

# Chemical oxidation of organic matter in secondary-treated municipal wastewater by using methods involving ozone, ultraviolet radiation and TiO<sub>2</sub> catalyst

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**Abstract** The efficiencies of chemical oxidation of organic matter in genuine secondary-treated municipal wastewater by using O<sub>3</sub>, O<sub>3</sub>/UV, O<sub>3</sub>/TiO<sub>2</sub>, UV/TiO<sub>2</sub> and O<sub>3</sub>/UV/TiO<sub>2</sub> methods were compared experimentally. Effects of carbonates on these efficiencies were also investigated. Elimination of carbonates from the water increased TOC reduction efficiency of all the methods. The effect of the carbonates on the O<sub>3</sub> method was less significant than that on the other methods. The O<sub>3</sub>/UV method was the most effective for reducing TOC under both carbonate-present and decarbonated conditions. The catalytic ozone process (O<sub>3</sub>/TiO<sub>2</sub>) showed a tendency to increase the ozonation efficiency at the beginning of the reaction under the decarbonated condition, but the addition of the TiO<sub>2</sub> catalyst inhibited the ozonation under the carbonate-present condition. The photocatalytic oxidation process (UV/TiO<sub>2</sub>) did not reduce TOC as much as the other methods, but it could reduce TOC over a long time. And the O<sub>3</sub>/UV/TiO<sub>2</sub> method did not show a synergistic effect of ozonation and photocatalytic oxidation. Furthermore, ozonation prior to coagulation increased TOC reduction efficiency of coagulation, but this effect was also affected by the carbonates in water.

**Keywords** Coagulation; municipal wastewater; ozonation; refractory organic matter; TiO<sub>2</sub> catalyst; UV irradiation

## Introduction

Reduction of refractory organic matter in wastewater is important from the viewpoint of wastewater reclamation, recycling and reuse. Refractory organic matter is, however, difficult to degrade by biological treatment such as an activated sludge process. Chemical oxidation processes are therefore, attractive methods for reducing or mineralizing organic matter in water. Advanced oxidation processes (AOPs) are particularly promising methods for this purpose. The concept of AOPs was established by Glaze *et al.* (1987). AOPs were defined as those which involve the generation of hydroxyl radicals in sufficient quantity to affect water purification. And AOPs generally use different combinations of oxidation agents, irradiation and catalysts in order to generate hydroxyl radicals. So various AOPs have been developed (Huang *et al.*, 1993).

Different chemical oxidation methods have recently been investigated and compared for reducing specific organic compounds and organic matter in some kinds of industrial wastewater (Ruppert *et al.*, 1994; Trapido *et al.*, 1998). But oxidation characteristics of refractory organic matter in genuine municipal wastewater have been rarely investigated (Ito *et al.*, 1998). The aim of this study was to utilize different chemical oxidation methods for reducing refractory organic matter in municipal wastewater and to compare their reduction efficiencies. In this study, the methods involving ozone (O<sub>3</sub>), ultraviolet radiation (UV) and titanium-dioxide catalyst (TiO<sub>2</sub>) were investigated. Hereafter, these methods are referred to as O<sub>3</sub>, O<sub>3</sub>/UV, O<sub>3</sub>/TiO<sub>2</sub>, UV/TiO<sub>2</sub> and O<sub>3</sub>/UV/TiO<sub>2</sub> methods.

The O<sub>3</sub> method (ozonation) is chemical oxidation by ozone, which is the most widely used oxidant for water treatment. The O<sub>3</sub>/UV method is a well known AOP; it utilizes generation of hydroxyl radicals by photolysis of aqueous ozone. The O<sub>3</sub>/TiO<sub>2</sub> method, called

