Research Article

Visible-Light-Driven Photocatalytic Degradation of Aniline over NaBiO$_3$

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Aniline was almost completely degraded in 30 min in given conditions. It was found that pH and NaBiO$_3$ dosage had played important role in the photocatalytic degradation. To scrutinize the mechanistic details of the aniline photodegradation, several critical analytical methods including spectroscopy and GC/MS were utilized to detect the temporal course of the reaction. Intermediates and several small molecular products were separated and identified, such as C$_2$H$_5$O$_3$N, C$_{10}$H$_{13}$O$_2$N, and C$_{12}$H$_{10}$N$_2$. Then two possible photodegradation pathways of aniline over NaBiO$_3$ were proposed: ring opening and mineralization.

1. Introduction

Aniline is widely used in the chemical industry, mainly as a raw material for obtaining isocyanate. Aniline is also applied to the manufacture of accelerators, antioxidants, pesticides, dyes, and pigments [1]. The negative effects of aniline on human health and the environment are depending on the amount and exposure time. Aniline can enter the aqueous environment via dyes and nitro aromatic compounds and has been identified as a potential carcinogen [2]. Nowadays, more attention is focused to remove it from environment.

Among chemical methods, photocatalysis technology can play an important role in removing harmful organic compounds, which enables human to have comfortable and safe lives [3]. Being the most common photocatalyst among semiconductors, TiO$_2$ possesses various merits such as low cost, high photocatalytic activity, chemical activity, and nontoxicity [4]. As its photoresponse is only limited in the UV region, which accounts for less than 5% of the earth-reaching solar irradiation [5, 6], it requires a high power UV excitation source [7]. Therefore, it is meaningful to explore a new photocatalyst which can utilize visible light.

Lots of studies have been devoted to developing visible-light-driven photocatalysis. Apart from TiO$_2$ doped with metallic elements, for instance, Cr^{3+} and V^{5+} [8], new materials such as AgNbO$_3$ and InNbO$_4$ are previously reported to absorb visible light [9, 10]. However, the activity of the photocatalyst was hardly enhanced, and the low reaction rate severely blocked the development of photocatalysis technology.

Seeking for new materials with higher photocatalytic activity has become a key solution to this problem. Particularly, Bi(V)-containing oxides are potential materials as the candidates of visible light sensitive oxides [11]. In fact, some Bi(V)-containing oxides have indicated the ability of absorption of visible light. Among them, NaBiO$_3$ is studied as it displayed the visible light absorption because of its hybridized valence band. The large dispersion of the hybridized orbitals in the conduction band increases the mobility of the photoexcited electrons, thus suppressing the recombination of photoexcited electron-hole pairs and enhancing activities [11]. Kou and coworkers [12] utilized NaBiO$_3$ in photooxidation of PAHS. Yu and coworkers [13] utilized NaBiO$_3$ in photooxidation of rhodamine B under visible light irradiation and found that heating temperature
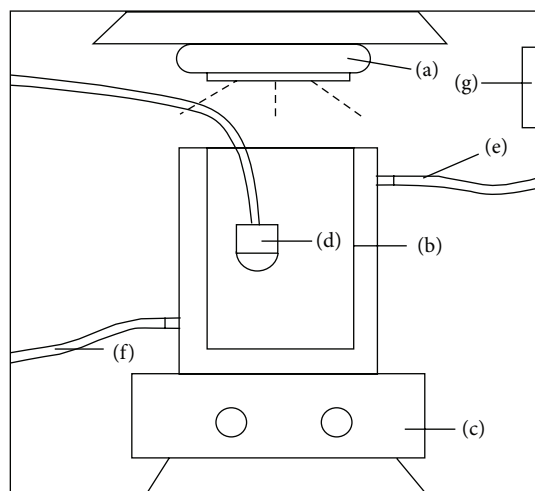
FIGURE 1: Photoreaction chamber. (a) Xenon lamp, (b) double-deck beaker, (c) magnetic stirrer, (d) oxygen pump, (e) outlet, (f) inlet, and (g) fan.

