Improved O_3/H_2O_2 oxidation process for wastewater reclamation

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Abstract A continuous two step O_3/H_2O_2 oxidation system, in which the waste gas from the former reactor was reused in the latter step with an ejector, was established for the purpose of wastewater reclamation in electronics industries. ORP monitor was combined into the system to obtain the optimum ratio of H_2O_2 to O_3 by automatically adjusting the dosage of H_2O_2, and ion exchange resin was used for removing organic acids formed during oxidation. The effectiveness of the O_3/H_2O_2 oxidation system for TOC removal was investigated under various conditions by using IPA, DMSO, and NMP as model substances. The optimum H_2O_2/O_3 for oxidizing IPA was in a range above 0.15, and it increased with the increase of O_3 dose. A sudden drop of ORP from ca. 800 mV to a little more than 200 mV was observed when H_2O_2/O_3 was approaching the optimum point from the lower end. An ORP between 250 mV and 300mV or 800 mV and 900 mV was proper for H_2O_2/O_3 control. The treatability of the model substances was in an order of IPA<<DMSO<NMP, being consistent with the magnitude of the energy of the highest occupied molecular orbital (ε_{HOMO}). The two step treatment system developed in this study was found to be more efficient than the conventional single step system. With the help of H_2O_2 dosing control and two step treatment using waste O_3, the system could save about 40% O_3 in comparison with the conventional O_3/H_2O_2 oxidation process.

Keywords AOP; H_2O_2 dosing control; ORP; O_3/H_2O_2 method; TOC removal; wastewater reclamation

Introduction

Ultra pure water is extensively used for silicone wafer cleansing in the electronics industry. Most of the spent ultra pure water is recovered for the purposes of saving water and cutting water treatment cost, and the recovery rate has exceeded 70% in Japan. The spent ultra pure water contains a small amount of organic compounds, which must be removed before the recovered water is returned to ultra pure water production lines. Biological treatment methods, UV oxidation method, UV/O_3 method, thermo-chemical oxidation process using persulfate as the oxidant, and O_3/H_2O_2 method and so on have been applied to TOC removal for spent ultra pure water reclamation (Hango *et al*., 1981; Morita *et al*., 1996). Of the above, the O_3/H_2O_2 oxidation process is considered to be one of the most promising methods.

The O_3/H_2O_2 oxidation process has been considered to be one of the simplest and most practical advanced oxidation processes (AOP), and has long been employed for advanced treatment and reclamation of wastewater (Nakayama *et al*., 1979; Kawaai *et al*., 1997). It is also used for decomposition of pesticides and chlorinated organics like TCE and PCE in ground water (Glaze *et al*., 1988; Meijiers *et al*., 1995; Schwammlein *et al*., 1995). One of the important parameters affecting oxidation efficiency of the process is the ratio of H_2O_2 to O_3. As shown in Eq. (1) (Schulte *et al*., 1995), O_3 is an oxidant and H_2O_2 a reducing agent when they react to give OH radicals in an O_3/H_2O_2 process. While the stoichiometric ratio of H_2O_2 to O_3 in Eq. (1) is 0.354 in weight, the optimum ratio varies in a range between 0.24 and 0.50, according to treatment conditions and wastewater species (Glaze *et al*., 1988; Bellamy *et al*., 1991; Kawaai *et al*., 1997). It is therefore desirable that the optimum ratio of H_2O_2 to O_3 can be automatically controlled.

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$$2O_3 + H_2O_2 = 2 \cdot OH + 3O_2 \tag{1}$$

In most cases, organic acids, most of which are carboxylic acids, are formed before the objective compounds are completely mineralized by OH radicals. Since organic acids can be easily removed by reverse osmosis (RO) or ion exchange treatment step, it is economically preferable that TOC oxidation is carried out to the point at which most of the residual organics are converted into organic acids.

