



## Rapid photocatalytic degradation of PCP–Na over NaBiO<sub>3</sub> driven by visible light irradiation

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### ABSTRACT

The photocatalytic performance of sodium pentachlorophenate (PCP–Na) over NaBiO<sub>3</sub> under visible light irradiation was first investigated systematically. After 1 h of photocatalytic reaction, the degradation rate of PCP–Na could reach to 90.5% in appropriate conditions. •OH is the dominant photooxidant rather than O<sub>2</sub><sup>•−</sup> based on the experiment results and density of states (DOS) analysis. The PCP–Na solution became basic (pH value increased to ~9) with the progress of photocatalytic reaction which may be attributed to the PCP<sup>−</sup> oxidized to the pentachlorophenoxy radical by an attack on PCP<sup>−</sup> by •OH. The photocatalytic reaction over NaBiO<sub>3</sub> follows the rule of first-order reaction according to the Langmuir–Hinshelwood model. The initial concentration of the PCP–Na, the initial pH value of PCP–Na aqueous solution and the amount of NaBiO<sub>3</sub> used have great influences on the photocatalytic performance. Three kinds of photocatalytic systems (P25, Bi<sub>2</sub>O<sub>3</sub> and P25–Bi<sub>2</sub>O<sub>3</sub> heterojunction) exhibited relative lower photocatalytic activity compared to NaBiO<sub>3</sub> powder.

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### 1. Introduction

Pentachlorophenol (PCP) and its salts, most notably sodium pentachlorophenate (PCP–Na), are widely used as biocides for the protection of timber and textiles all over the world [1]. PCP and its salts have attracted great attention worldwide owing to their toxicity, endocrine disturbing effect, mutagenicity, carcinogenicity, and bioaccumulation. PCP has been listed as a priority pollutant by the U.S. Environmental Protection Agency [2] and recently, many studies, which concern the endocrine system disrupting effects of PCP and its salts, were carried out [3,4].

Because of the various advantages, such as optical and electronic properties, low cost, high photocatalytic activity, chemical stability and non-toxicity, TiO<sub>2</sub> has been widely used as a popular catalyst [5–7]. However, a critical drawback of titania is that it has a large band gap (3.2 eV), which is too large to allow efficient absorption of most sunlight. Therefore, a lot of works have been done to develop visible light sensitive photocatalysts. The modification of TiO<sub>2</sub> by doping with nonmetallic elements [8] (such as S, N etc.), establishment of the p–n heterojunction by two semiconductor compounds with different energy band structures [9,10] and development of new materials are the main strategies to develop visible-light-sensitive photocatalysts. Bi-containing oxides

such as Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [11], Bi<sub>2</sub>WO<sub>6</sub> [12,13] and BaBiO<sub>3</sub> [14] have been reported to be promising photocatalysts under visible light irradiation.

NaBiO<sub>3</sub> is another new efficient photocatalyst which was firstly demonstrated by Tetsuya Kako et al. Their results show that NaBiO<sub>3</sub> showed a higher photocatalytic activity towards methylene blue compared to some other visible light sensitive semiconductor compounds such as N doped TiO<sub>2</sub> and BiVO<sub>4</sub> [15]. To the best of our knowledge, however, a systematic study based on photocatalytic performance research of NaBiO<sub>3</sub> has not been reported so far. Herein, we first evaluate the photocatalytic performance of PCP–Na over NaBiO<sub>3</sub> under visible light irradiation and the initial catalytic mechanism was discussed in this paper.

### 2. Experimental

#### 2.1. Materials

The following chemicals were used as received: PCP–Na, *tert*-butanol, hydrochloric acid and sodium hydroxide are of analytical reagent grade, methanol (HPLC grade, Dikma Pure, >99.9%), TiO<sub>2</sub> (product name P25, particle diameter 30 nm, surface area 50 m<sup>2</sup> g<sup>−1</sup>) is commercially supported by Degussa Corporation. NaBiO<sub>3</sub> was prepared according to the previous report [16]. Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> semiconductor heterojunctions, which were used as a reference photocatalysts, were fabricated according to the reference [10].

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## 2.2. Photocatalytic process

The photocatalytic reactor consists of two parts: a 250 ml quartz glass reactor and a 500 W Xe lamp, which was positioned parallel to the quartz glass reactor. 2 M NaNO<sub>2</sub> aqueous solution was used to remove the radiation below 400 nm and to ensure the irradiation of the photocatalytic system occurred only by visible-light wavelengths [17]. The photocatalytic reaction temperature was kept at room temperature by a water cooler machine (Lab Tech Company).

