Practical Application of UV/H_2O_2 Treatment Technique to DMSO Wastewater

By Arata TOYODA,* Keiji HIRANO,* Tatsuya KOITO* and Tsutomu TAIRA†

ABSTRACT A UV/H_2O_2 technique has been developed for treating Dimethyl Sulfoxide (DMSO, $(CH_3)_2SO$) wastewater which has so far been dealt with as industrial waste. The treatment conditions for various actual wastewater containing several organic compounds in addition to DMSO was studied, and a practical treatment system based on this technique was installed in a factory which has an existing biological treatment plant. Through the operation of this system, it was demonstrated that DMSO wastewater can be treated completely without generating any noxious compounds and industrial waste, and that considerable reductions in treatment cost are possible.

KEYWORDS **DMSO (Dimethyl Sulfoxide), Wastewater, Treatment, UV (Ultraviolet) light, Hydrogen Peroxide (H_2O_2), Organic Compound, Biological Treatment**

1. INTRODUCTION

In the semiconductor manufacturing industry, solvents containing Dimethyl Sulfoxide (DMSO, $(CH_3)_2SO$) are used in photoresist stripping processes. However, treating DMSO wastewater is difficult because DMSO can produce very noxious compounds by the conventional biological treatment[1]. Because of this, DMSO wastewater is normally separated from other organic wastewater and handled as industrial waste.

Previously, we reported a UV/H_2O_2 treatment technique for reducing the cost of treating a simple DMSO wastewater without generating industrial waste[2]. In this work, we studied several treatment conditions to treat various actual wastewater containing DMSO using an evaluation plant and altered the practical treatment system for the factory site to make this technique more practical and to prove that treatment costs can be reduced.

2. TOTAL TREATMENT PROCESS

Figure 1 illustrates the fundamental flow diagram of the DMSO wastewater treatment process that we developed. DMSO in wastewater is decomposed promptly into Metanesulfonic Acid (MSA) with the coexistence of Hydrogen Peroxide (H_2O_2) as an oxidizing agent under the irradiation of ultraviolet light (UV/H_2O_2 treatment). After this process, the generated MSA is decomposed into H_2SO_4 through a conventional biological treatment process without generating any noxious compounds.

3. EXPERIMENT AND RESULTS

3.1 Evaluation Plant

The UV/H_2O_2 treatment conditions were examined using an evaluation plant in order to design a more practical treatment system and determine its operational conditions.

The evaluation plant consisted of a 16*l* photoreactor, a 50*l* circulation tank and a pump. The photoreactor had three 65W low-pressure mercury lamps (main wavelength: 254nm). Wastewater was circulated through the system by the pump at rate of $1.5m^3/h$.

3.2 Decomposition Characteristics with UV Irradiation

An examination on the DMSO decomposition effect of the cumulative UV irradiation was carried out using 40*l* simple wastewater containing 1,000mg/*l* of DMSO with 1,200mg/*l* of H_2O_2 and an initial pH of 3.

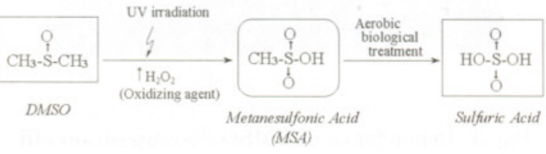

Fig. 1 Flow diagram of DMSO wastewater treatment process.

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Figure 2 shows concentration change in three kinds of compounds (DMSO, MSA, and H_2SO_4) versus cumulative UV irradiation. It was found that while DMSO decomposed easily into MSA, there was very little decomposition of MSA into H_2SO_4.

Because MSA can be easily treated biologically, MSA decomposition with UV/H_2O_2 treatment is not necessary. The DMSO in the wastewater (total weight 40g) was decomposed completely into MSA with $10kWh/m^3$ cumulative UV irradiation.

3.3 Dependence of H_2O_2 Concentration

Optimum oxidizing agent concentration was also studied. Figure 3 shows the dependence of the DMSO decomposition rate on initial H_2O_2 /DMSO rate at different levels of cumulative UV irradiation. The DMSO decomposition rate shows the rate of the decomposed DMSO concentration against the initial DMSO concentration. From the result, it can be seen that H_2O_2 concentration is adequate if it is at least 1.4 times that of DMSO regardless of the cumulative UV irradiation. Therefore, the most economical H_2O_2 concentration is 1.4 times that of DMSO.

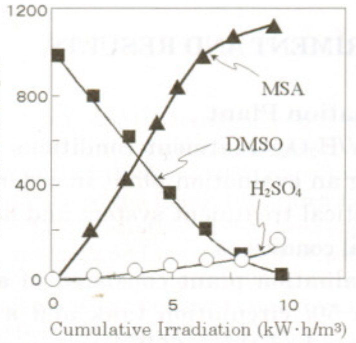

Fig. 2 Concentration change of each compound the cumulative UV irradiation.