Since ORP (oxidation-reduction potential) indicates the ratio of oxidants to reducing agents in the solution, the possibility of employing ORP for H_2O_2 dosing control was investigated in this study. Then a waste pure water reclamation system was established by incorporating a two step O_3/H_2O_2 process for oxidizing organic compounds into organic acids and a subsequent ion exchange step for removing the organic acids. The second step was designed to oxidize the residual organics further with the residual O_3 from the exhaust gas of the first step. The effectiveness of the spent ultra pure water reclamation system was verified by using IPA (iso-propyl alcohol), DMSO (dimethyl sulfoxide), and NMP (N-methyl pyrolidone) as model substances.

Material and methods

Figure 1 shows the schematic diagram of the wastewater reclamation system employed in this study. A glass column (I.D., 16.5 cm; H, 200 cm; water level, 180 cm) with two stainless end plates was used as the bubble H_2O_2/O_3 reactor (R1). Synthetic wastewater was fed continuously into the bubble reactor from the top with a flow rate ranging from $20 \, l \, h^{-1}$ to $120 \, l \, h^{-1}$, and O_3 gas produced from PSA (pressure swing adsorption) O_2 was introduced from the bottom through a sintered glass diffuser (effective diameter, 2 cm). The gas flow rate was varied from 60 to $240 \, l \, h^{-1}$ (linear velocity, $2.8–11.2 \, m \, h^{-1}$) and the rated output of the ozonizer (SG-01A-PSA4, Sumitomo Fine Mechanical Co., Japan) was $25 \, g \, h^{-1}$. A pH electrode, ORP electrode (TOA Electric Waves Co., Japan), and dissolved O_3 electrode (Orbisphere, USA) were inserted into the effluent water line of R1, respectively, and the effluent pH was automatically controlled at given values by adding NaOH solution of proper concentrations. In some experiments, the H_2O_2 feeding rate was adjusted automatically with a PID (proportional-integral-differential) controller based on the measured ORP values. An on-line TOC meter (Model720, Toray Co., Japan) continuously monitored the TOC of the effluent.

About $10 \, l \, h^{-1}$ effluent water from R1 was used for TOC measurement. The remaining water flowed into a stainless tank (R2; effective volume, 46 l), and could be treated further with the waste O_3 gas from R1 through an ejector. The recirculation rate for the ejector was varied in a range from 0 to $600 \, l \, h^{-1}$. The TOC of the organic acid was removed by ion exchange resin (IER) after the residual O_3 and H_2O_2 were decomposed by an activated car-
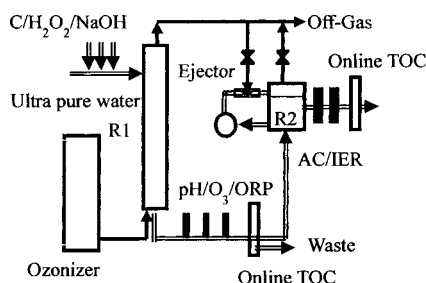

Figure 1 Schematic diagram of experimental setup
R1: Glass column, I.D.=16.5cm, H=2.5m.
R2: Stainless tank, effective volume = 46l.

bon column (SV50–100 h^{-1}). Another on-line TOC meter (Sievers 810, Sievers Co., USA) was installed for measuring the residual TOC after IER treatment. The conductivity of IER effluent was continuously monitored for indicating the timing for exchange of IER.

IPA, DMSO, and NMP, the typical chemicals used in electronics industry, were used as model substances. Stock synthetic wastewater of proper concentrations was prepared by dissolving one of the above chemicals into ultra pure water. The influent TOC concentration was adjusted by controlling the ratio of the feeding rate of stock solution to that of ultra pure water. Each condition was tested for ca. 24 h, and 2 to 3 samples were taken in an interval of 1 to 2 hours for each condition. The values of pH, ORP, O_3, TOC, etc, were read at the same time. Data for each condition were calculated on an average.

The highest occupied molecular orbital energy (ε_{HOMO}) of the 3 objective compounds was calculated by MOPAC Ver.6 included in CAChe 3.2 for Windows (Oxford Molecular) and PM3 was used as the calculation keyword (Hu *et al*. 2001).