In a typical photocatalytic process, 100 mg NaBiO<sub>3</sub> powders were added into 150 ml PCP–Na solution (50 ppm). The suspensions were magnetically stirred in dark for 1 h to ensure an adsorption–desorption equilibrium before the irradiation. Then, the suspensions containing PCP–Na and photocatalysts were irradiated using the Xenon lamp with continuous stirring. The slurry of reaction mixture was taken out and filtered to remove NaBiO<sub>3</sub> sample at certain intervals.

## 2.3. Chemical analysis

Determination of PCP–Na solutions was performed by HPLC Shimadzu model LC-9A equipped with UV detector at 249 nm, and C-18 phenomenex column. The mobile phase was 80% methanol in phosphate buffer (pH 2) with the flow rate of 0.5 ml min<sup>-1</sup>. The UV spectra of PCP–Na solutions were measured on UV–visible spectroscopy (DR 5000, HACH Corporation). Chloride ion concentrations were monitored by ion chromatography system (ICS-1000, Dionex Corporation). Digital pH meter was used to measure the pH value of the solution.

## 3. Results and discussion

### 3.1. Photodegradation and catalyst durability

Fig. 1(a) presents the irradiation time dependence of PCP–Na degradation in the presence of NaBiO<sub>3</sub>, and meanwhile, PCP–Na which was only photolyzed and bleached in the dark was also studied as comparison. The result shows that PCP–Na cannot be efficiently decomposed only by photolysis, and NaBiO<sub>3</sub> powders had limited adsorption capability for PCP–Na (the adsorption rate was less than 10% after stirring in the dark for 1 h). However, NaBiO<sub>3</sub> exhibited high photocatalytic activity for PCP–Na under the visible light irradiation and the removal rate can reach to 90.5% after 1 h irradiation.

The UV spectral changes taking place during the photodegradation of PCP–Na over NaBiO<sub>3</sub> were displayed in Fig. 1(b). PCP–Na shows a major absorption peak at 320 nm, which is attributed to the conjugated structure. The absorption value at 320 nm was decreased with the photocatalytic process and the absorption peak was not obvious after 1 h reaction. On the other hand, this result was further confirmed by HPLC measurement. From Fig. 2, it can be seen clearly that the signal intensity of the peak decreased after the photocatalytic process, indicating PCP–Na was degraded rather than simply bleached. In the meantime, the HPLC result also indicates that the destruction of the conjugated structure leads to the formation of some other new molecules in the PCP–Na solution because some other weak chromatographic signals with different retention times (e.g. 9.372 min) could be observed from Fig. 2b. And the detailed degradation products and pathway are being further investigated.

As a kind of heterogeneous photocatalyst, NaBiO<sub>3</sub> can be easily recycled by simple filtration and its photocatalytic activity did not change even after 6 cycles of photodegradation (Fig. 3). However, it is found that such catalyst was not stable under the strong acidic condition; when the initial pH value of PCP–Na solution was set

