization of organics. Previous blank tests have indicated that the volatility of PEG under the experimental conditions is negligible. Furthermore, the PEG elimination in the electroplating solution by virtue of sole UV radiation has tested as insignificant. However, with the synergistic effect of ozonation with UV radiation, the PEG removal is found remarkable. The enhanced phenomenon results from the free radical reactions of highly active oxidants such as hydroxyl radicals produced because of the ozone photolysis reactions.

The degradations of PEG and PEG-like structure substances by the ozonation without UV radiation in the aqueous solution have been studied by Suzuki (1976) and Andreozzi et al. (1996a). The occurrence of intermediates such as glycolic aldehyde, glycolic acid derivatives, and compounds with a terminal hydroxyl group and esters was noted. The reaction rate expressions of ozone *A* and PEG-like substances *B* in the aque-

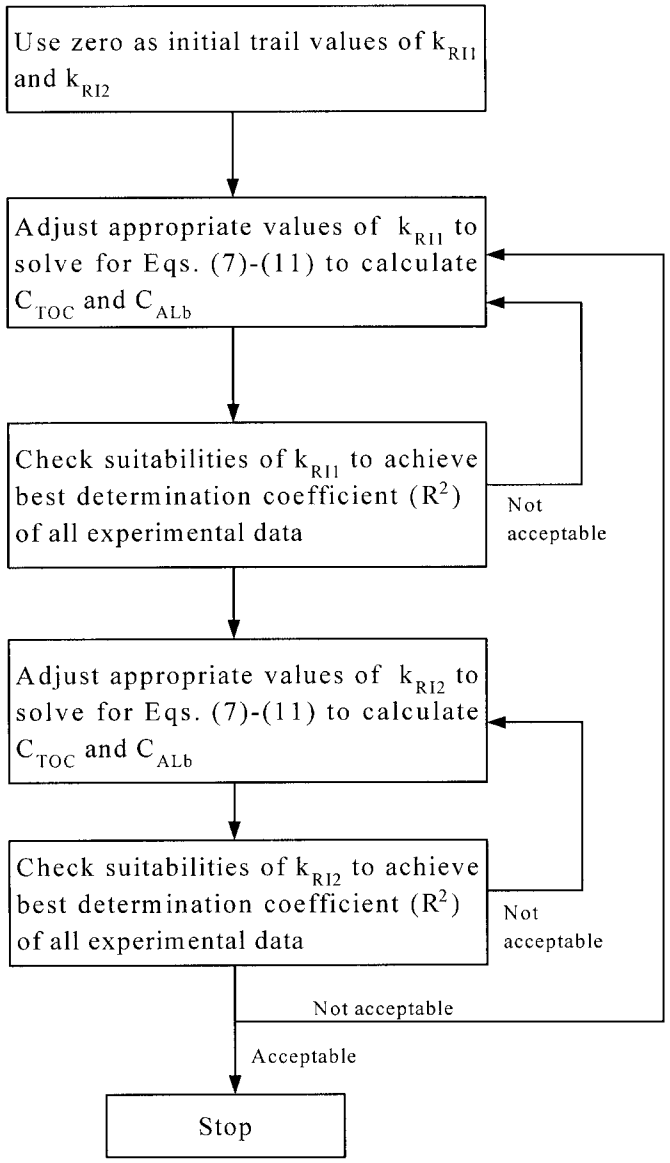

FIG. 6. Procedures to Determine Kinetics Parameters (k_{RI1}, k_{RI2}) of PEG Ozonation with UV Radiation in Electroplating Solution