Results and discussion
Possibility of using ORP for H2O2 dosing control

As discussed above, the optimum ratio of H_2O_2 to O_3 for oxidation reaction varies according to wastewater being applied. The main reason for the change of the optimum ratio is perhaps due to the existence of O_3 consumption matters, including the objective organics and their oxidation intermediates, in water. So, the normal practice of treating water under a given H_2O_2/O_3 is not reasonable. In order to find a parameter to reflect the state of oxidation reaction of the O_3/H_2O_2 process with a high sensitivity, the ORP and residual O_3 of the treated water were continuously monitored, and the residual H_2O_2 was analyzed manually. IPA was used as the model substance. The experimental conditions were as follows: TOCin (influent TOC), ca.7000ppb; pH, 6.6–6.8; effective O_3/TOC (weight ratio of O_3 absorbed to TOCin), 15–31; R2, not being operated. Variations of ORP, the residual H_2O_2 and O_3, and the ratio of TOCout (effluent TOC) to TOCin with H_2O_2/O_3 (defined here as gH_2O_2added/gO_3absorbed) for R1 are respectively shown in Figure 2a, b, and c.

Figure 2a and b indicate that the ORP and residual O_3 decreased with the increase of H_2O_2/O_3, and the residual H_2O_2 increased at the same time. Variations of the residual H_2O_2 and O_3 were basically a continuous one. However, there appeared an inflection point for ORP with the increase of H_2O_2/O_3. The ORP dropped from ca. 800 mV to a little more than 200 mV around the H_2O_2/O_3 of 0.15. Figure 2c indicates that the minimum TOCout/TOCin, i.e. the best TOC decomposition performance, was also obtained near the inflection point of ORP. By comparing Figure 2c with Figure 2a, it is clear that ORP sensitively reflected the state of the oxidation reaction in the reactor and the reflection point of ORP indicates possibly the point of optimum H_2O_2/O_3.

In order to investigate if the reflection point of ORP could be used for H_2O_2 dosing control, treatment under controlled ORP was carried out. In this test, electric signals from ORP monitor were sent to the pump controller for adjusting the feeding rate of H_2O_2, and the effective O_3/TOC was in a range between 11 and 15. The other conditions were same with the above experiment.

Both of the TOCout/TOCin and TOC after IER are shown in Figure 3a. The lowest TOCout/TOCin and TOC after IER were obtained around an ORP between 250 mV and 800 mV. It was almost impossible to keep a constant ORP in the range of 300 mV<ORP<800 mV. It is interesting that the TOC removal efficiency decreased significantly with the decrease of ORP around 200 mV. That is to say, overdose of H_2O_2 was not only a waste, but also harmful to the oxidation reaction. On the other hand, treatment even at an ORP as high as 900 mV did not affect TOC decomposition efficiency much, which provided a very wide ORP range for selection. Therefore, an ORP between 250 mV and 300 mV

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(low range) or between 800 mV and 900 mV (high range) is proper for efficient H_2O_2 dosing control. The two ranges of ORP could be selected according to need, which is very convenient in some cases. For example, the lower range of ORP could be used when undesirable side reactions occur in the higher range of ORP. Figure 3a also indicates that near 70% TOC was completely mineralized in R1 under a proper ORP, and ca. 80 to 85% of the remaining TOC in R1 was comprised of organic acids, which were removed by the successive IER column. Figure 3b shows variation of residual H_2O_2 with ORP. The residual H_2O_2 was 750ppb or lower in an ORP range of 250–900 mV. Raising ORP could decrease the residual H_2O_2 to some extent. However, ORP was not the only factor being related with the residual H_2O_2, the effective O_3/TOC was also an affecting factor. The value of H_2O_2/O_3 is also indicated in the figure. The H_2O_2/O_3 was between 0.15 and 0.25 in an ORP range from 250 mV to 900 mV in this experiment.

