



## Formaldehyde degradation by UV/TiO<sub>2</sub>/O<sub>3</sub> process using continuous flow mode

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### Abstract

The degradation of formaldehyde gas was studied using UV/TiO<sub>2</sub>/O<sub>3</sub> process under the condition of continuous flow mode. The effects of humidity, initial formaldehyde concentration, residence time and ozone adding amount on degradation of formaldehyde gas were investigated. The experimental results indicated that the combination of ozonation with photocatalytic oxidation on the degradation of formaldehyde showed a synergetic action, e.g., it could considerably increase decomposing of formaldehyde. The degradation efficiency of formaldehyde was between 73.6% and 79.4% while the initial concentration in the range of 1.84–24 mg/m<sup>3</sup> by O<sub>3</sub>/TiO<sub>2</sub>/UV process. The optimal humidity was about 50% in UV/TiO<sub>2</sub>/O<sub>3</sub> process and degradation of formaldehyde increases from 39.0% to 94.1% when the ozone content increased from 0 to 141 mg/m<sup>3</sup>. Furthermore, the kinetics of formaldehyde degradation reaction could be described by Langmuir-Hinshelwood model. The rate constant  $k$  of 46.72 mg/(m<sup>3</sup>·min) and Langmuir adsorption coefficient  $K$  of 0.0268 m<sup>3</sup>/mg were obtained.

**Key words:** UV/TiO<sub>2</sub>/O<sub>3</sub> process; formaldehyde; continuous flow mode

### Introduction

The pollution of indoor formaldehyde has been increasingly concerned in recent years. Conventional purification methods, including thermal destruction, chemical oxidation, incineration, adsorption etc., have been applied to reduce the pollution. These methods, however, have different kinds of drawbacks. Recently, many scientists have been exploring some better techniques to solve this problem.

The photo-catalytic process is considered to be one of the new purification methods, because the catalyst can be used in room temperature and pressure, and also the process is simple to be carried out. There are some reports on the photocatalytic degradation of aromatic contaminant such as benzene, toluene, xylene (Maira *et al.*, 2001; Lewandowski and Ollis, 2003a, b, c; Duan *et al.*, 2002; Sun *et al.*, 2005; Wang and Ku, 2003; Cao *et al.*, 2000; Blount and Falconer, 2002; Belver *et al.*, 2003), trichloroethylene (Yamazaki *et al.*, 1996; Wang *et al.*, 2002), chloroform, tetrachloroethylene (Avila *et al.*, 2002), vinyl chloride (Madjid and Arnaud, 2003), dichloromethane, 1-butanol, 1-butylamine (Florcnce *et al.*, 2000), 1-butene (Cao *et al.*, 1999), methanol (Muggli *et al.*, 2001), ethanol (Pillai

and Sahle, 2002), acetone (Coronado *et al.*, 2003) and formaldehyde (Yang *et al.*, 2000; Shang *et al.*, 2003; Liu *et al.*, 2004). Most of the studies on the degradation of gas contaminants were in the condition of bench mode, and indicated that only UV/TiO<sub>2</sub> process alone was not enough in degradation of gaseous contaminant, so UV/TiO<sub>2</sub>/O<sub>3</sub> process was suggested, in which the ozone process and the UV/TiO<sub>2</sub> process are combined. This new UV/TiO<sub>2</sub>/O<sub>3</sub> process has been applied on gaseous contaminant such as toluene (Zhang *et al.*, 2003) and TCE (Shen and Ku, 2002). To the authors knowledge, the degradation of formaldehyde by UV/TiO<sub>2</sub>/O<sub>3</sub> process has not been reported.

In this work, the degradation of gaseous formaldehyde was studied using continuous flow mode in UV/TiO<sub>2</sub>/O<sub>3</sub> process. A series of factors affecting the degradation level was also investigated.

### 1 Experimental

#### 1.1 Preparation of TiO<sub>2</sub> catalyst

TiO<sub>2</sub> catalyst was prepared by a sol-gel process, in which a porous nickel sheet was used as the catalyst carrier. The thickness of the nickel sheet was 1.6 mm. The porosity of the nickel sheet was reduced from 93% to 52% after coating with the catalyst. The concrete procedure of TiO<sub>2</sub> preparation was described elsewhere (Duan *et al.*, 2002).