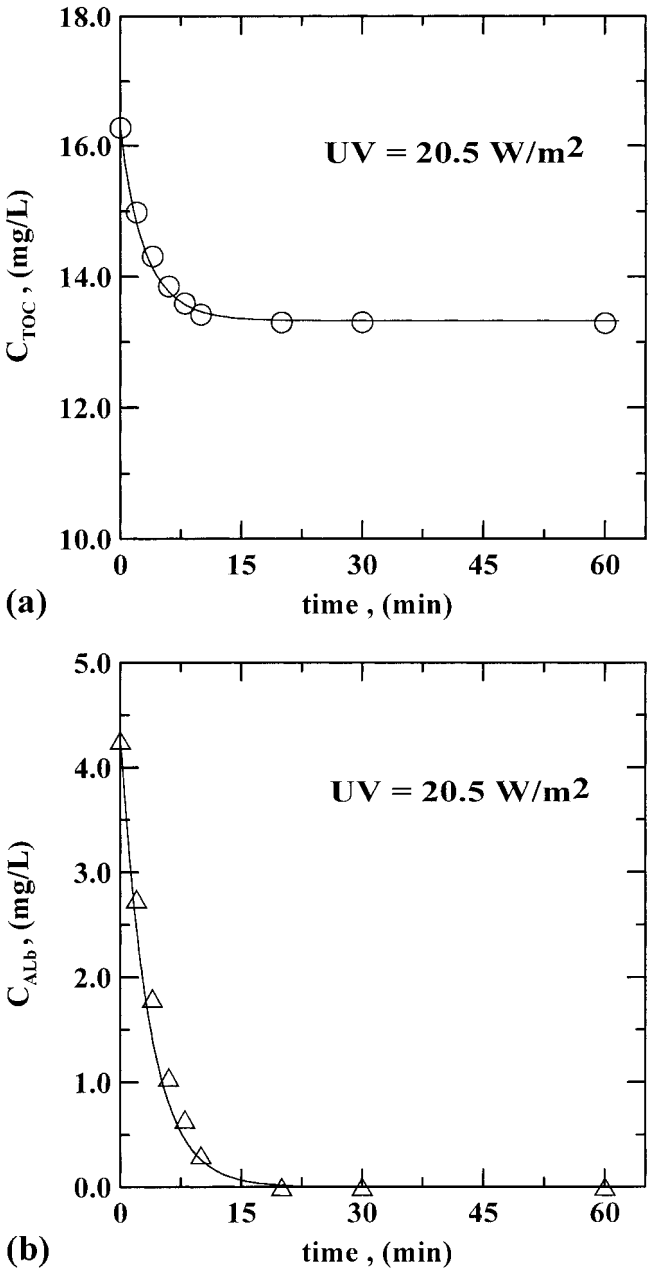

FIG. 7. Concentration Variations of C_{TOC} and C_{ALb} of PEG Ozonation with UV Radiation of 20.5 W/m^2 in Electroplating Solution of Batch System [Symbols: Experiments; Lines: Prediction: (a) C_{TOC}: $R^2 = 0.993$; (b) C_{ALb}: $R^2 = 0.983$]