catalytic ozonation, combines ozone with the adsorptive and oxidative properties of titanium oxide catalyst to achieve mineralization of aqueous organic matter (Paillard *et al.*, 1991; Allemane *et al.*, 1993; Luck *et al.*, 1997; Volk *et al.*, 1997), and the UV/TiO<sub>2</sub> method, called photocatalytic oxidation, utilizes positive holes and electrons which are produced at an irradiated semiconductor catalyst surface. These positive holes and electrons can oxidize organic matter directly and/or generate hydroxyl radicals (Huang *et al.*, 1993). Comparison between the UV/TiO<sub>2</sub> and the O<sub>3</sub>/UV methods depends on the experimental conditions (Mansilla *et al.*, 1997; Ruppert *et al.*, 1994), but Mansilla *et al.* (1997) reported that the UV/TiO<sub>2</sub> method was more effective than the O<sub>3</sub>/UV method for degrading phenolic and polyphenolic compounds present in an elemental chlorine-free bleaching effluent. Also the O<sub>3</sub>/UV/TiO<sub>2</sub> method benefits from a synergistic effect of ozonation and photocatalytic oxidation (Tanaka *et al.*, 1992).

In this study, effects of carbonates (carbonate/bicarbonate ions), known as radical scavengers that inhibit oxidation of organic matter (Beltran *et al.*, 1997; Camel *et al.*, 1998), were investigated. The effects of each method on both carbonate-present and decarbonated test water were examined, and combined processes of ozonation (as a typical chemical oxidation method) and coagulation were investigated from the viewpoint of reducing organic matter.

## Experimental procedures

### Experimental apparatus and method

All experiments were performed using the experimental set-up shown in Figure 1. The cylindrical reactor vessel made of quartz glass was 80 mm in diameter and 500 mm high. For every experiment, the reactor was filled with 2 L of test water. The test water was continuously stirred during the reaction, and the sample waters for analysis were taken from the sample port at an appropriate time interval.

**Ozonation.** Ozone generated by an ozonizer (SG-01-PSA2, Sumitomo Precision Co.) was continuously supplied to the reactor through the gas distributor at an air flow rate of 160 mL/min and an ozone gas concentration of 42 mg/L. The supplied ozone gas concentration was continuously measured by an ozone-gas sensor (OZ-20, TOA Electronics Ltd.) and appropriately adjusted.

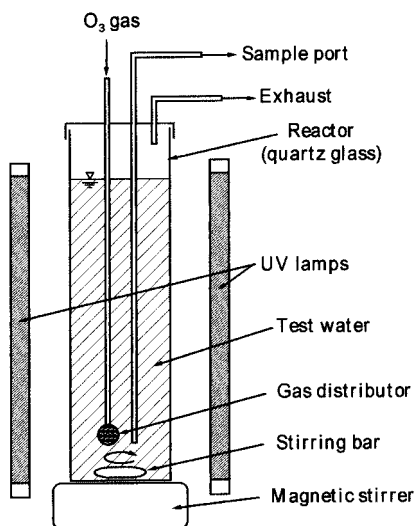


Figure 1 Experimental reactor set-up

**UV-irradiation.** The test water was dosed with UV-irradiation was dosed by four low-pressure mercury lamps located around the reactor. UV-intensity at a 254 nm wavelength emitted by each lamp (15 W) was 1 mW/cm<sup>2</sup> (measured at the centre of the reactor). The total UV-intensity emitted by the four lamps was thus approximately 4 mW/cm<sup>2</sup>.

**TiO<sub>2</sub> catalyst.** Powdered TiO<sub>2</sub> catalyst (ST-01 (predominantly anatase), Ishihara Techno Co.) was added and suspended in the test water at a concentration of 1000 mg/L.

**Coagulation.** Aluminium sulphate was employed as a coagulant (for coagulation experiments) and added in the test water at a concentration of 85 mg/L (as Al). This procedure consisted of the following steps: rapid mix (160 rpm) for 1 min, flocculation (50 rpm) for 10 min, and settling for 30 min.

### Test water and its analysis

Test waters studied in this work were secondary-treated (i.e. activated-sludge processed) municipal wastewater obtained from a domestic wastewater-treatment plant of a factory in Ibaraki, Japan. In some experiments, the test waters were decarbonated by the following procedure: adjust pH to 2 or less, purge with air for one hour, and adjust pH again to the initial value.

Total organic carbon (TOC) and chemical oxygen demand, which was determined by the method of potassium permanganate oxidation (COD<sub>Mn</sub>), were determined at appropriate time intervals during the reaction. TOC was determined by a Shimadzu TOC analyzer (TOC-5000A). Prior to the TOC analysis, inorganic carbon (IC) in the sample water was removed by purging with purified air at pH 2 or less. The TiO<sub>2</sub> catalyst powder contained in the sample water was removed by centrifugation (2000G, 15 min). In all experimental procedures, H<sub>2</sub>SO<sub>4</sub> and NaOH solutions were used to adjust pH.