FIGURE 2: Control experiment. (a) Light+ NBH, (b) NBH alone, (c) light alone, and (d) none.

significantly influenced the photocatalytic activity of the catalyst. As $NaBiO_3$ has the properties of strong oxidation, electromagnetism, and electrochemical activity, it has been applied to industries such as organic synthesis, superconductor, and electrochemistry [14]. It is meaningful to explore the feasibility of the photodegradation of aniline over $NaBiO_3$.

In this study, aniline was chosen as the target organic pollutant to investigate its degradation behavior over $NaBiO_3$ under visible light irradiation. The goal was aimed at the investigation of aniline degradation and the presentation of mechanistic details of the photochemical process.

2. Experimental Section

2.1. Materials and Reagents. Aniline was bought from Ke Long Chemical Company, and $NaBiO_3 \cdot 2H_2O$ (NBH) was purchased from Guang Fu Chemical Products Institute. All other chemicals were of analytical grade and used without further purification.

2.2. Photoreaction Chamber. Photodegradation experiments were performed in a chamber which was displayed in Figure 1. A 500 W xenon lamp (Chengdu Na Pu Photoelectricity Company, China) was positioned to ensure visible light. The reactor was a double-deck beaker equipped with an inlet and an outlet which can draw into water circulation to make sure experiments performed in adequate temperature. A 50 W fan was used to keep the chamber at ambient temperature. A stir was used to ensure that photocatalyst distributes well in the suspension. Oxygen pump was used to provide enough oxygen to ensure that oxidation performed sufficiently.

2.3. Experimental Procedures and Analysis Methods. In the experiments, the dispersions containing aniline and $NaBiO_3$ photocatalyst were prepared by adding NBH to an aqueous solution of aniline in a beaker.
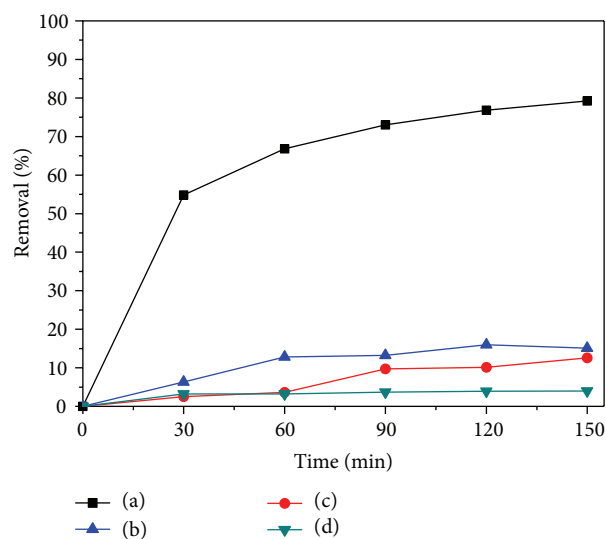
A 500 mL double-deck beaker was used as a reactor. The NBH was added to 200 mL aniline solution, which was magnetically stirred at a constant speed to ensure continuous contact between the solution and $NaBiO_3$ when they were under visible light irradiation emitted from xenon lamp. At given time intervals, samples (10 mL) were centrifuged immediately. The samples were analyzed by a V-1100D spectrophotometer. The intermediates were detected by GC/MS (GCMS-QP2010 Plus).

3. Results and Discussions

3.1. Control Experiment. The decreases of aniline concentration as a function of reaction time were shown in Figure 2. In the control experiment, when utilizing NBH (1 g/L) alone, a slight decrease of aniline concentration was observed; this could be attributed to surface adsorption. Aniline was relatively stable in aqueous solution under visible light irradiation as expected. Therefore, aniline was not significantly decomposed by either under ambient conditions used in the experiment. Aniline can be degraded rapidly only in the circumstance of both NBH and visible light irradiation.

3.2. Nitrogen Transformation. As there is an amidogen in the aniline structure, it will be harmful to environment if it transforms into nitrite nitrogen. It is important to study the transformation of nitrogen in the photodegradation process of aniline.