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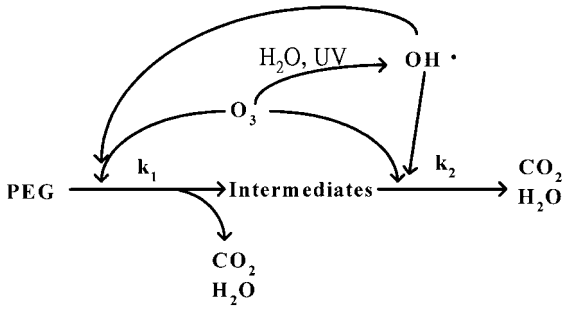
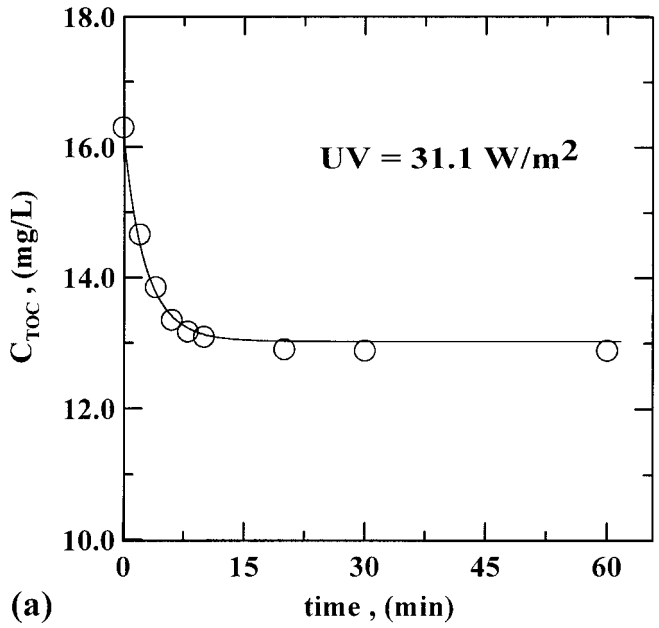
ous solution were described as $-dC_A/dt = -dC_B/dt = k_B C_A C_B$ (Andreozzi et al. 1996a). In the ozonation process of other organics such as phenol (Andreozzi et al. 1996b) and chlorophenol (Hautaniemi et al. 1998), and some solutes such as 2-propanol, *o*-xylene, toluene, and benzene (Hoigné and Bader 1983), the reaction rates have been reported to be first orders with respect to ozone, reactants, and intermediates. These findings support that the ozonation reaction rates may be generally considered first orders with respect to ozone *A*, reactant *B*, and intermediates int formed during ozonation (Gurol 1985). Based on the above works, one may propose a two-step reaction model for the reactions of ozone with PEG and its reaction intermediates (for example: glycolic acid or glycolic aldehyde). The simplified scheme of the decomposition pathways of PEG ozonation with UV radiation is



It is apparent that the PEG decomposition in the O_3/UV process includes direct oxidation by means of ozone and indirect oxidation by means of hydroxyl radicals. In the acidic condition, hydroxyl radicals (OH·) are generated mainly from the ozone photolysis reaction. Referring to the works of Gurol (1985) and Hautaniemi et al. (1998), one has the following rate expressions for ozone *A*, PEG *B*, and intermediates int:



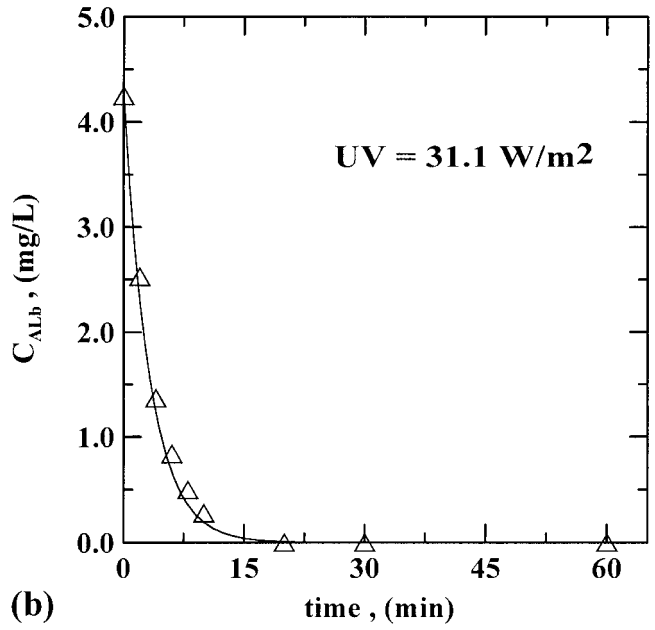
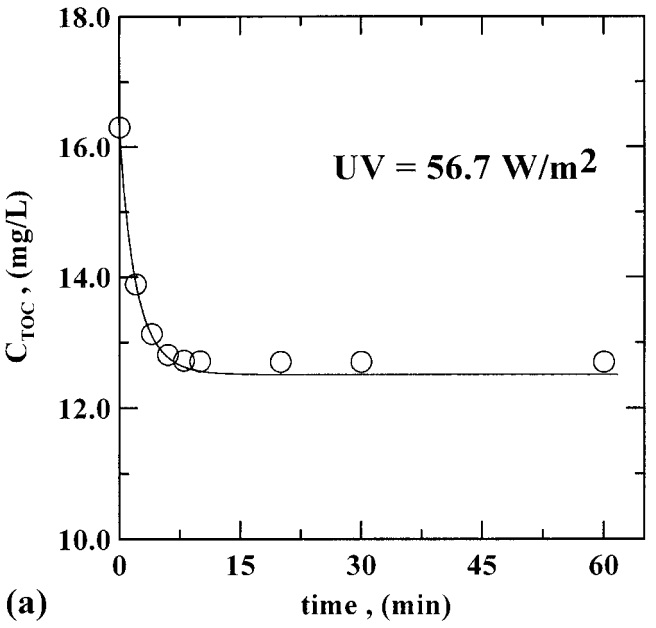