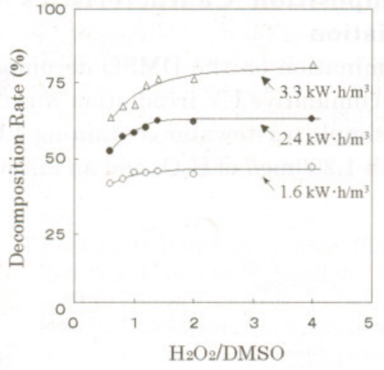

Fig. 3 Dependence of DMSO decomposition efficiency on H_2O_2 concentration at different levels of cumulative UV irradiation (Initial DMSO: 500mg/*l*, Initial pH: 3).

3.4 Dependence of DMSO Concentration

Figure 4 shows decrease in DMSO concentration against the cumulative UV irradiation for three kinds of initial DMSO concentration. The three lines are almost linear and parallel one another at the range from approximately 150 to 2,600mg/*l*. This means that the decrease rate of DMSO concentration was approximately proportional to the cumulative UV irradiation regardless of the DMSO concentration of 150~2,600mg/*l*.

3.5 Influence of Coexistent Materials

The semiconductor manufacturing process uses various organic compounds, and the actual DMSO wastewater from a semiconductor factory does not always contain only DMSO. According to an analysis of actual wastewater, the DMSO concentration was always in the rage of 500~1,000mg/*l* and the concentration of Isopropyl Alcohol (IPA) was very high (more than 50 times that of DMSO). Since other organic compounds (Monoethanolamine, Acetic Acid, etc.) had lower concentrations, we studied the influence of IPA on the decomposition reaction.

Figure 5 shows the dependence of DMSO decomposition rate on IPA concentration. At the same cumulative UV irradiation, the DMSO decomposition rate decreased with an increase in IPA concentration. Therefore, IPA concentration should be reduced to the minimum permissible concentration.

We examined several IPA removal techniques,

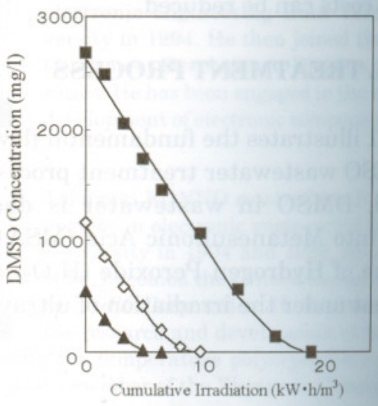

Fig. 4 DMSO concentration versus the cumulative (■: Initial DMSO: 2,500 mg/*l*, ◇: Initial DMSO: 1,000 mg/*l*, ▲: Initial DMSO: 500 mg/*l*).

and finally decided to remove it through the aeration of wastewater by heating it to over 80°C. Using this technique, IPA concentration was easily reduced to below 500mg/*l*, which is the minimum permissible concentration for practical treatment.

3.6 Influence of Water Temperature

For irradiation output, the optimum temperature condition of the UV lamps in this photoreactor is around 35°C. Since DMSO wastewater must be heated to high temperature for the IPA removal process, it was estimated that an extremely long cooling time or some kind of system would be needed for a practical system. Therefore, we studied the influence of water temperature on DMSO decomposition rate on water temperature for three levels of cumulative UV irradiation. As the figure shows, it was found that in this photoreactor, the efficiency was higher for a water temperature of around 60°C than for one around 20°C.

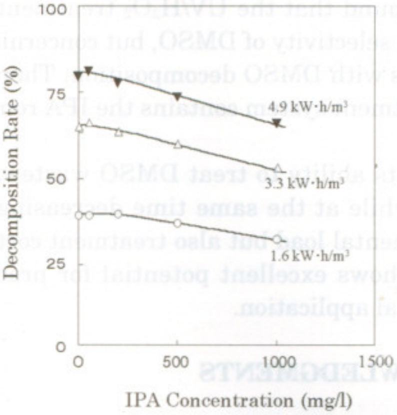

Fig. 5 Dependence of DMSO decomposition on IPA concentration at different levels of UV irradiation (Initial DMSO: 500 mg/*l* , Initial pH: 3, Initial H_2O_2: 700 mg/*l*).

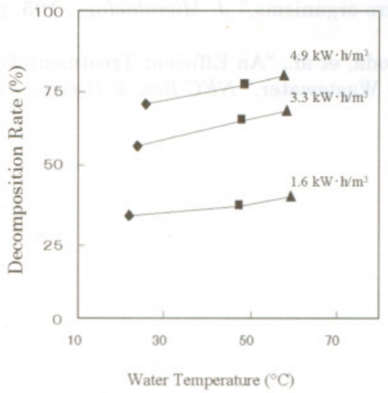

Fig. 6 Dependence of DMSO decomposition rate on water temperature for each cumulative UV irradiation (Initial IPA: 1,000 mg/*l*, Initial DMSO: 500 mg/*l*, Initial H_2O_2: 700mg/*l*).

