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Photocatalytic degradation kinetics of unsymmetrical dimethylhydrazine in aqueous solution by Fe³⁺ doped Bi₂O₃

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Abstract. The Fe³⁺ doped Bi₂O₃ photocatalyst was prepared by sol-gel method. The photocatalytic degradation experiment was carried out using unsymmetrical dimethylhydrazine (UDMH) simulated wastewater as the target pollutant. The results showed that Fe³⁺ doping significantly improved the degradation efficiency of UDMH with an optimum doping concentration of 2.0%. The reaction kinetics study indicated that the reaction was heterogeneously catalyzed and the kinetic fitting results were consistent with pseudo first-order reaction kinetics model. According to the results of linear fitting, the kinetic reaction rate constant of Fe³⁺ doped Bi₂O₃ (2.0%) was the largest, about 1.9 times as much as that of undoped Bi₂O₃. Finally, a possible mechanism was proposed to explain the enhanced photocatalytic activity.

1. Introduction

As a high-energy liquid propellant, unsymmetrical dimethylhydrazine (UDMH) is widely used in missiles and satellite launch vehicles. In the process of production, storage, and use of UDMH, a large amount of wastewater will be produced. Such wastewater is highly toxic and has a wide range of concentration. If directly discharged, the hazardous wastewater will have adverse effects on people and environment. At present, the main treatment methods for UDMH wastewater are physical method, biological method, chemical method, etc. [1-3], all of which have various drawbacks, such as incomplete oxidation, secondary pollution, and equipment corrosion.

Photocatalytic oxidation is a kind of advanced oxidation processes (AOPs), which has the unique advantages of complete oxidation process, fast reaction rate, low cost, and easy operation. Photocatalysis is widely used in the fields of air purification, degradation of organic pollutants, and advanced treatment of water [4-7]. Most of the photocatalysts used for degradation of organic pollutants are semiconductor materials. Bismuth oxide (Bi₂O₃), an important metal oxide semiconductor with a wide energy change, has received considerable interests because of its excellent physicochemical properties, good charge mobility, thermal property, and outstanding photoconductivity [8-12]. Due to these remarkable characteristics, Bi₂O₃ has been considered to be one of the most promising photocatalysts. In this paper, Fe³⁺ doped Bi₂O₃ prepared by sol-gel method [13] was used as photocatalyst, and photocatalytic degradation experiments were carried out using UDMH wastewater as target pollutants.

2. Experiment

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



2.1. Synthesis of Fe^{3+} doped Bi_2O_3 photocatalyst

The Fe^{3+} doped Bi_2O_3 photocatalyst was prepared by sol-gel method and the detailed synthesis procedure was as follows: 5.0 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 20.0 mL HNO_3 aqueous solution (HNO_3 3.3 mL, H_2O 16.7 mL). Then 4.0 mL PEG200, 2.0 g citric acid and 3.5 mL $t\text{-Oct-C}_6\text{H}_4\text{-(OCH}_2\text{CH}_2)_x\text{OH}$ ($x=9\text{--}10$) were added in the above solution. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to obtain the different molar ratio of Fe/Bi (0, 0.5%, 1.0%, 2.0%, 3.0%). The above solution was stirred for 10 h at room temperature. After that, pieces of $50 \times 100 \text{ mm}^2$ quartz glass were dipped into the colloidal sol where they would be kept for 3 min, and then withdrawn at a rate of 4.0 cm/min. These pieces of quartz glass were dried up at 100°C in a baking oven. At last the samples were annealed at 550°C with a heating rate of $1^\circ\text{C}/\text{min}$, and at this temperature 2 h plateau was maintained.

2.2. Photocatalytic activity test

The photocatalytic activity of Fe^{3+} doped Bi_2O_3 was investigated by degradation of target pollutants UDMH in aqueous solution under UV-light irradiation (Philips, 8 W, wavelength 253.7 nm). The experiment conditions were $20\text{--}25^\circ\text{C}$ in temperature, and $20\text{--}30\%$ in humidity. The distance from the UV lamp to the photocatalysts was 10 cm. The samples of UDMH were taken every 20 minutes, which were determined by spectrophotometry (GB18063-2000).