However, the optimum H_2O_2/O_3 was not only related with ORP, it also varied according to O_3 dosage as shown in Figure 4. The data of Figure 4 was obtained under a controlled ORP (between 770 mV and 830 mV). Although a scattering of data exists, it is apparent that the H_2O_2/O_3 increased gradually with the increase of effective O_3/TOC ratio although the ORP was controlled at a relatively constant value. The experiment was conducted under 3 TOC concentrations: 3000ppb, 7000ppb, and 10000ppb, and the variation of TOCin did not
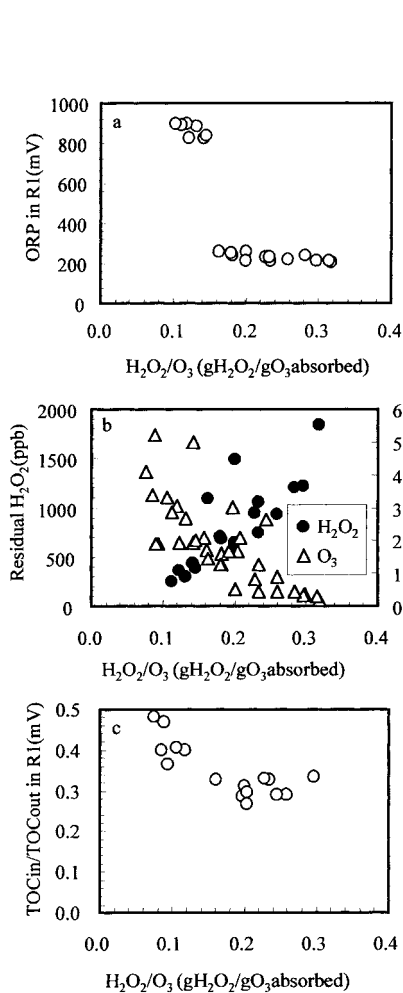

Figure 3 TOC removal under controlled ORP

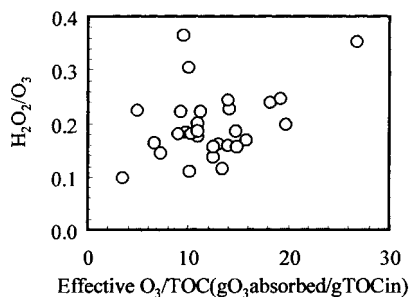314   **Figure 2** Effects of H_2O_2/O_3 on TOC decomposition   **Figure 4** Effects of O_3 dosage on H_2O_2/O_3 ratio

make any significant differences. The result further indicates that the optimum H_2O_2/O_3 was not a fixed one, and a proper control method like the one used in this study was necessary for efficient TOC removal.

Effects of chemical structures of objective compounds on their treatability

Figure 5a and b show the relationship between TOC removal extent of IPA, DMSO, and NMP and their respective O_3 demands under the following conditions: TOCin, 6000–7000ppb; pH, 6.6–6.8; H_2O_2/O_3, 0.15–0.35; HRT, 0.33–1.8 h; R2, not being operated. It was found that both of the logarithms of TOCout/TOCin and TOC after IER could be approximately linearly related to logarithm of effective O_3/TOC. The result demonstrates that oxidation of the remaining TOC required more O_3. The ratio of TOCout/TOCin indicates the extent of mineralization of the TOC, and the TOC after IER represents the unionized portion of TOCout (the ionized portion, mainly organic acid, was removed by IER). It is apparent that oxidation of IPA required much more O_3 than that of the other two, either from the viewpoint of complete TOC decomposition, or from the viewpoint of TOC removal through formation of organic acids. That is to say, the compounds easier to be oxidized to organic acids were also easier to be completely decomposed. It should be noted that variation of HRT from 1.8 to 0.33 h did not affect TOC removal performance significantly.

The structures and their respective HOMO energy (ε_{HOMO}) of the 3 objective compounds are shown in Table 1. In an OH-radical reaction, the initial decomposition rates have been found to be dependant on ε_{HOMO} of the objective compounds in gas phase reactions (Bartolotti *et al.*, 1994). The higher the ε_{HOMO}, the higher the initial decomposition rate of the objective compound. As shown in Table 1, the result of this study seemed also to be in conformity with the conclusion. NMP, which has the highest ε_{HOMO} value, consumed least O_3 for a given value of TOCout/TOCin or TOC after IER. While the compound number was very limited and further verification studies are needed, the result in this study