FIG. 8. Concentration Variations of C_{TOC} and C_{ALb} of PEG Ozonation with UV Radiation of 31.1 W/m^2 in Electroplating Solution of Batch System [Symbols: Experiments; Lines: Prediction: (a) C_{TOC}: R^2 = 0.991; (b) C_{ALb}: R^2 = 0.994]



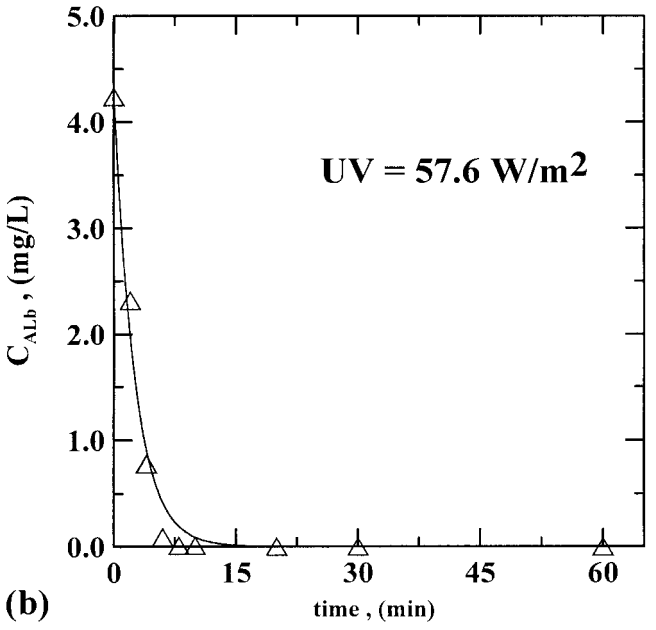


FIG. 9. Concentration Variations of C_{TOC} and C_{ALb} of PEG Ozonation with UV Radiation of 57.6 W/m^2 in Electroplating Solution of Batch System [Symbols: Experiments; Lines: Prediction: (a) C_{TOC}: R^2 = 0.985; (b) C_{ALb}: R^2 = 0.985]

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TABLE 2. Comparison of Ozonation Kinetic Expressions and Experimental Methods of PEG Removal between This Work and Others

Author	Experimental Method: Solution	Reactor type	pH	UV radiation	Target substance	Rate constant
Suziki (1976)	Aqueous	Semibatch	2, 12	No	PEG 8000	NA[a]
Andreozzi et al. (1996a)[b]	Aqueous	Semibatch	4, 6, 7, 8.8	No	PEG 2000	k_B = 5.182 $M^{-1}s^{-1}$
					DEG	k_B = 0.348 $M^{-1}s^{-1}$
Li et al. (2000)[c]	Electroplating solution	Semibatch and batch	0.18–0.42	No	PEG 6000	k_{R1} = 13.525 $M^{-1}s^{-1}$
						k_{R2} = 0.751 $M^{-1}s^{-1}$
This work[d]	Electroplating solution	Semibatch and batch	0.18–0.42	Yes	PEG 6000	k_{R1} = 13.525 $M^{-1}s^{-1}$
						k_{R2} = 0.751 $M^{-1}s^{-1}$
						k_{RI1} = 0.683 $m^2W^{-1}M^{-1}s^{-1}$
						k_{RI2} = 0.042 $m^2W^{-1}M^{-1}s^{-1}$

