Study on Photocatalytic Degradation of Unsym-Dimethylhydrazine Wastewater by Bi_2O_3 Thin Films

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Abstract: The Bi_2O_3 thin films were prepared by sol-gel method for photocatalytic degradation of unsym-dimethylhydrazine (UDMH) wastewater. The effects of initial concentration of UDMH, initial pH value of solution and H_2O_2 addition were investigated. Besides, the reaction kinetics and mechanism were studied. The results showed that when the initial concentration of UDMH was between 100 mg/L and 500mg/L, the concentration had little effect on the degradation efficiency; initial pH value of solution had noticeable impact on the degradation of UDMH and higher removal efficiency can be achieved in neutral or weakly alkaline condition; the addition of H_2O_2 can effectively improve the degradation. The kinetic study showed that the reaction kinetics were well fitted by the pseudo first-order rate model and Langmuir-Hinshelwood model.

1 INTRODUCTION

Unsym-dimethylhydrazine (UDMH) is a high-energy fuel and its wastewater is usually produced in the engine test, propellant transfer and rail tank cleaning process, which contains a variety of toxic and hazardous substances (Liang et al., 2016). In recent years, with the increase of spacecraft launching, the use of UDMH has increased significantly, and the pollution of UDMH wastewater has attracted extensive attention (Angaji and Ghiaee, 2015). Advanced oxidation processes (AOPs) are a set of chemical treatment procedures designed to remove organic materials in wastewater by oxidation through reactions with hydroxyl radicals (·OH). Photocatalytic oxidation is one of the AOPs which began in the 1970s (Fujishima and Honda, 1972). It has the unique advantages of high efficiency, low cost and environmental friendliness, and is considered to be an ideal wastewater treatment method (Hoffmann et al., 1995). In recent years, many researchers have used photocatalysts to degrade UDMH wastewater to obtain satisfactory results (Khalid et al., 2013; Bessekhouad et al., 2005; Zhu et al., 2011).

Bi_2O_3 is an effective and stable photocatalyst with a narrow band gap (about 2.8 eV), many oxygen vacancies, strong redox capability, and high photocatalytic activity. Since 1988, Bi_2O_3 was introduced into the field of photocatalysis (Anthony et al., 1988), many scholars have achieved good results in treating organic wastewater with Bi_2O_3 as photocatalyst (Zhang et al., 2006). However, most of the current researches focus on the suspension photocatalysts (Li et al., 2013), which have the disadvantages of easy agglomeration, difficult separation, and low photon utilization. Therefore, scholars turn to the study of supported Bi_2O_3 film (Fruth et al., 2005; Leontie et al., 2005; Qin et al., 2014). In this study, the supported Bi_2O_3 thin films were prepared on the quartz glass substrate by sol-gel method (Qin et al., 2014), and the photocatalytic degradation of UDMH wastewater was studied.

2 EXPERIMENT

All chemicals were of reagent grade and used without further purification. Distilled water was used throughout this experiment.

2.1 Photocatalyst Preparation

The Bi_2O_3 thin films were prepared according to the following procedure: 5.0 g Bi $(NO_3)_3 \cdot 5H_2O$ was dissolved in 20.0 mL HNO_3 aqueous solution (HNO_3

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3.3 mL, H_2O 16.7 mL). Then 4.0 mL PEG200 and 2.0 g citric acid were added in the above solution, and 3.5 mL t-Oct-C_6H_4-$(OCH_2CH_2)_xOH$ (x=9-10) was added as surfactant. The above solution was stirred for 10 h at room temperature. After that, pieces of 50×100 mm^2 quartz glass were dipped into the sol solution where they would be kept for 3 min, and then withdrawn at a rate of 4.0 cm/min. All the films were preliminarily treated at a heating rate of 1 °C/min to 390 °C, during the process of which two 30 min plateaus at 275 °C and 390 °C were maintained, respectively. The films were then annealed at 550 °C with a heating rate of 1 °C/min, and at this temperature 2 h plateau was maintained.

2.2 Photocatalytic Experiments

A certain concentration of UDMH aqueous solution (100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L, 500 mg/L) was prepared as simulated wastewater. The photocatalytic activity of Bi_2O_3 was evaluated by degrading UDMH wastewater under irradiation of an UV-light source (Philips, 8 W, wavelength 253.7 nm). The UV-light irradiated perpendicularly to the surfaces of the samples and the distance from the UV-light source to the samples was 10 cm. The ambient temperature was 20~25°C and the humidity was 20~30%. 5 mL UDMH solution was taken every 30 minutes and the concentration changes of UDMH with the irradiating time were measured by spectrophotometry (GB18063-2000).