3. Results and Discussion

3.1. Influence of Fe^{3+} doping on photocatalytic activity of Bi_2O_3

The degradation of UDMH under UV-light was used to test the influence of Fe^{3+} doping on Bi_2O_3 photocatalytic activity and the results were shown in Figure 1. Obviously, the incorporation of a small amount of Fe^{3+} resulted in a sharp increase of UDMH degradation efficiency. As the Fe^{3+} doping concentration increased to 2.0%, the doped Bi_2O_3 showed the highest photocatalytic degradation efficiency (about 100%), after which the photodegradation efficiency decreased. Such a phenomenon can be ascribed mainly to the fact that redundant Fe^{3+} ions could serve as the recombination centers of photogenerated electrons and holes because of the well-known effect of concentration quenching. Generally, the Fe^{3+} doped Bi_2O_3 exhibited higher photocatalytic activities than the undoped.

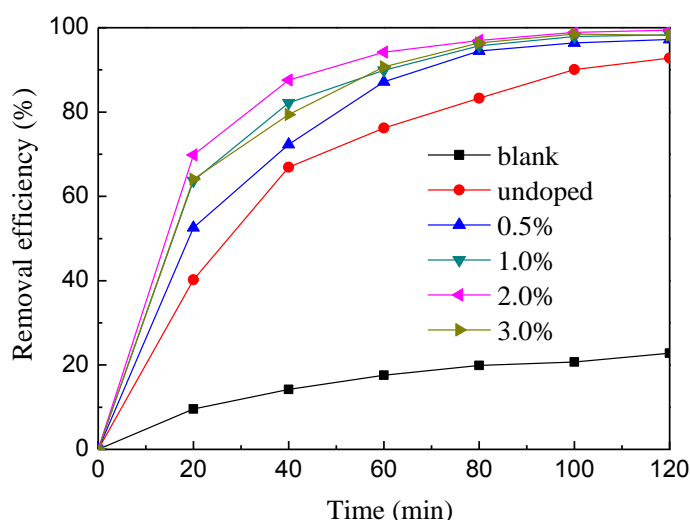


Figure 1. The influence of Fe^{3+} doping on removal efficiency of UDMH.

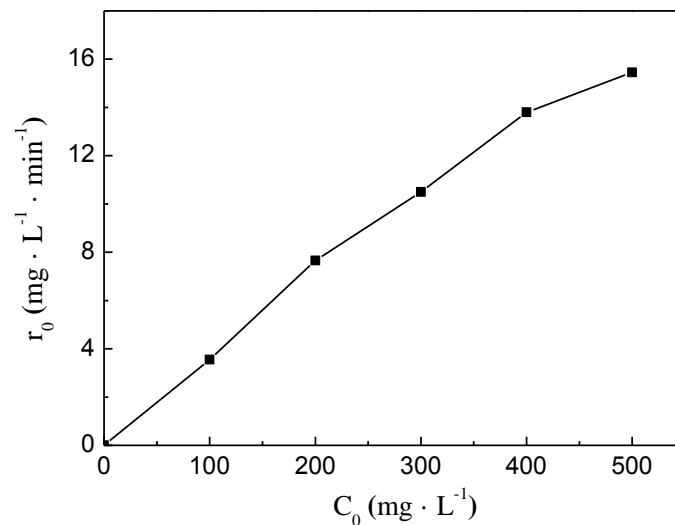


Figure 2. The relationship graph between initial concentration of UDMH (C_0) and initial reaction rate (r_0).