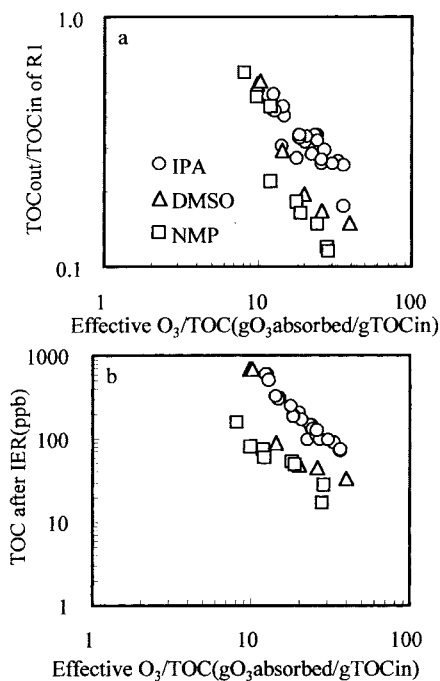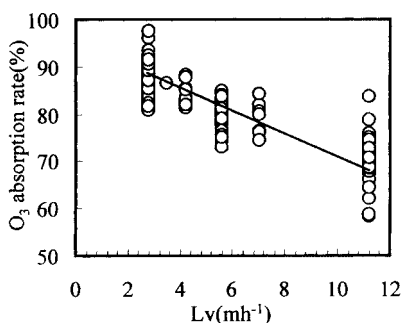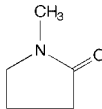**Figure 6** Effects of *Lv* on O_3 absorption rate

Table 1 Calculated ε_{HOMO}

	IPA	DMSO	NMP
	$(CH_3)_2COH$	$(CH_3)_2S=O$	
ε_{HOMO}	−11.052	−9.323	−9.151

Figure 5 TOC removal and O_3 demand

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demonstrates that it is possible to estimate O_3 consumption for decomposing an organic compound from its ε_{HOMO} value. This result is very important since the treatability of a substance could be estimated without experiment.

Effectiveness of waste gas utilization

O_3 absorption rate of the bubble reactor versus gas Lv (linear velocity) over the whole experimental period is shown in Figure 6. The scattering of data was perhaps because they were obtained under various experimental conditions. However, it is clear that O_3 absorption rate decreased with the increase of Lv. As the gas Lv increased from 2.8 m h^{-1} to 11.2 m h^{-1}, the O_3 absorption rate decreased from a value around 90% to ca. 70%. That is to say, ca. 10 to 30% O_3 produced was not utilized and had to be decomposed in the waste gas treatment reactor. If dried air was used for O_3 production, the O_3 absorption rate would be much lower because of much lower O_3 concentration in the gas (only one sixth of that used in this study). Since O_3 production accounts for a major percentage of the whole initial and running cost of an O_3/H_2O_2 oxidation process, it is important to reduce O_3 requirement. One method for reducing O_3 requirement is to reuse the waste O_3 gas. The second reactor (R2) was setup to treat further the effluent water from R1 with the waste O_3.

Since the waste O_3 gas was fed with an ejector, it was difficult to measure gas flow rate directly. The flow rate of the reciuculation pump for driving gas was used instead. Figure 7 shows the effects of recirculation rate on TOC removal under the following conditions: IPA; TOCin, ca.7000ppb; pH, 6.6–6.8; effective O_3/TOC of R1, 15; H_2O_2/O_3, 0.20; water flow rate to R1 and R2, 120 l h^{-1} and 110 l h^{-1}; gas flow rate to R1, 120 l h^{-1} (gas Lv in R1: 5.6 m h^{-1}). TOC after IER decreased from more than 300 ppb to ca. 200 ppb when the recirculation rate was increased from 0 to more than 400 l h^{-1}. It is clear that the waste O_3 gas from R1 was effectively utilized in R2. From Figure 5 it is clear that similar effects could be obtained only by raising the effective O_3/TOC from 15 to 20. The O_3 absorption rate in R1 was 80%. So it was impossible to raise the effective O_3/TOC of the two step oxidation system to 20 even if all of the residual O_3 gas from R1 was absorbed in R2. The result indicates that the two step treatment system developed in this study was more efficient than a single step system if same amount of O_3 was consumed. Similar phenomenon has been reported by Furukawa *et al*. (1997) who found that organic compounds were removed with less O_3 consumption by injecting O_3 into the reactor through multiple ports provided serially. In this case, injecting O_3 through multiple ports could be considered as multiple step treatment.