3 RESULTS AND DISCUSSION

3.1 Initial Concentration of UDMH

The influence of initial concentration of UDMH on photocatalytic degrading efficiency was studied and the results were shown in Figure 1. It showed that the removal efficiency of UDMH increased rapidly with the extension of reaction time, and the removal efficiency increased slowly after 60 minutes. It can be easily concluded from the figure that there was no obvious difference among the photocatalytic degrading when the initial concentration of UDMH was between 100 mg/L and 500 mg/L. The removal efficiency of UDMH with different initial concentrations were above 90% (120 min). It can be seen from the above that the initial concentration of UDMH has little effect on the degradation efficiency.

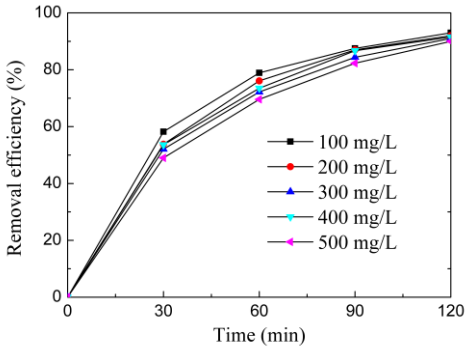

Figure 1: Influence of initial concentration on removal efficiency of UDMH.

3.2 Initial pH Value of the Solution

In order to investigate the degradation effect of initial pH value on UDMH, H_2SO_4/NaOH was added into the UDMH aqueous solution (300 mg/L) to adjust the pH of the solution to 4, 6, 8, 10, and the reaction time was 60 min. The results were shown in Figure 2.

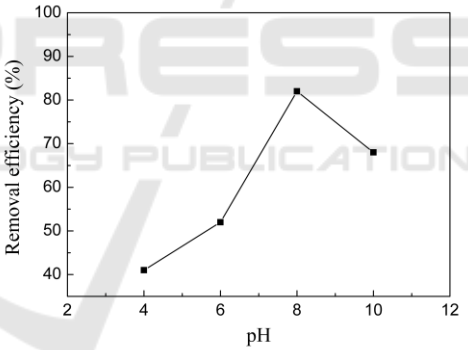

Figure 2: Influence of initial pH value on removal efficiency of UDMH.

It can be inferred that the degradation efficiency of UDMH increased first and then decreased with the increase of pH value, and reached a maximum when the pH value was about 8. This is mainly related to the existence state of UDMH under acidic or strongly alkaline conditions and the surface electrical properties of the catalyst. UDMH is an organic weak base which is mainly present as $(CH_3)_2NNH^{3+}$ in acidic medium. At this time, the surface of the catalyst is positively charged. Under strong alkaline conditions, it is mainly in the presence of $(CH_3)_2NNH_2OH^-$ and the surface of the catalyst is negative. So UDMH can not be adsorbed effectively under acidic or strongly alkaline

conditions. The ideal adsorption effect be achieved in neutral or weakly alkaline condition.

3.3 Addition of H_2O_2

The unequal amount of H_2O_2 (30 wt%) was added to the reaction system to make the concentration of H_2O_2 0.5, 1.0 and 1.5 g/L, respectively. The influence of H_2O_2 on removal efficiency of UDMH were shown in Figure 3.

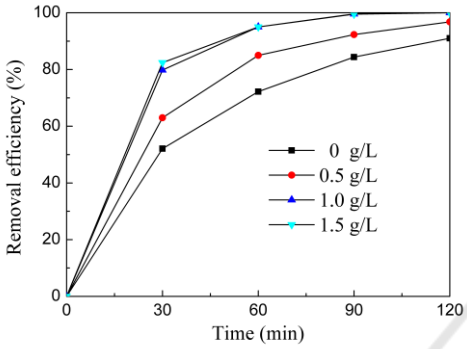

Figure 3: Influence of H_2O_2 on removal efficiency of UDMH with Bi_2O_3 as photocatalyst.

Obviously the addition of H_2O_2 can significantly improve the photocatalytic degradation efficiency of UDMH. To further understand the role of H_2O_2 in photocatalytic reaction, the blank photodegradation experiments without Bi_2O_3 were conducted and the results were shown in Table 1.

Table 1: Influence of H_2O_2 concentration on removals of UDMH without B_2O_3 (120 min).