3.2. Photocatalytic reaction kinetics

In order to investigate the relationship between initial concentration of UDMH (C_0) and initial reaction rate (r_0), Fe^{3+} doped Bi_2O_3 (Fe/Bi 2.0%) was placed in five different concentrations of UDMH simulated wastewater (100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L, 500 mg/L) for photocatalytic degradation experiments, and the results were shown in Figure 2. Obviously, the initial rate (r_0) of photocatalytic degradation increased with the increase of initial concentration (C_0). Plot the reciprocal of the initial reaction rate ($1/r_0$) to the reciprocal of the initial concentration ($1/C_0$) and the relationship graph was shown in Figure 3. There was a linear relationship between $1/C_0$ and $1/r_0$, and the relation equation is:

$$\frac{1}{r} = 27.1739 \times \frac{1}{C} + 0.0045 \quad (1)$$

The linear equation indicated that the relationship between the initial reaction rate (r_0) and the initial concentration (C_0) were consistent with Langmuir-Hinshelwood (L-H) model.

$$r = -\frac{dC}{dt} = \frac{KK_1C}{1 + K_1C} \quad (2)$$

$$\frac{1}{r} = \frac{1}{K} + \frac{1}{KK_1C} \quad (3)$$

The Langmuir-Hinshelwood equation is the basic kinetic equation describing the heterogeneous catalytic reaction. The experimental results showed that the photocatalytic degradation of UDMH by Fe^{3+} doped Bi_2O_3 was heterogeneous catalytic reaction, indicating that the reaction was carried out at the interface between photocatalyst and solution under UV-light. Because of the low reactant concentration (C_0), L-H equation can be simplified to pseudo first-order kinetic equation.

$$\left(1 + \frac{1}{K_1C}\right)dC = Kdt \quad (4)$$

$$\ln\left(\frac{C}{C_0}\right) + K_1(C - C_0) = -KK_1t \quad (5)$$

$$\ln\left(\frac{C}{C_0}\right) = -KK_1t = -k_{app}t \quad (6)$$

where C_0 and C are the concentrations of UDMH at times 0 and t , respectively, and k_{app} (min^{-1}) is the apparent reaction rate constant determined from the linear fitting data as shown in Figure 4.

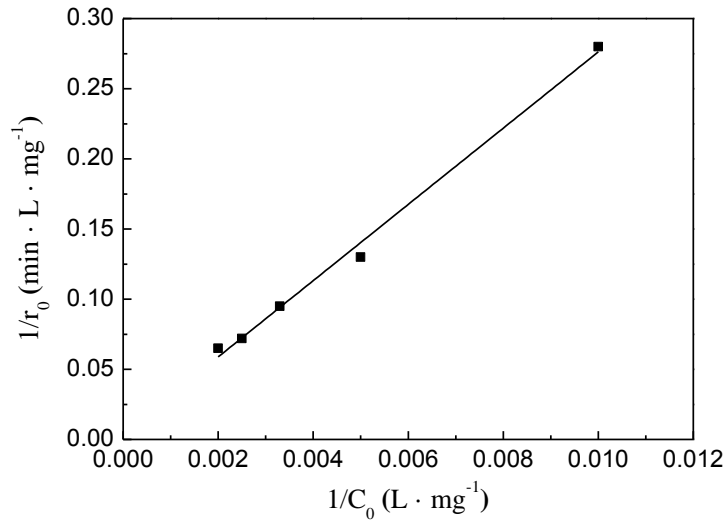


Figure 3. The relationship graph between reciprocal of initial concentration ($1/C_0$) and reciprocal of initial reaction rate ($1/r_0$).