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## 1.2 Set-up of continuous flow reactor

Fig.1 displays the schematic diagram of the photocatalytic reaction system for degrading formaldehyde in continuous flow mode. The system consists of three sections: feed system, photoreactor and gas detection apparatus. The feed system includes air pump, drier, several flow meters, humidifier, and a mixer, which can adjust and control the inlet concentration of formaldehyde, relative humidity and ozone content in the feed. The photoreactor was made of stainless steel tubing (100 mm inside diameter and 640 mm in length). The UV-lamp (main wavelength 254 nm) was located at the axis of the reactor. The porous nickel sheet (400 cm<sup>2</sup>) that was coated with TiO<sub>2</sub> particles (33.2 g) was installed inside the reactor. The detection system consists of gas chromatography and humidity meter, which can analyze the formaldehyde concentration and the relative humidity of the reactor.

## 1.3 Degradation experiment of formaldehyde

The reaction system reaches equilibrium in three steps: (1) mixer equilibrium. Three or four gas streams, formaldehyde, water vapor and dilute gas or ozone, mix in the mixer. When the inlet concentration and relative humidity, controlled by adjusting the ratio of the gas flow rates and maintaining the total gas flow constant, reach the appropriate values, the mixed gas enters the reactor. (2) Adsorption equilibrium. In this process, the inlet concentration and relative humidity of the inlet and outlet of the reactor are detected. When the inlet and outlet values are the same, a dynamic equilibrium between adsorption and desorption is achieved, and the UV-lamp is switched on. (3) Degradation equilibrium. In this process, the concentration of outlet decreases gradually, and finally stabilizes when the degradation reaction has reached equilibrium, and the experimental data can be collected.

Formaldehyde concentrations at the inlet and outlet were monitored in interval. All formaldehyde concentrations were analyzed by gas chromatography (HP6890) using a flame ionization detector with an Porapak Q column. The conversion was calculated from the inlet and outlet concentrations.

## 2 Results and discussion

### 2.1 Effect of initial formaldehyde concentration on its degradation

The photocatalytic ozonation of formaldehyde compared to the photocatalytic oxidation and ozonation is shown in Fig.2 under the condition of different initial formaldehyde concentrations. Formaldehyde degradations were obtained at various initial formaldehyde concentrations while keeping the relative humidity at 35%, and with total flow rates of 5000 ml/min.

The results showed that the degradations of formaldehyde in the UV/TiO<sub>2</sub>, UV/TiO<sub>2</sub>/O<sub>3</sub> and O<sub>3</sub>/TiO<sub>2</sub> processes were decreased when the inlet concentration of formaldehyde increased. In heterogeneous catalysis, the factors that determine the rate-controlling step are mass transfer and surface reaction. At the speed of 5000 ml/min, low formaldehyde inlet concentration has high degradation efficiency, indicating that the rate-controlling step is surface reaction on concentration from 1.84 to 24 mg/m<sup>3</sup>. However, there were significant differences among them. Fig.2 shows that, as the initial concentration increased from 1.84 mg/m<sup>3</sup> to 24 mg/m<sup>3</sup>, the formaldehyde degradation efficiencies decreased from 72% to 43.4% in the UV/TiO<sub>2</sub> process, decreased from 79.4% to 73.6% for the UV/TiO<sub>2</sub>/O<sub>3</sub> process, and decreased from 19.8% to 16.6% in O<sub>3</sub>/TiO<sub>2</sub> process, This indicates that the formaldehyde degradation was low in TiO<sub>2</sub>/O<sub>3</sub> process, but the presence of O<sub>3</sub> could greatly enhance the degradation of formaldehyde in UV/TiO<sub>2</sub>/O<sub>3</sub> process. The high degradation by UV/TiO<sub>2</sub>/O<sub>3</sub> at high concentrations was the reason of the synergistic action with the ozone. In this case, the degradation rate of more than 70% could be achieved provided that the formaldehyde concentration was kept below 24 mg/m<sup>3</sup> at 5000 ml/min speed.