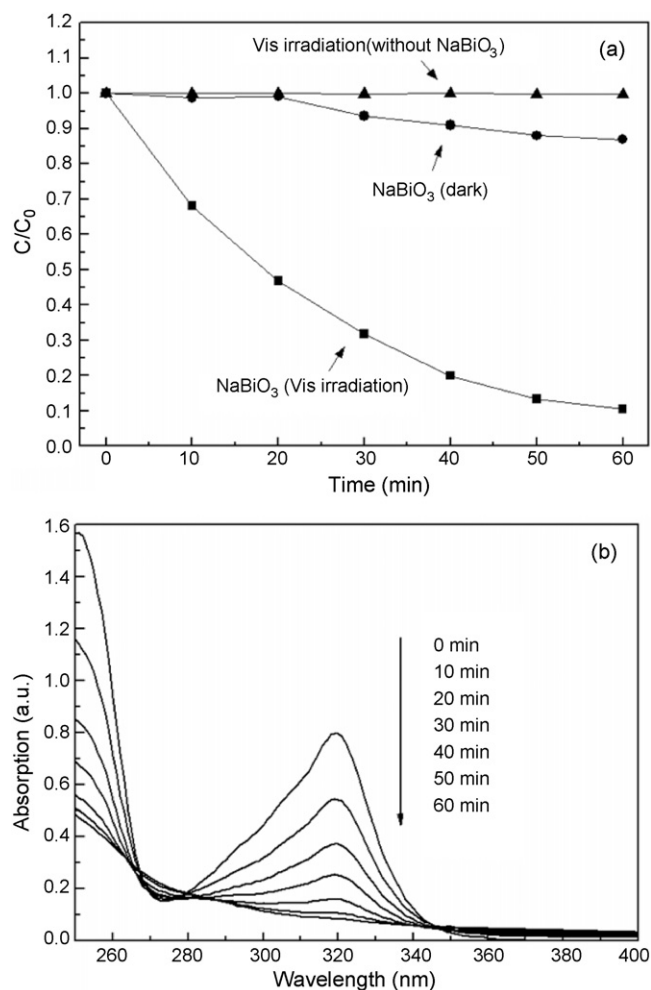


Fig. 1. PCP–Na was only photolyzed (▲), bleached in the dark (●) and photocatalytically degraded (■) over NaBiO<sub>3</sub> (a) and UV spectral changes of PCP–Na in NaBiO<sub>3</sub> dispersions as a function of irradiation time (b).

to less than 3, the yellow colored NaBiO<sub>3</sub> turned into white colored powder (it should be further detected via X-ray diffraction method) and the photocatalytic activity was extremely low (less than 8%), indicating that NaBiO<sub>3</sub> was not chemically stable under the high H<sup>+</sup> concentration.

### 3.2. Photocatalytic degradation mechanism

In order to further study the catalytic process, a comparison of the photocatalytic activity in the presence of dissolved oxygen, continuous saturated N<sub>2</sub> and 1 ml *tert*-butanol was carried out. The result is displayed in Fig. 4(a). The photocatalytic activity was not decreased under the existence of continuous saturated N<sub>2</sub> after 1 h irradiation. This observation suggests the presence of dissolved oxygen and nitrogen has no effect on the photocatalytic performance over NaBiO<sub>3</sub>, indicating that O<sub>2</sub><sup>-</sup> was not the dominant photooxidant during the photocatalysis.

*tert*-Butanol has the reaction rate constant of 5.0 × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup> with •OH, as a stronger radical scavenger, it can react with •OH and then generates inert intermediates, which do not predominantly produce the HO<sub>2</sub><sup>-</sup> and O<sub>2</sub><sup>-</sup> radicals, thus causing the termination of the radical chain reaction [18]. The results from Fig. 4(a) also indicate that the addition of *tert*-butanol has a negative influence on the degradation efficiency of PCP–Na, indicating that *tert*-butanol can consume •OH in aqueous solution to block the photocatalytic reaction. The results also suggest that •OH was the

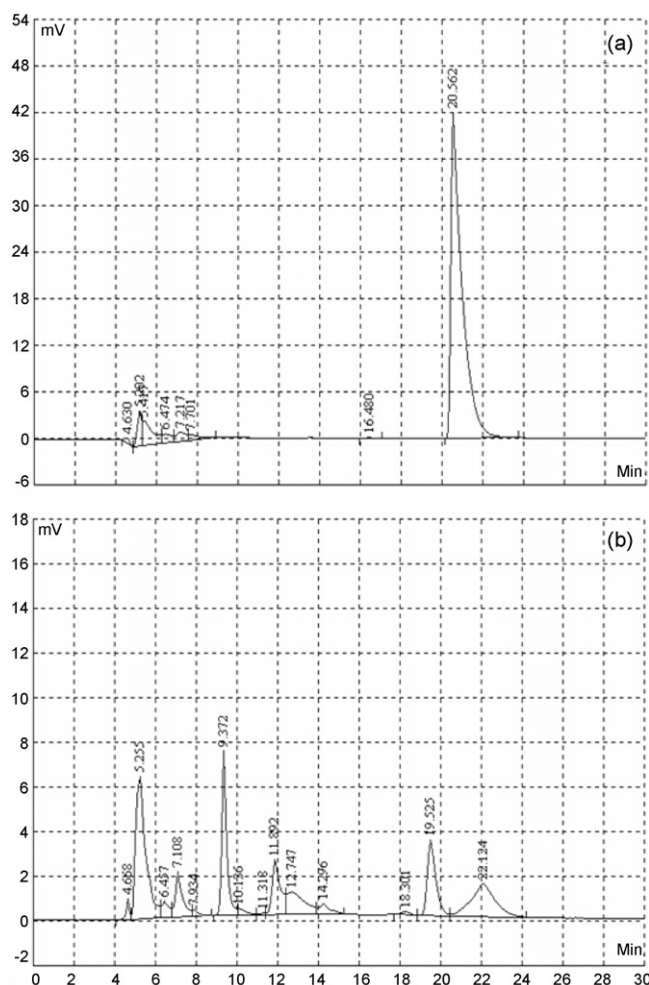


Fig. 2. HPLC chromatograms of the sample solutions without photocatalysis (a) and after photocatalysis for 1 h (b).