Characteristics of the test waters are listed in table 1. DOC, BOD, E<sub>260</sub> and SS are abbreviations of dissolved organic carbon, biochemical oxygen demand, UV absorbance at a 260 nm wavelength and suspended solid, respectively. The concentration of SS was relatively low, and almost all TOC was DOC. Since the concentration of BOD was much lower than that of COD<sub>Mn</sub>, it can be concluded that refractory organic matter, which is hard to degrade biologically, comprises the majority of the organic matter in the test water. The raw test water contained a large quantity of carbonates (approximately 200 mg/L as IC), while the decarbonated test water hardly contained any carbonates (approximately 2 mg/L as IC).

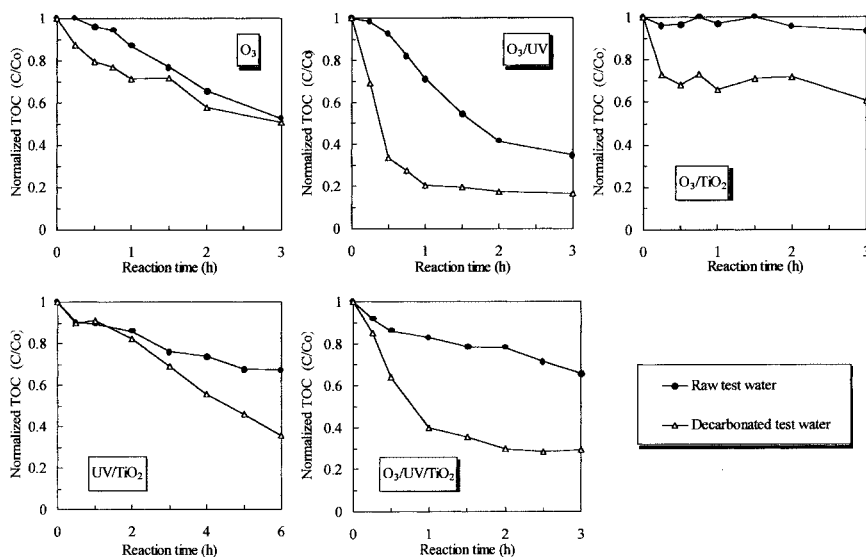
## Results and discussion

### Effects of carbonates

Figures 2 and 3 show the reduction of TOC and COD<sub>Mn</sub>, respectively, by each chemical oxidation method (O<sub>3</sub>, O<sub>3</sub>/UV, O<sub>3</sub>/TiO<sub>2</sub>, UV/TiO<sub>2</sub> and O<sub>3</sub>/UV/TiO<sub>2</sub>). TOC and COD<sub>Mn</sub> are

**Table 1** Characteristics of test waters

Water samples	TOC (mg/L)	DOC (mg/L)	COD <sub>Mn</sub> (mg/L)	BOD (mg/L)	E <sub>260</sub> (1/cm)	SS (mg/L)	IC (mg/L)	pH
Raw test water	6.5 (6.4–6.6)	6.3	11.0 (10.8–11.1)	1.3	0.21 (0.20–0.21)	3	204 (201–207)	8.5 (8.4–8.7)
Decarbonated test water	6.6 (6.5–6.7)	–	10.5 (9.8–11.1)	–	0.19 (0.19–0.20)	–	1.7 (1.3–2.2)	8.4 (8.0–8.6)