4. DESIGN AND CONSTRUCTION OF THE ALTERED PRACTICAL SYSTEM

On the basis of these results, we designed and constructed an altered practical treatment system.

4.1 Total System Constitution

The process flow of the UV/H_2O_2 decomposition system is illustrated in Fig. 7 and an external photograph of the system is shown in Fig. 8. The system consists of a 64*l* photoreactor, which is equipped with sixteen 65W low-pressure UV lamps, a 2m³ circulation tank, a 2m³ IPA removal tank with a steam heating system, and a 1.8m³ activated carbon tank to remove residual H_2O_2. The system is 10m wide, 5m deep and 3m high.

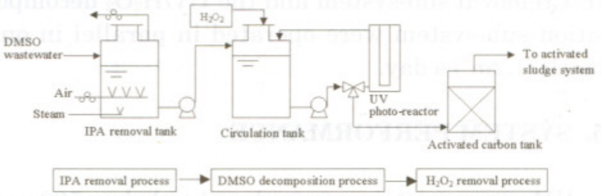

Fig. 7 Process flow diagram of UV/H_2O_2 decomposition system for DMSO wastewater containing IPA.

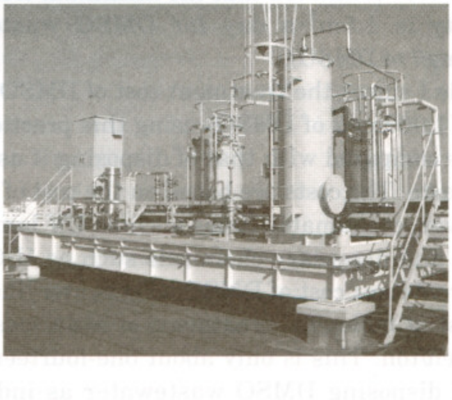

Fig. 8 UV/H_2O_2 decomposition system for DMSO wastewater. Size: 10 m (w) × 5 m (d) × 3 m (h). Electric-power consumption for photoreactor: 1.6 kW. Capacity: 1.5 m³/day (1,000 mg/*l* of DMSO).

4.2 IPA Removal Sub-System

IPA is removed through the aeration of wastewater by heating it to over 80°C. Considering heating cost and efficiency, steam supplied from a co-generation system at the factory site was set at $0.2 m^3$/min. The IPA removed from the wastewater is recollected by a condensation trap.

4.3 UV/H_2O_2 Decomposition Sub-System

According to the results obtained in an experiment on the influence of water temperature, we determined it was not necessary to cool DMSO wastewater in the decomposition process. To enable the system to withstand temperatures as high as 80°C, the system was built using heat-resistant materials and equipment.

4.4 Residual H_2O_2 Removal Sub-System

We introduced activated carbon for removing residual H_2O_2 because of its low maintenance requirements and low cost.

4.5 Operation of the System

In order to increase the treatment capacity, the IPA removal sub-system and the UV/H_2O_2 decomposition sub-system were operated in parallel in one batch ($1.2 m^3$) a day.

5. SYSTEM PERFORMANCE

IPA concentration was reduced to below 500mg/*l* from an initial concentration of 30,000mg/*l* after a 9-hour removal treatment. Then DMSO was decomposed to a concentration below 8mg/*l* from an initial value of approximately 500mg/*l* after a 10-hour UV/H_2O_2 decomposition treatment. Based on these results, it is estimated that the maximum treatment capacity is $1.5 m^3$ a day for DMSO wastewater (1,000mg/*l* of DMSO).

Table I shows the treatment cost of DMSO wastewater (1,000mg/*l* of DMSO) using this practical system, as compared with that of disposing it as industrial waste. The costs are based on the cost of electrical power, consumable items such as UV lamps and steam, and necessary chemicals such as H_2O_2. The total treatment cost of DMSO wastewater, including the cost of biological treatment of MSA was about 2,900yen/ton. This is only about one-fourteenth the cost of disposing DMSO wastewater as industrial waste, which we assume to be approximately 40,000yen/ton.

Table I Treatment cost of DMSO wastewater (1,000 mg/*l*. $1.2 m^3$/day) at the treatment system.

Means	Cost (yen/ton)
●UV/H_2O_2 Treatment ($DMSO \rightarrow MSA$) + Biological Treatment ($MSA \rightarrow H_2SO_4$)	2,900
● Collected as Industrial Waste	40,000

6. CONCLUSION

We have developed a practical system to treat DMSO wastewater containing various organic compounds, using UV/H_2O_2 treatment technique.

We optimized the several treatment conditions, and we found that the UV/H_2O_2 treatment has considerable selectivity of DMSO, but concerning IPA, it interferes with DMSO decomposition. Therefore, our new treatment system contains the IPA removal sub-system.

With its ability to treat DMSO wastewater completely while at the same time decreasing not only environmental load but also treatment cost, the new system shows excellent potential for practical and economical application.

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