dominant photooxidant during the photocatalytic process. Then we try to explain the photocatalytic mechanism through the band and electronic structure of  $\text{NaBiO}_3$ . It is noted that the composition of  $\text{NaBiO}_3$  valance band is very different from other Bi-containing semiconductor compounds, such as  $\text{Bi}_2\text{WO}_6$  [19] and  $\text{BaBiO}_3$  [14].

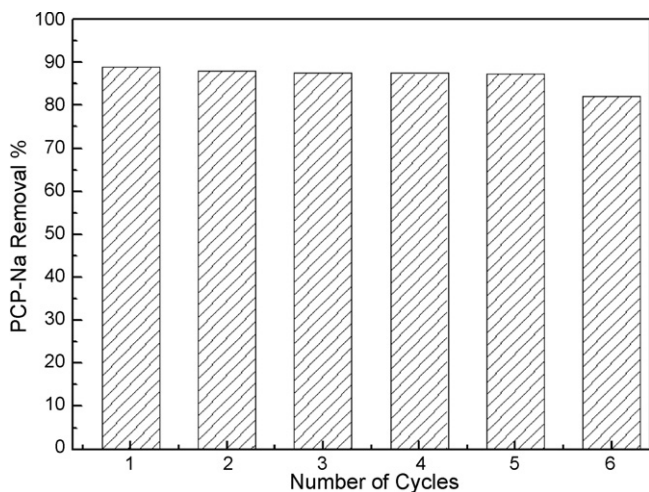


Fig. 3. Durability of  $\text{NaBiO}_3$  photocatalysis from the repeatable degradation of PCP-Na under visible light irradiation.

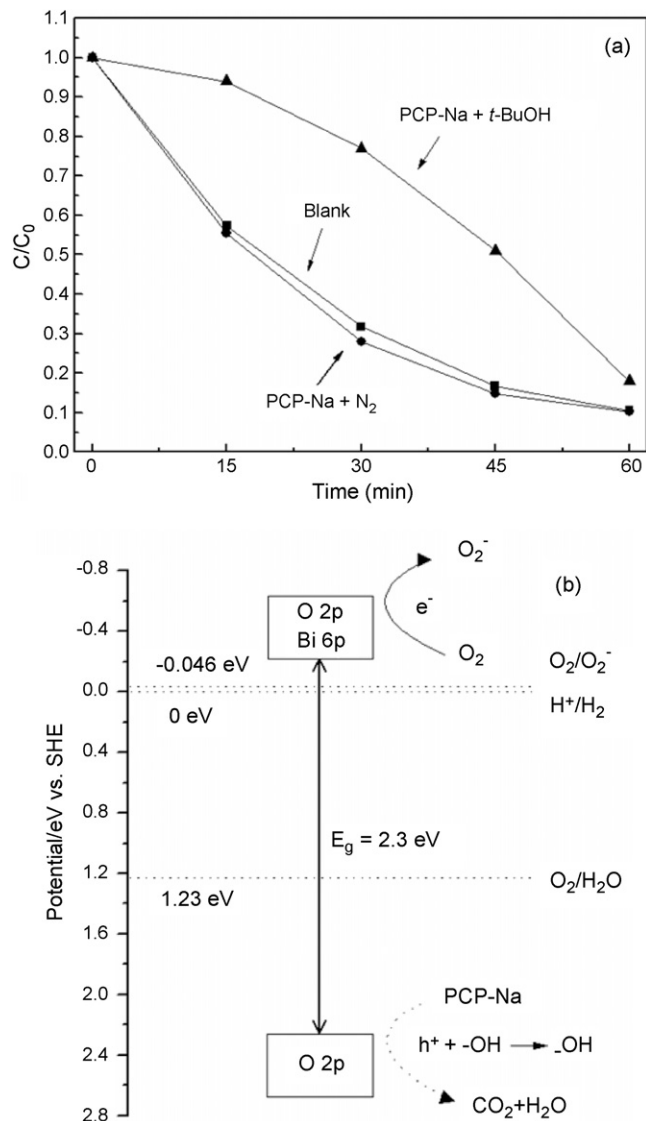
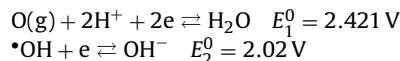


Fig. 4. (a) Photocatalytic degradation of PCP-Na over  $\text{NaBiO}_3$  in the presence of dissolved oxygen (■), continuous saturated  $\text{N}_2$  (●) and 1 ml *tert*-butanol (▲); (b) Schematic band structures of  $\text{NaBiO}_3$  and the possible photocatalytic reaction process.