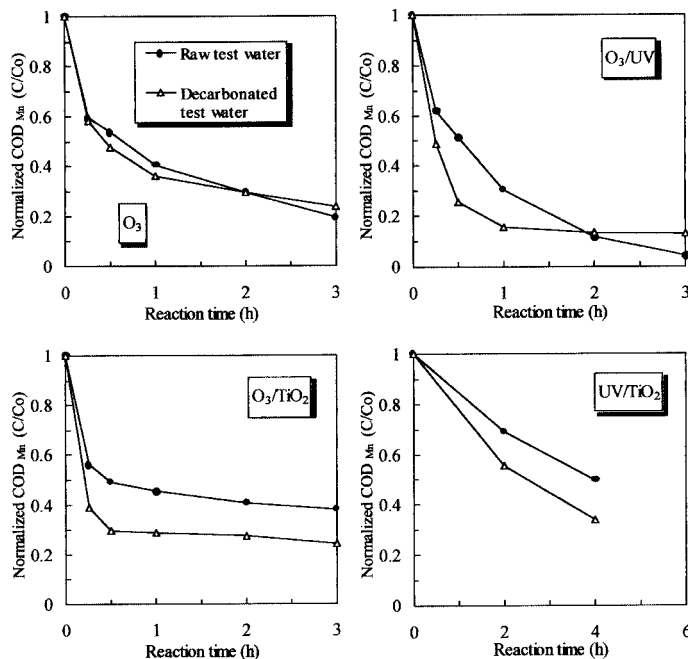
**Figure 2** Effect of carbonates on TOC reduction by  $O_3$ ,  $O_3/UV$ ,  $O_3/TiO_2$ ,  $UV/TiO_2$  and  $O_3/UV/TiO_2$  methods

normalized by the initial concentrations ( $C/C_0$ ). The plots of the  $UV/TiO_2$  method cover a six-hour reaction, while the others cover three-hour reactions. And all reactions are under both carbonate-present (i.e. raw test water) and decarbonated (i.e. decarbonated test water) conditions.

Figure 2 shows that elimination of carbonates increases TOC reduction efficiency of all the methods. However, for  $COD_{Mn}$  reduction, the effect of eliminating carbonates is not seen clearly; especially, the  $O_3$  method hardly shows any effect at all. Similarly, for TOC reduction, the  $O_3$  method was not affected so much by carbonates. Ozone can have two reaction modes: direct ozonation and free-radical (such as hydroxyl radicals) decomposition (Huang *et al.*, 1993). Because the carbonates can generally act as radical scavengers, they have less effect on the efficiency of the  $O_3$  method, which mainly has direct-ozonation reactions (not free-radical-decomposition reactions). On the other hand, the methods involving both ozone and UV radiation (i.e.  $O_3/UV$  and  $O_3/UV/TiO_2$ ) mainly involve free-radical-decomposition reactions. They were therefore notably affected by the carbonates as radical scavengers.

As for the  $UV/TiO_2$  method, the carbonates effect was not clearly found at the beginning of the reaction (up to 3 hours), but after three hours, carbonates decreased TOC reduction; after six hours of reaction, TOC reduction efficiency reached 60% under the decarbonated condition, as compared with 30% under the carbonate-present condition. It is therefore supposed that the free-radical-decomposition reactions also dominate the  $UV/TiO_2$  method.

TOC could hardly be reduced by the  $O_3/TiO_2$  method under the carbonate-present condition; namely, the carbonates also inhibited TOC reduction by the  $O_3/TiO_2$  method. However, in the case of oxalic acid degradation, Paillard *et al.* (1991) reported that the catalytic ozonation process was hardly affected by addition of alkalinity in the form of sodium bicarbonate. At any rate, the hydroxyl radicals are rarely produced by this process. The effect of carbonates could therefore be caused by something else, such as interaction between the catalyst surface and organic matter or oxidants (i.e. adsorption and desorption), not by the radical scavenging.



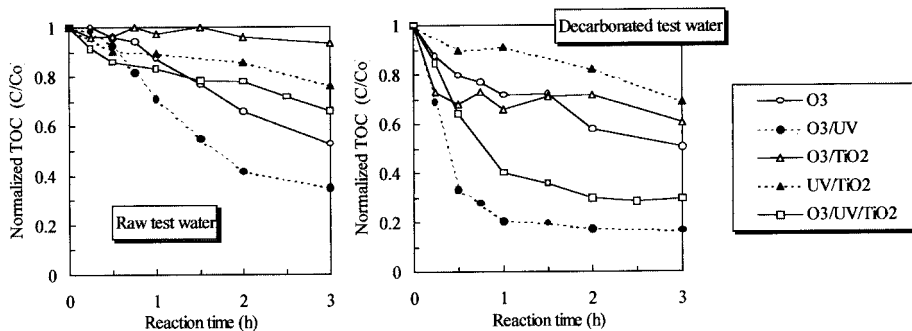
**Figure 3** Effect of carbonates on  $\text{COD}_{\text{Mn}}$  reduction by  $\text{O}_3$ ,  $\text{O}_3/\text{UV}$ ,  $\text{O}_3/\text{TiO}_2$  and  $\text{UV}/\text{TiO}_2$  methods