### 2.2 Effect of relative humidity on formaldehyde degradation

The tests in UV/TiO<sub>2</sub>/O<sub>3</sub> system were carried out at various relative humidity while maintaining the total flow rate at 5000 ml/min and the inlet concentration of

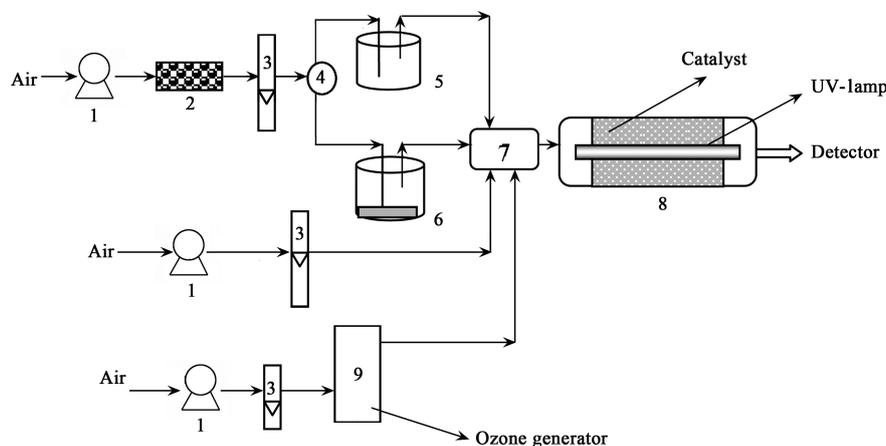


Fig. 1 Schematic diagram of continuous flow reactor for photocatalysis. (1) air pump; (2) drier; (3) flow meters; (4) three-way valve; (5) humidifier; (6) formaldehyde saturator; (7) mixer; (8) photoreactor; (9) ozone generator.

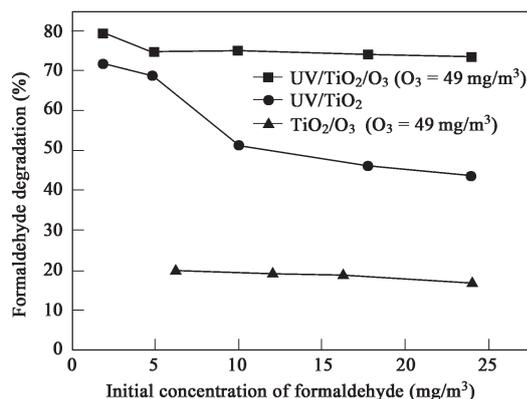


Fig. 2 Effect of initial formaldehyde concentration on its degradation. Conditions: relative humidity 35%; total flow rate 5000 ml/min.

formaldehyde at 22.2–24.0 mg/m<sup>3</sup>.

The results presented in Fig.3 show the effects of relative humidity on degrading formaldehyde for both UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub>/O<sub>3</sub> processes. It can be seen that with the increase of relative humidity the degradation of formaldehyde was first enhanced until reaching the highest point then decreased for both the processes. It is well known that water vapor is an important source of surface hydroxyl radicals in gas-solid photocatalytic oxidations, and its presence in the reactant mixture is necessary to maintain the catalytic activity. If the water vapor content in the reactor is too high, adsorbed water must compete with formaldehyde molecules, which can decrease the adsorption of formaldehyde and lead to a slow degradation rate. In the absence of water vapor, the conversion must be decreased due to a lack of hydroxyl radicals and an excess of products can be accumulated on the catalyst surface. Therefore, it is necessary to maintain an optimal amount of water vapor in the system for photocatalytic oxidation of formaldehyde in which the degrading formaldehyde reaches the highest value. The optimal humidity range is about 50% for UV/TiO<sub>2</sub>/O<sub>3</sub> process with the degrading formaldehyde equal to 78% and approximately 35% for UV/TiO<sub>2</sub> process with the degrading formaldehyde equal to 47%. The degradation efficiencies of UV/TiO<sub>2</sub>/O<sub>3</sub> process is 1.7–3.0 times higher than that of TiO<sub>2</sub>/UV process.