[a]Not reported.
[b]$dC_B/dt = -k_BC_AC_B$, C_A and C_B = liquid concentrations of ozone and PEG or DEG.
[c]$dC_B/dt = -k_{R1}C_AC_B$, $dC_I/dt = k_{R1}C_AC_B - k_{R2}C_AC_I$, C_I = liquid concentration of intermediates.
[d]$dC_B/dt = -(k_{R1} + k_{RI1}[I_{uv}])C_AC_B$, $dC_I/dt = (k_{R1} + k_{RI1}[I_{uv}])C_AC_b - (k_{R2} + k_{RI2}[I_{uv}]C_AC_I$.

$$r_A\ (=dC_{ALb}/dt) = -k_AC_{ALb} - k_1C_{ALb}C_{BLb} - k_2C_{ALb}C_{ILb} \quad (7)$$

$$r_B\ (=dC_{BLb}/dt) = -k_1C_{ALb}C_{BLb} \quad (8)$$

$$r_{int}\ (=dC_{ILb}/dt) = k_1C_{ALb}C_{BLb} - k_2C_{ALb}C_{ILb} \quad (9)$$

with $k_A = k_{Am} + k_I[I_{uv}]$, $k_1 = k_{R1} + k_{RI1}[I_{uv}]$, and $k_2 = k_{R2} + k_{RI2}[I_{uv}]$.

The concentration of TOC in the electroplating solution is

$$C_{\mathrm{TOC}} = \alpha C_{BLb} + \beta C_{ILb} \quad (10)$$

The applicable initial conditions of the system at $t = 0$ are

$$C_{ILb} = 0; \quad C_{BLb} = C_{BLb0}; \quad C_{ALb} = C_{ALb0}; \quad C_{\mathrm{TOC}} = C_{\mathrm{TOC0}} = \alpha C_{BLb0} \quad (11)$$

The initial concentration of PEG is 30 mg/L, which is equivalent to TOC of 16.3 mg/L. The values of α, β, k_{R1}, k_{R2} were obtained by Li et al. (2000) as 271.7 MM^{-1}, 155 MM^{-1}, 13.525 $M^{-1}s^{-1}$, and 0.751 $M^{-1}s^{-1}$, respectively. The variations of C_{TOC} and C_{ALb} under different experimental conditions are measured at successive reaction time intervals. Solving for (7)–(11) by the fourth-order Runge-Kutta method with the Turbo C program, one may obtain the predicted values with presumed kinetics parameters (rate constants: k_{RI1} and k_{RI2}). The values of k_{RI1} and k_{RI2} are estimated by comparing the predicted results with the experimental data with minimum differences. The simulation procedures are shown in Fig. 6. As a result, k_{RI1} and k_{RI2} are determined as 0.683 and 0.042 $m^2W^{-1}M^{-1}s^{-1}$. It is obvious that the reaction rate constants of PEG (k_{R1} and k_{RI1}) are greater than those of intermediates (k_{R2} and k_{RI2}). The findings are consistent with the results of Andreozzi et al. (1996a) that the intermediates of PEG had lower ozonation reactivity than PEG. Figs. 7–9 compare the predicted results of the two-step reaction model with experimental data, indicating good agreements. The TOC removal efficiency increases with UV radiation intensity with the same initial ozone dosage (C_{ALb0} = 4.24 mg/L). Thus, the UV radiation enhances the PEG decomposition rate. The reaction rate expressions of the concentrations of the liquid phase ozone C_{ALb}, PEG C_{BLb}, and intermediates C_{ILb} are $r_A\ (=dC_{ALb}/dt) = -(0.0036 + 4.654 \times 10^{-5}[I_{uv}])C_{ALb} - (13.525 + 0.683[I_{uv}])\cdot C_{ALb}C_{BLb} - (0.751 + 0.042[I_{uv}])C_{ALb}C_{ILb}$; $r_B\ (=dC_{BLb}/dt) = -(13.525 + 0.683[I_{uv}])C_{ALb}C_{BLb}$; and $r_{int}\ (=dC_{ILb}/dt) = (13.525 + 0.683[I_{uv}])C_{ALb}C_{BLb} - (0.751 + 0.042[I_{uv}])C_{ALb}C_{ILb}$. These reaction rate expressions are useful and referable for the proper design of the ozonation system with UV radiation for the treatment of PEG in the PWB electroplating solution.