#### Comparison of the chemical oxidation methods

Figures 4 and 5 compare the chemical oxidation methods for reducing TOC and  $\text{COD}_{\text{Mn}}$ , respectively (under both carbonate-present (raw test water) and decarbonated (decarbonated test water) conditions). For TOC reduction, the  $\text{O}_3/\text{UV}$  method was the most effective under both conditions. The least effective methods were  $\text{O}_3/\text{TiO}_2$  under the carbonate-present condition and  $\text{UV}/\text{TiO}_2$  under the decarbonated condition. For  $\text{COD}_{\text{Mn}}$  reduction, the  $\text{O}_3/\text{UV}$  method was also the most effective under both conditions; the least effective method was  $\text{UV}/\text{TiO}_2$  under both conditions.

The methods involving ozone could rapidly reduce about 50% of  $\text{COD}_{\text{Mn}}$  at the beginning of the reaction (up to 1 hour). Moreover, the  $\text{COD}_{\text{Mn}}$  reduction efficiencies of each of the methods were not so different. This result suggests that the reduced  $\text{COD}_{\text{Mn}}$  was easily oxidized by the direct ozonation reactions.

However, reduction efficiencies of TOC, especially of the  $\text{O}_3$  and  $\text{O}_3/\text{TiO}_2$  method were lower than that of  $\text{COD}_{\text{Mn}}$ . Under the decarbonated condition, TOC reduction efficiency reached more than 80% by the  $\text{O}_3/\text{UV}$  method after one hour but less than 50% by the  $\text{O}_3$



**Figure 4** Comparison of  $\text{O}_3$ ,  $\text{O}_3/\text{UV}$ ,  $\text{O}_3/\text{TiO}_2$ ,  $\text{UV}/\text{TiO}_2$  and  $\text{O}_3/\text{UV}/\text{TiO}_2$  methods for TOC reduction

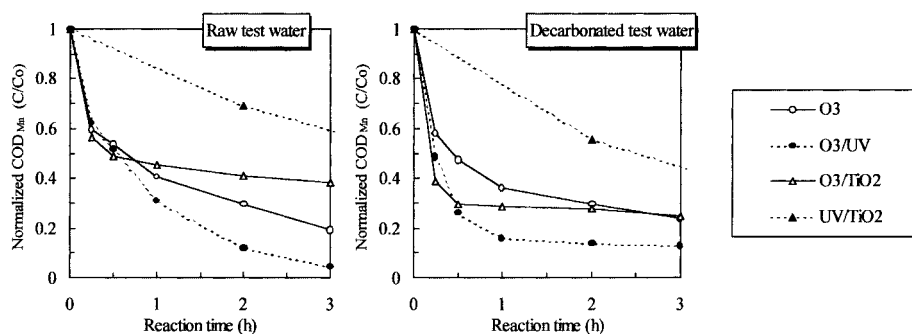


Figure 5 Comparison of O<sub>3</sub>, O<sub>3</sub>/UV, O<sub>3</sub>/TiO<sub>2</sub> and UV/TiO<sub>2</sub> methods for COD<sub>Mn</sub> reduction

and O<sub>3</sub>/TiO<sub>2</sub> methods after three hours. These results suggest that the free-radical-decomposition reactions involving hydroxyl radicals, which have a higher oxidation-reduction potential than ozone, are needed to mineralize organic matter in the test water.

The O<sub>3</sub>/TiO<sub>2</sub> method showed a tendency to increase the ozonation efficiency at the beginning of the reaction (up to 1 hour) under the decarbonated condition, but the addition of the TiO<sub>2</sub> catalyst inhibited the ozonation under the carbonate-present condition (especially TOC reduction). As mentioned above, it was supposed that the presence of carbonates affected adsorption and desorption at the catalyst surface. Acceleration of ozonation by addition of TiO<sub>2</sub> catalyst was not clearly seen over the entire reaction under the experimental conditions in this study.