As it was shown in Figure 3, the removal rose in the first 30 min of the degradation aniline; the concentration of ammonia nitrogen and nitrate were increasing and tended towards stability in 120 min. Nitrites were produced as the intermediates of nitrate, and the concentration was low on the whole.
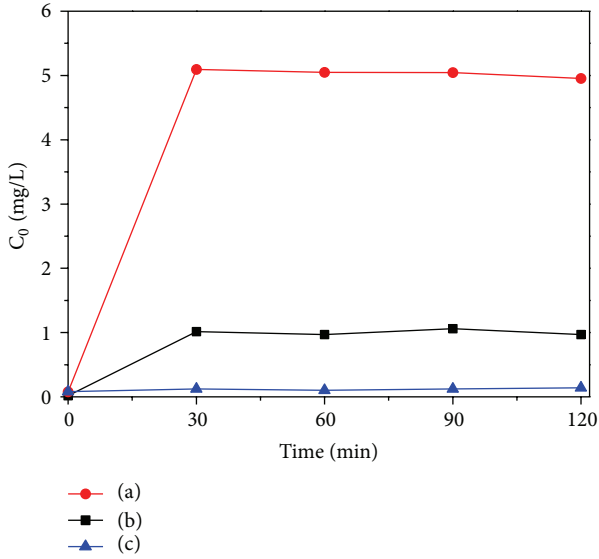
FIGURE 3: Temporal change in the concentration of nitrogen during the photodegradation. (a) Nitrate, (b) ammonia nitrogen, and (c) nitrite.

FIGURE 4: Effect of initial pH value. (a) pH = 2, (b) pH = 4, (c) pH = 8, (d) pH = 6, and (e) pH = 10.

3.3. Kinetic Model. The reaction mechanism of photocatalytic degradation was the process of absorption-surface-reaction-desorption whose kinetic model was in coincidence with the Langmuir-Hinshelwood model [15, 16]. The kinetic model was as below [17]:

$$-\frac{dc}{dt} = Kc, \tag{1}$$

where t is time and c is instantaneous concentration of aniline. The equation below is the integration of it when t is from 0 to t:

$$\ln c = -Kt + \ln c_0. \tag{2}$$

When initial aniline concentration was 30 mg/L, the pseudo first order rate constant for photocatalytic degradation, light reaction, and dark reaction was 0.0402 min^{-1}, 0.00182 min^{-1}, and 0.000987 min^{-1}, respectively. The kinetic study proved that the effect of NBH on aniline degradation is great.

3.4. Influence Factors

3.4.1. pH Value Effect. In the photocatalytic oxidation, the solution pH had an instant influence on the agglomeration of particles, electric charge, and absorption of organic on the surface [18]. In Figure 4, the remainder aniline in the acidity was less than that in the neutral and alkaline condition. When pH was 2, the aniline concentration was reduced to 0.98 mg/L in the 120 min with a removal of 97%. The main reason was that the oxidation was in the dominant position. It was found that the NBH effect was better in the acidity condition. The removal rate can reach 75% in the 5 minutes, whereas the removal rate in the neutral and alkaline condition was 20% and 16%, respectively. In the acidity condition, [BiO$_3$]