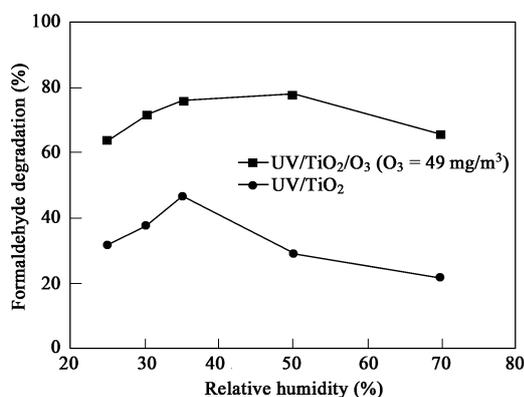


Fig. 3 Effect of relative humidity on degrading formaldehyde. Conditions: initial concentration 22.2–24.0 mg/m<sup>3</sup>; flow rate 5000 ml/min.

### 2.3 Effect of ozone content on formaldehyde degradation

The effect of ozone to degrading formaldehyde has been studied while keeping the total flow rate 5000 ml/min (retention time 58 s), the relative humidity at 30% and the inlet formaldehyde concentration at 22.0–24.9 mg/m<sup>3</sup>. The results are showed in Fig.4. It shows that the degradation of formaldehyde increases from 72.4% to 94.1% when the ozone content increases from 49 to 141 mg/m<sup>3</sup>. In fact, ozone was used to capture the excited electron and prevent the electron-hole pair from recombining. Ozone forms O<sub>3</sub><sup>-</sup>, which can directly participate in the reaction. In the absence of ozone, the conversion of formaldehyde declines to 39.0%.

For the ozone enhanced photocatalysis (UV/TiO<sub>2</sub>/O<sub>3</sub>), the generation of hydroxyl radical can be generally described as follows (Zhang *et al.*, 2003):



### 2.4 Effect of residence time on formaldehyde degradation

Figure 5 gives the effect of residence time on the degradation of formaldehyde, where the formaldehyde inlet concentration was set at 10 mg/m<sup>3</sup> and the relative humidity was adjusted to 30%. The relationship between gas flow rate and residence time is showed in Table 1. It indicates that the degradation of formaldehyde increases along with prolong residence time for both UV/TiO<sub>2</sub>/O<sub>3</sub> and UV/TiO<sub>2</sub> processes. When residence time is low (ca. 40 s), the degradation of formaldehyde is 33.3% for UV/TiO<sub>2</sub> process, and 64.1% for UV/TiO<sub>2</sub>/O<sub>3</sub> process,

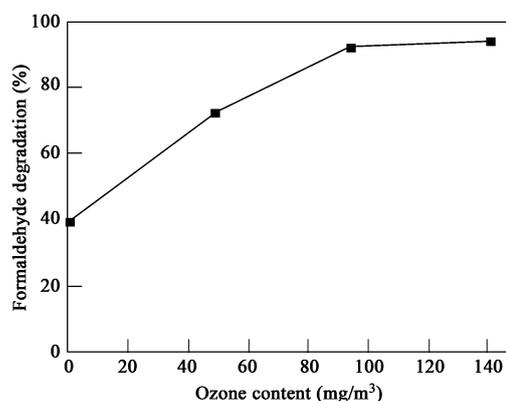


Fig. 4 Effect of quantity of ozone on degrading formaldehyde. Conditions: relative humidity 30%; inlet formaldehyde concentration 22–24.9 mg/m<sup>3</sup>; total flow rate 5000 ml/min.

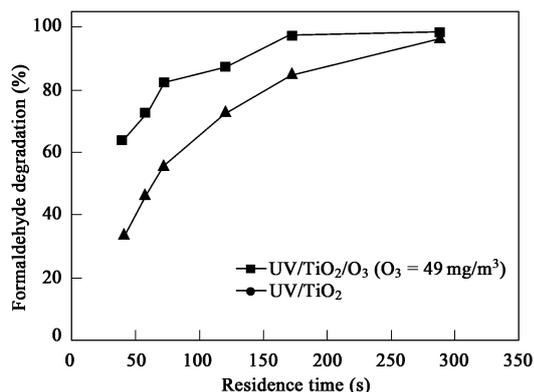


Fig. 5 Effect of residence time on degrading formaldehyde. Conditions: inlet formaldehyde concentration 10 mg/m<sup>3</sup>; relative humidity 30%; flow rate is corresponding to Table 1.