Figure 8a and b show the effects of two step oxidation under controlled ORP by comparing the results with those obtained in single step treatment. The conditions of two step treatment were: TOCin, 7000ppb; ORP, ca. 800 mV; HRT, 0.33 h; gas flow rate to R1, 240 l h^{-1} (gas Lv in R1: 11.2 m h^{-1}); recirculation rate of R2, 600 l h^{-1}; H_2O_2 dose in R2, 2.95 mgl^{-1}. For the single step treatment, the conditions were as follows: H_2O_2/O_3, 0.15–0.35; HRT, 0.33–1.8h. Since the effective O_3 absorption rate of R2 could not be obtained, the term of O_3 dosage rate (O_3added/TOCin) was used instead of the effective O_3/TOC. Figure 8a indicates that for IPA a TOC after IER of 100 ppb could be obtained at an O_3 dosage rate of 20 gO$_3$/gTOC during two step treatment. Without ORP control in R1 and the second step treatment, however, the O_3 dosage rate for the same TOC objective increased to 35 gO$_3$/gTOC, a 40% up compared with the former case. That is to say, with the help of H_2O_2 dosing control and the second step treatment using the waste O_3 gas from R1, a total effect of saving 40% O_3 could be obtained. As shown in Figure 8b, similar effects could also be obtained for treating wastewater containing DMSO and NMP although the two compounds consumed much less O_3.
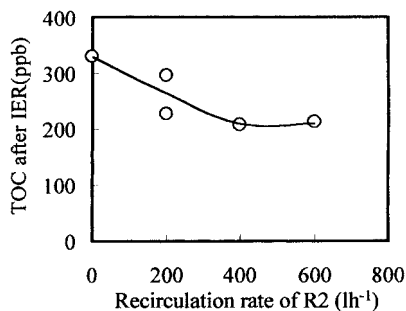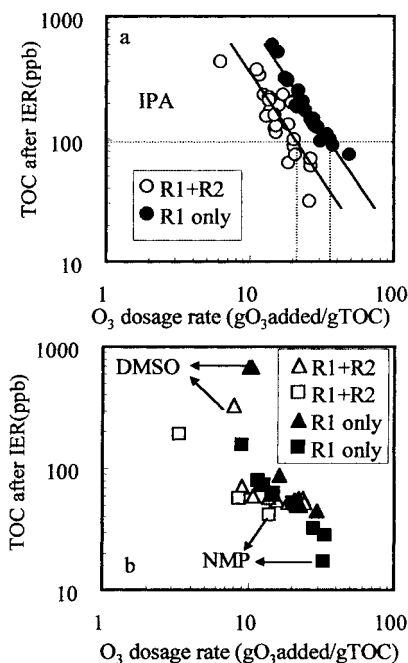
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Figure 7 Effects of recirculation rate

Figure 8 Comparison of treatment performance

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Conclusion

The continuous two step O_3/H_2O_2 oxidation system with ORP monitor incorporated for H_2O_2 dosing control was established for the purpose of wastewater reclamation in electronics industries, and its performance was evaluated on synthetic waste ultra pure water under various conditions. ORP was found to be very sensitive to the reaction state of the solution, and a very sharp reflection point of ORP was observed near the point of optimum H_2O_2/O_3. When IPA synthetic wastewater was treated, the ORP decreased suddenly from ca. 800 mV to a little more than 200 mV on approaching the optimum H_2O_2/O_3 of 0.15 from the lower end. An ORP between 250 mV and 300 mV or 800 mV and 900 mV was proper for H_2O_2/O_3 control. The treatability of the model substances was in an order of IPA<<DMSO<NMP, being consistent with the magnitude of ε_{HOMO}. Waste O_3 gas from the first step was effectively utilized in the second step, and the system with two step treatment was found to be more efficient that that of single treatment. With H_2O_2 dosing control by ORP and waste O_3 reuse in the second step, the system could save about 40% O_3 in comparison with the conventional O_3/H_2O_2 oxidation process.

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