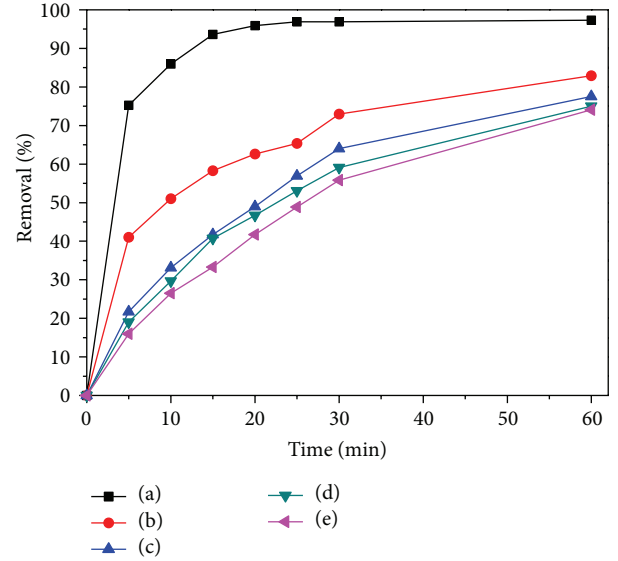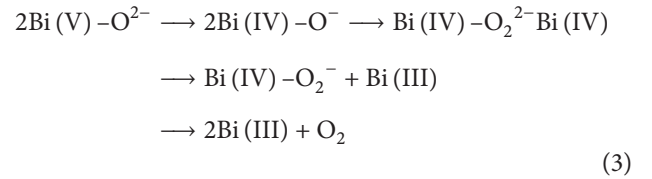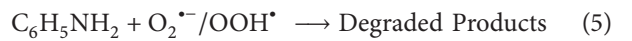can turn into [BiO$_6$] more easily, while the latter's crystal structure was relatively weak. During reduction of Bi(V), oxygen which had higher activity was released [13]. The equation was as below:

$$2\text{Bi (V)} -\text{O}^{2-} \longrightarrow 2\text{Bi (IV)} -\text{O}^- \longrightarrow \text{Bi (IV)} -\text{O}_2{}^{2-}\text{Bi (IV)}$$

$$\longrightarrow \text{Bi (IV)} -\text{O}_2{}^- + \text{Bi (III)}$$

$$\longrightarrow 2\text{Bi (III)} + \text{O}_2$$

$$\tag{3}$$

In this case, aniline was oxidized mainly by O$_2{}^\bullet$. The reaction progress was not part of photocatalytic oxidation.

The photocatalytic oxidation of aniline was as below:

$$\text{O}_2{}^{\bullet-} + \text{H}^+ \longrightarrow \text{OOH}^\bullet \tag{4}$$

$$\text{C}_6\text{H}_5\text{NH}_2 + \text{O}_2{}^{\bullet-}/\text{OOH}^\bullet \longrightarrow \text{Degraded Products} \tag{5}$$

H$^+$ has played an important role in the photocatalytic oxidation. In the weak acidity condition, H$^+$ can combine with active oxygen to produce more $^\bullet$OH which increases the reaction rate. In the neutral and alkaline condition, the oxidation electric potential decreased as the pH increases. As a result, the removal had a decline [19].

3.4.2. NBH Dosage Effect. The result of aniline degradation over NBH dosage was given in Figure 5. The result showed that the oxidation efficiency was increasing with NBH dosage increasing correspondingly in the first 30 min. When NBH dosage was 0.5 g, there was a significant rise in the removal, as the aniline concentration was decreased to 12.7 mg/L in the 10 min. However, the removal in the 120 min was 84%, lower when compared with 0.2 g and 0.1 g, which were both around 87%. Referring to the fact that over NBH dosage could hinder the suspension transparency, which would be an obstacle
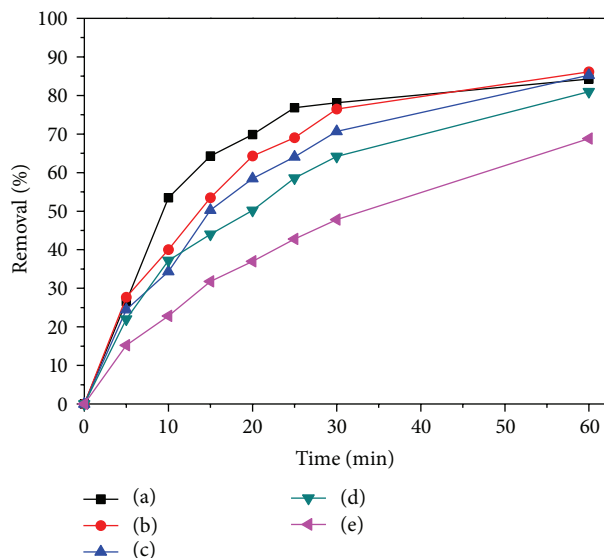
FIGURE 5: Effect amount of NBH. (a) 0.5 g, (b) 0.2 g, (c) 0.1 g, (d) 0.05 g, and (e) 0.025 g.