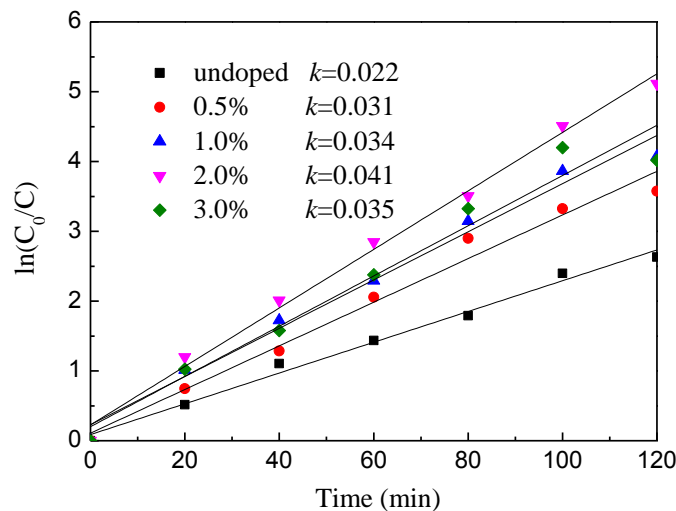


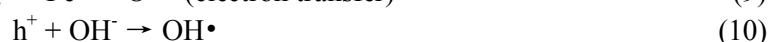
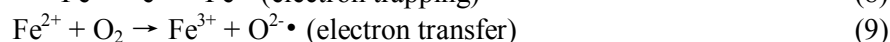
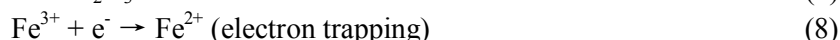
Figure 4. Photocatalytic kinetic linear fitting of UDMH.

The results indicated that the reaction kinetics of all the samples were well fitted by the pseudo first-order reaction kinetics model. Clearly, the kinetic reaction rate constant of Fe^{3+} doped Bi_2O_3 (2.0%) was the largest (0.041 min^{-1}), about 1.9 times as much as that of undoped Bi_2O_3 (0.022 min^{-1}).

3.3. Possible photocatalytic mechanism

To explain the enhanced photocatalytic activity of the Fe^{3+} doped Bi_2O_3 , a possible mechanism was proposed that Fe^{3+} can act as electron scavenger during the photocatalytic reaction. Under UV-light

irradiation, the photogenerated electrons (e^-) on the valence band are excited to the conduction band, and at the same time, correspondingly photogenerated holes (h^+) are generated on the valence band. The Fe^{3+} ions doped into Bi_2O_3 would capture the photogenerated electrons and the reduced state of Fe^{2+} ions, which are instable, would participate in the O_2 reduction reaction to form $O_2^{\cdot-}$. In the meantime, the holes in the valence band react with surface hydroxyl group to produce OH^{\cdot} . The photogenerated holes (h^+), OH^{\cdot} , and $O_2^{\cdot-}$ can act as major reactive species due to their strong oxidation property. It can be described as follows:



Therefore, the electron trapping-transfer process caused by Fe^{3+} in Bi_2O_3 lattice induces an effective charge carriers separation, leading to higher photocatalytic efficiency.

4. Conclusions

In summary, the photocatalyst Bi_2O_3 with different doping concentrations of Fe^{3+} were synthesized by sol-gel method. The exceptional photocatalytic performance of Fe^{3+} doped Bi_2O_3 for the degradation of UDMH under UV-light irradiation was superior over that of undoped Bi_2O_3 and the doped Bi_2O_3 with 2.0% of Fe^{3+} exhibited the highest photodegradation efficiency. The reaction kinetics study showed that the photocatalytic degradation of UDMH by Fe^{3+} doped Bi_2O_3 was heterogeneous catalytic reaction, indicating that the reaction was carried out at the interface between photocatalyst and solution under UV-light. The reaction kinetics of all the samples were well fitted by the pseudo first-order reaction kinetics model and the kinetic reaction rate constant of Fe^{3+} doped Bi_2O_3 (2.0%) was the largest (0.041 min^{-1}), about 1.9 times as much as that of undoped Bi_2O_3 (0.022 min^{-1}). A possible mechanism was proposed that the enhancement of photocatalytic activity was attributed to the electron trapping-transfer process caused by Fe^{3+} .

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