Note that the values of k_{R1} (13.525 $M^{-1}s^{-1}$) and k_{R2} (0.751 $M^{-1}s^{-1}$) for the sole ozonation of PEG 5000–7000 in the electroplating solution studied by Li et al. (2000) are about 2 times those of k_B of PEG 2000 (5.182 $M^{-1}s^{-1}$) and DEG (0.348 $M^{-1}s^{-1}$) in the aqueous solution reported by Andreozzi et al. (1996a), as shown in Table 2. This may be due to the high ionic strength of the electroplating solution. Table 2 also compares the results of this work with those of other related studies. The results clearly indicated that the intermediates are more refractory than PEG.

Further noted is that H_2O_2/UV or other advanced oxidation processes with the addition of OH^- may give higher removal of PEG than O_3/UV because of the generation of more hydroxyl radicals. Nevertheless, the application of O_3/UV without changing the substrate recipe of the electroplating solution is preferred for the reutilization purpose. The cost of the power consumption of generating O_3 is vital for adopting the O_3/UV.

CONCLUSIONS

Ozonation combined with UV radiation is an effective way to remove PEG in the electroplating solution. The ozone photolysis reaction rate is proportional to the dissolved ozone concentration and UV radiation intensity. The mineralization rate of PEG ozonation is accelerated by the UV radiation. The following conclusions may be drawn:

- The kinetic expression of ozone *A* decomposition reaction with UV radiation in the acidic electroplating solution has been established. The results give the reaction rate expression as $r_A\ (=dC_{ALb}/dt) = -(k_{Am} + k_I[I_{uv}])C_{ALb}$, with k_{Am} = 0.0036 s^{-1} and $k_I = 4.654 \times 10^{-5}$ $s^{-1}/(Wm^{-2})$.
- In PEG *B* ozonation with UV radiation, the reaction kinetics may be expressed by a two-step reaction mechanism involving PEG and intermediates int. The predicted results of C_{ALb} and C_{TOC} agree with the experimental data.
- The kinetic equations of PEG ozonation with UV radiation may be expressed as $r_A\ (=dC_{ALb}/dt) = -(0.0036 + 4.654 \times 10^{-5}[I_{uv}])C_{ALb} - (13.525 + 0.683[I_{uv}])C_{ALb}C_{BLb} - (0.751 + 0.042[I_{uv}])C_{ALb}C_{ILb}$; $r_B\ (=dC_{BLb}/dt) = -(13.525 + 0.683[I_{uv}])C_{ALb}C_{BLb}$; and $r_{\mathrm{int}}\ (=dC_{ILb}/dt) = (13.525 + 0.683[I_{uv}]C_{ALb}C_{BLb} - (0.751 + 0.042[I_{uv}])C_{ALb}C_{ILb}$.
- The reactivity of ozonation of PEG is higher than that of intermediates.

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NOTATION

The following symbols are used in this paper:

C_A, C_{ALb} = concentration of A or ozone in bulk liquid (M or mg/L);
C_{AGe} = gas concentration of ozone in free volume (M or mg/NL);
$C_{AGe,ss}$ = gas concentration of ozone in free volume at steady state (M or mg/NL);
C_{AGi0} = gas concentration of ozone of inlet gas (M or mg/NL);
$C_{ALb,ss}$ = C_{ALb} at steady state (M or mg/L);
C_{ALb0} = concentration of ozone in bulk liquid at time = 0 (M or mg/L);
C_B, C_{BLb} = concentration of B or PEG in bulk liquid (M or mg/L);
C_{BLb0} = initial concentration of PEG in bulk liquid (M or mg/L);
$\underline{C_e}$ = experimental concentration data (M or mg/L);
$\overline{C_e}$ = average value of experimental concentration data (M or mg/L);
C_{ILb} = concentration of intermediates in reaction of PEG decomposed by ozonation (M);
C_p = predicted concentration values (M or mg/L);
$C_{\rm TOC}$ = concentration of TOC (M or mg/L);
$C_{\rm TOC0}$ = initial concentration of TOC (M or mg/L);
$[I_{uv}]$ = light intensity of UV lamp (W/m^2);
i = reaction order of UV radiation of ozone photolysis reaction;
int = intermediates produced by ozonation reaction;
k_A = reaction rate constant of ozone decomposition, $=k_{Am} + k_I[I_{uv}]$ (s^{-1});
k_{Am} = acidic decomposition rate constant of ozone [$(M)^{1-m}$ s^{-1}];
k_{aI} = reaction rate constant reported by Ikemizu et al. (1987) [$(M)^{-0.5}s^{-1}$];
k_{aK} = decomposition rate constant of ozone reported by Ku et al. (1996) [$(M)^{-0.5}s^{-1}$];
k_B = reaction rate constant of $-dC_B/dt = k_BC_AC_B^n$ ($M^{-n}s^{-1}$);
k_{bI} = reaction rate constant reported by Ikemizu et al. (1987) (s^{-1});
k_I = reaction rate constant of ozone photolysis [$(Wm^{-2})^{-i}(M)^{1-u}s^{-1}$];
k_{II} = reaction rate constant of ozone photolysis reported by Ikemizu et al. (1987) [$(Wm^{-2})^{-1}s^{-1}$];
k_{IK} = reaction rate constant of ozone photolysis reported by Ku et al. (1996) [$(Wm^{-2})^{-0.9}(M)^{-0.5}s^{-1}$];
k_{Iu} = reaction rate constant of ozone photolysis in (1) [$(M)^{1-u}s^{-1}$];
k_{R1} = reaction rate constant of PEG reacted with ozone ($M^{-1}s^{-1}$);
k_{R2} = reaction rate constant of intermediates reacted with ozone ($M^{-1}s^{-1}$);
k_{RI1} = reaction rate constant of PEG reacted with OH$\cdot$ induced by UV ($m^2W^{-1}M^{-1}s^{-1}$);
k_{RI2} = reaction rate constant of intermediates reacted with OH$\cdot$ induced by UV ($m^2W^{-1}M^{-1}s^{-1}$);
k_1 = PEG decomposition reaction rate constant ($M^{-1}s^{-1}$);
k_2 = intermediates decomposition reaction rate constant ($M^{-1}s^{-1}$);
m = acidic decomposition reaction order of ozone of (1) or (2);
n = reaction order of kinetic expression of $-dC_B/dt = k_BC_AC_B^n$, or (1);
$[OH^-]$ = molar concentration of OH^- ions (M);
$[O_3]$ = molar concentration of dissolved liquid ozone (M);
Q_G = ozone-containing gas flow rate (L s^{-1});
r_A, r_B, r_{int} = reaction rates of formations of A, B, and int (Ms^{-1}, Ms^{-1}, Ms^{-1});
r_{Ad} = reaction rate of ozone self-decomposition without UV radiation (Ms^{-1});
r_{Au} = reaction rate of ozone photolysis reaction (Ms^{-1});
R^2 = determination coefficient, $1 - [\Sigma (C_e - C_p)^2/\Sigma (C_e - \overline{C_e})^2]$;
r^2 = correlation coefficient;
T = temperature (K);
t = reaction time (s);
u = reaction order of ozone photolysis reaction;
V_L = liquid volume (L);
α = initial ratio of concentrations of TOC to PEG (M M^{-1}); and
β = ratio of concentrations of TOC associated with intermediates int to int (M M^{-1}).

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