TABLE 1: Identification of the small molecular intermediates of aniline during the photoreaction by GC/MS.

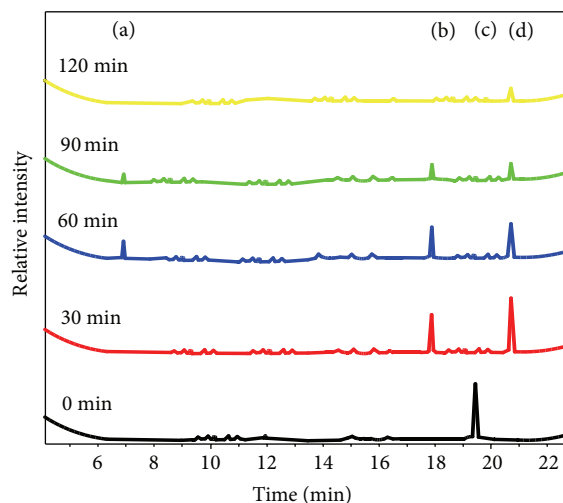| Product	Rt (min)	Mw	Formula	Name
1	7	91	$C_2H_5NO_3$	2-Nitroethanol
2	18	179	$C_{10}H_{13}NO_2$	3-Hydroxy-N-phenylbutanamide
3	18.5	93	C_6H_7N	Aniline
4	21	182	$C_{12}H_{10}N_2$	Azobenzene

FIGURE 6: GC chromatograph of intermediates. (a) $C_2H_5O_3N$, (b) $C_{10}H_{13}O_2N$, (c) C_6H_7N, and (d) $C_{12}H_{10}N_2$.

to absorb light and decrease photocatalytic degradation efficiency eventually, as a result, excessive NBH dosage could lead to a downward trend shown in the oxidation effect.

3.4.3. GC/MS Analysis. In the given condition, aniline could be degraded completely in the 30 min. Analysis on the intermediates and final products can help to clarify the details of the reaction. They were identified by GC/MS (GCMS-QP2010 Plus) and shown in Table 1 and Figure 6.

In the chromatograph of initial sample, there was a peak representing aniline, which disappeared in the 30 min. The chromatomap of 60 min resembled that of 30 min, as the peak of $C_{10}H_{13}O_2N$ and azobenzene existed, while their top area was decreasing. It proved that the above intermediates of aniline have been degraded to other products. There was a peak at about 7 min in the picture of 60 min, which was $C_2H_5O_3N$, the product of $C_{10}H_{13}O_2N$ and azobenzene. In the chromatomap of 90 min, $C_2H_5O_3N$ was not detected, which meant it had been mineralized into CO_2. The peak of $C_{10}H_{13}O_2N$ had disappeared in the chromatomap of 120 min. The organics containing nitrogen only was azobenzene, and its peak area had decreased to a small part.

The photohole, generated by $NaBiO_3$ under visible light, could make reaction with aniline and produce azobenzene. Azobenzene produces $C_{10}H_{13}O_2N$ by $^\bullet OH$ and h^+. As the reaction goes on, azobenzene could still react with $^\bullet OH$ or h^+ until its loop opens. $C_{10}H_{13}O_2N$ would go into two parts by the effect of $^\bullet OH$ and h^+. One could produce $C_2H_5O_3N$ and then be mineralized, while the other one is mineralized after ring opening.

4. Conclusion

Aniline could be easily degraded by $NaBiO_3$ under visible light irradiation. In the experiment. Aniline was decomposed largely under visible light over $NaBiO_3$ in 120 min, which could reach 95% in some conditions. Moreover, three small molecular products were also identified by GC/MS. On the basis of the data collected, the mechanism of aniline photodegradation on $NaBiO_3$ had been elucidated. Aniline could react with $^\bullet OH$ or h^+. Its products would go into two parts. One part would be mineralized directly, while the other part opened ring and produced $C_2H_5O_3N$ then was mineralized; meanwhile, N-ionogen turned into mineral nitrogen.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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