The UV/TiO<sub>2</sub> method did not reduce TOC and COD<sub>Mn</sub> as much as the other methods, but it could reduce TOC over a long time (as shown in Figure 2). It is therefore suggested that the reaction rate of the UV/TiO<sub>2</sub> method is low under this experimental condition, but it could mineralize refractory organic matter like the O<sub>3</sub>/UV method does.

Finally, the efficiency of TOC reduction by the O<sub>3</sub>/UV/TiO<sub>2</sub> method was lower than that of the O<sub>3</sub>/UV method; that is, the O<sub>3</sub>/UV/TiO<sub>2</sub> method did not show a synergistic effect of ozonation and photocatalytic oxidation under the experimental conditions in this study.

### Combined process of ozonation and coagulation

The coagulation process (CP), which is an available unit process to upgrade water quality for reclamation of wastewater, can remove a part of the dissolved organic matter. In this study, combinations of coagulation and ozonation were also tested under both carbonate-present and decarbonated conditions.

Figure 6 shows TOC reduction by a process of ozonation prior to coagulation (O<sub>3</sub>+CP) and a process of coagulation prior to ozonation (CP+O<sub>3</sub>). In these experiments, reaction

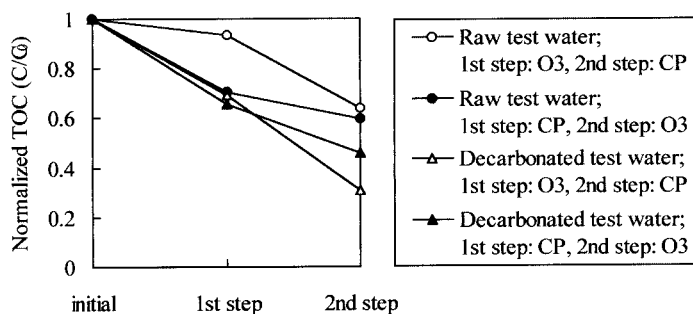


Figure 6 TOC reduction by combined processes of ozonation (O<sub>3</sub>) and coagulation (CP)

time of the ozonation was 30 min. Under the carbonate-present condition, TOC reduction efficiencies of the each unit process ( $O_3$  and CP) do not depend on the sequence of the processes. Consequently, total TOC reduction efficiencies of the combined processes ( $O_3$ +CP and CP+ $O_3$ ) are almost the same. However, under the decarbonated condition, TOC reduction efficiency of the CP on the  $O_3$ +CP process is higher than that of the CP on the CP+ $O_3$  process. As a result, total TOC reduction efficiency of the  $O_3$ +CP process is higher than that of the CP+ $O_3$  process. It is suggested that the ozonation process changes the characteristics at the surface of organic matter in water and therefore increases the coagulation process, but its effectiveness is affected by carbonates in water.

## Conclusions

Chemical oxidation processes involving ozone, ultraviolet radiation and  $TiO_2$  catalyst (i.e.  $O_3$ ,  $O_3/UV$ ,  $O_3/TiO_2$ ,  $UV/TiO_2$  and  $O_3/UV/TiO_2$ ) were effective for reducing refractory organic matter in secondary-treated municipal wastewater. Particularly, the  $O_3/UV$  method was the most effective for reducing TOC. However, carbonates inhibited the reduction of all the methods. The effect of carbonates on the  $O_3$  method was less significant than that on the other methods. The catalytic ozone process ( $O_3/TiO_2$ ) showed a tendency to increase the ozonation efficiency at the beginning of the reaction under the decarbonated condition, but the addition of the  $TiO_2$  catalyst inhibits the ozonation under the carbonate-present condition. The photocatalytic oxidation process ( $UV/TiO_2$ ) did not reduce TOC as much as the other methods, but it could reduce TOC over a long time. And the  $O_3/UV/TiO_2$  method did not show a synergistic effect of ozonation and photocatalytic oxidation. Furthermore, ozonation prior to coagulation increased TOC reduction efficiency of coagulation, but this effect was also affected by the carbonates in water.

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