Table 1 Relation of flow rate and residence time

Flow rate (ml/min)	1000	1670	2400	4000	5000	7000
Residence time (s)	288	172	120	72	58	41

almost 2 times of that for UV/TiO<sub>2</sub> process, indicating the UV/TiO<sub>2</sub>/O<sub>3</sub> process was more efficient in decomposing formaldehyde than UV/TiO<sub>2</sub> process at low residence time. When residence time increases to ca. 300 s, almost the same high formaldehyde degradations are achieved for both UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub>/O<sub>3</sub> processes (96.2% for UV/TiO<sub>2</sub> process and 98.5% for UV/TiO<sub>2</sub>/O<sub>3</sub> process).

### 2.5 Kinetics of formaldehyde degradation by UV/TiO<sub>2</sub>/O<sub>3</sub> process

The Langmuir-Hinshelwood model has been widely used to formulate the rate equations for the photocatalytic reaction for a surface-catalyzed reaction (Wang and Hsieh, 1998; Kim and Hong, 2002; Wang *et al.*, 1998; Bouzaza and Laplanche, 2002). The model uses the following equation to determine the reaction rate ( $R$ ) (Sun *et al.*, 2005):

$$R = -\frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (10)$$

where,  $R$  is the reaction rate (mg/(m<sup>3</sup>·min)),  $C$  is the initial concentration (mg/m<sup>3</sup>),  $k$  is the reaction rate constant (mg/(m<sup>3</sup>·min)), and  $K$  is the Langmuir adsorption coefficient (m<sup>3</sup>/mg). For a plug flow reactor, the relationship between retention time ( $\tau$ ) and the conversion ( $x$ ) can be expressed by

$$\tau = \frac{V_R}{V_0} = \int_0^x \frac{C_0 dx}{R} \quad (11)$$

where,  $V_R$  is the reactor volume,  $V_0$  is the gas flow rate. Combining Eq.(10) with Eq.(11) yields:

$$\begin{aligned} \tau &= \int_0^x \frac{C_0 dx}{\frac{kKC}{1 + KC}} = C_0 \int_0^x \frac{dx}{kKC} + C_0 \int_0^x \frac{dx}{k} \\ &= \int_0^x \frac{dx}{kK(1-x)} + C_0 \int_0^x \frac{dx}{k} \\ &= -\frac{1}{kK} \ln(1-x) + \frac{C_0}{k} x \end{aligned} \quad (12)$$

If  $C_0$  is fixed, the rate constant  $k$  and the Langmuir adsorption coefficient  $K$  can be obtained by using the least square method with data obtained at various retention time and conversions. The values of  $k$  and  $K$  for our reaction system in UV/TiO<sub>2</sub>/O<sub>3</sub> process were found to be 46.72 mg/(m<sup>3</sup>·min) and 0.0268 m<sup>3</sup>/mg, respectively.

### 3 Conclusions

On the basis of the above study, the following conclusions can be drawn. The process of UV/TiO<sub>2</sub>/O<sub>3</sub> can degrade the formaldehyde more efficiently than the UV/TiO<sub>2</sub> process under all the experimental conditions. The efficiency of the UV/TiO<sub>2</sub>/O<sub>3</sub> process is affected by initial concentration of formaldehyde, humidity and residence time. The degradation of formaldehyde is between 73.6% and 79.4% as the initial concentration in the range of 1.84–24 mg/m<sup>3</sup>, and the optimal relative humidity is approximately 50% in the UV/TiO<sub>2</sub>/O<sub>3</sub> process. Degradation of formaldehyde increases along with prolonging residence time.

In addition, the kinetics of photocatalytic degradation of formaldehyde can be described by the Langmuir-Hinshelwood model. From our calculation, the rate constants  $k$  and the Langmuir adsorption coefficient  $K$  were 46.72 mg/(m<sup>3</sup>·min) and 0.0268 m<sup>3</sup>/mg in UV/TiO<sub>2</sub>/O<sub>3</sub> process, respectively.

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