H_2O_2 concentration (g/L)	Removals (%)
0.5	32.5
1.0	38.7
1.5	36.5

It can be seen from Table 1 that the removal efficiency of UDMH in the presence of H_2O_2 without Bi_2O_3 were less than 40%, which mainly attributed to the strong oxidizing property of H_2O_2. As a comparison, the UDMH removals in solutions with different concentrations H_2O_2 with Bi_2O_3 as photocatalyst exceeded 90% (120 min). When the concentration of H_2O_2 reached 1.0 g/L, the removal efficiency of UDMH was 95% in 60 min and 100% in 120 min. The significantly improved photocatalytic efficiency can be attributed to the electron scavenger role of H_2O_2. As an effective electron trapping agent, H_2O_2 can be act as electron scavenger during the photocatalytic reaction which can reduce the recombination rate of photogenerated electrons/holes and prolong the effective life of photogenerated holes.

3.4 Reaction Kinetics

To quantitatively understand the reaction kinetics of UDMH degradation, the pseudo first-order kinetic equation (equation 1) with a simplified Langmuir-Hinshelwood model can be applied because of the low reactant concentration.

$$\ln(C_0/C) = k_{app}t \quad (1)$$

where C_0 and C are the reactant concentrations of dyes in solution at times 0 and t, respectively, and k_{app} (min^{-1}) is the apparent phtocatalytic reaction rate constant determined from a linear fit to the data as shown in Figure 4. The results indicated that the reaction kinetics of all the samples were well fitted by the pseudo first-order rate model and the photocatalytic reaction was carried out at the interface between Bi_2O_3 and the solution.

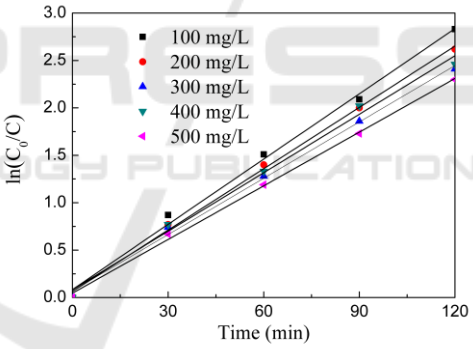

Figure 4: Photocatalytic kinetic linear fitting of UDMH.

3.5 Reaction Mechanism

At present, for the mechanism of semiconductor photocatalysis, the theory of hydroxyl radicals is generally accepted. Bi_2O_3 is a p-type semiconductor with an energy band structure, and it can be used as photocatalyst in connection with its semiconductor optoelectronic characteristics.

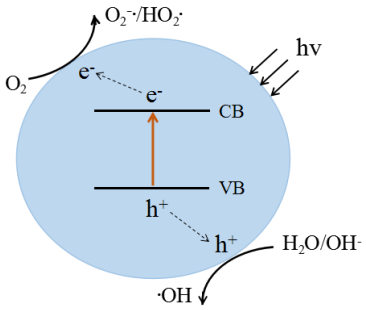

Figure 5: Schematic diagram of photocatalytic reaction.

As shown in Figure 5, the energy band of Bi_2O_3 is discontinuous, and there is a forbidden band between the electron-filled valence band (VB) and the empty conduction band (CB). When the photocatalyst is exposed to the light with an energy greater than the band gap, the photogenerated electrons (e^-) on the valence band are excited to transition to the conduction band, and at the same time, corresponding photogenerated holes (h^+) are generated on the valence band (equation 2).

$$Bi_2O_3 + h\upsilon \rightarrow h^+ + e^- \quad (2)$$

Under the action of the electric field, the photogenerated electrons and holes are separated to form oxidation-reduction system on the surface of the semiconductor. The holes can react with OH^- or H_2O to produce OH• (equation 3 and 4).

$$OH^- + h^+ \rightarrow OH\bullet \quad (3)$$
$$H_2O + h^+ \rightarrow OH\bullet + H^+ \quad (4)$$

4 CONCLUSIONS

(1) The Bi_2O_3 thin films which were prepared by sol-gel method showed high photocatalytic activity by degrading UDMH (above 90% in 120 min). The initial concentration of UDMH had little effect on the removal efficiency when the concentration was among 100~500 mg/L; in neutral or weakly alkaline conditions, the photocatalytic degradation efficiency of UDMH was higher; the addition of a small amount of H_2O_2 in the reaction system can significantly improve the degradation rate of UDMH.

(2) Reaction Kinetic studies showed that the reaction kinetics were well fitted by the pseudo first-order rate model and the photocatalytic reaction was carried out at the interface between Bi_2O_3 and the solution.

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