According to the density of states (DOS) analysis of  $\text{NaBiO}_3$  [15], broad valance band (VB) was mainly composed of the O 2p orbital owing to the empty Bi 6s and Na 3s orbitals. For the reaction [20]:



and the standard reduction potential of  $\text{O}(\text{g})/\text{H}_2\text{O}$  ( $\text{O}/\text{O}_2^-$ ) was more positive than that of  $\cdot\text{OH}/\text{OH}^-$  (+2.02 V), suggesting that the hole photogenerated on the surface of  $\text{NaBiO}_3$  could easily react with  $\text{OH}^-/\text{H}_2\text{O}$  to form  $\cdot\text{OH}$ .

In addition, the band edge of  $\text{NaBiO}_3$  semiconductor at the point of zero charge was calculated by the equation as follows:

$$E_{\text{CB}} = X - E^c - \frac{1}{2}E_g$$

where  $X$  is the absolute electronegativity of the semiconductor;  $E^c$  is the energy of free electrons on hydrogen scale ( $\approx 4.5$  eV) and  $E_g$  is the band gap of the semiconductor. The predicted band edge through the above equation of  $\text{NaBiO}_3$  was shown in Table 1. The CB

**Table 1**Absolute electronegativity, estimated band gap, calculated conduction band (CB) edge and valance band (VB) edge of NaBiO<sub>3</sub>.

Semiconductor	Absolute electronegativity ( $X$ )	Estimated band gap ( $E_g$ )	Calculated CB edge ( $E_{CB}$ )	Calculated VB edge ( $E_{VB}$ )
NaBiO <sub>3</sub>	5.49579 eV	2.3 eV	-0.15421 eV	2.14579 eV

bottom of NaBiO<sub>3</sub> semiconductors is close to H<sup>+</sup>/H<sub>2</sub> (0 eV vs SHE) and O<sub>2</sub>/O<sub>2</sub><sup>-</sup> (-0.046 eV vs SHE). Thus, we deduce that such small over-potential could suppress reducing O<sub>2</sub> to O<sub>2</sub><sup>-</sup>. Following the discussion above, we have reason to consider that the degradation of PCP-Na over NaBiO<sub>3</sub> may be the contribution of ·OH radicals, rather than O<sub>2</sub><sup>-</sup>. Fig. 4b gives a schematic band structure of NaBiO<sub>3</sub> and the possible photocatalytic reaction procedures.

### 3.3. Effect of initial pH value

Fig. 5 displays the changes of pH value as a function of irradiation time. From the pH value variation of PCP-Na solution, it can be found that the pH value increased from ~6.0 to ~9.0 after 1 h photocatalytic reaction. The PCP-Na solution became basic with the progress of photocatalytic reaction which may be attributed to the PCP<sup>-</sup> oxidized to the pentachlorophenoxy radical by an attack on PCP<sup>-</sup> by ·OH (see the inset of Fig. 5) [21,22]. On the other hand, the process of OH<sup>-</sup> forming during the photocatalysis indicates the reaction could be suppressed when the pH value of PCP-Na solution is under basic condition. What is more, the change of Cl<sup>-</sup> concentration was also detected. During the 1 h photocatalytic process, the dechlorination rate reached to 87.3%, demonstrating the cleavage of C–Cl bond during the photocatalytic degradation.

Fig. 6 shows the influence of pH value on the photocatalytic degradation ( $C/C_0$ ) after 1 h and adsorption of PCP-Na on the surface of NaBiO<sub>3</sub>. The initial pH value of PCP-Na solution was adjusted by hydrochloric acid and sodium hydroxide aqueous solution. When the initial pH value of PCP-Na solution was around 6.5, the photocatalytic degradation rate could reach to 90.5% after 1 h irradiation. Moreover, the degradation rate was more than 90.5% when the initial pH value of PCP-Na solution was adjusted to the range of 7.5–9.3 and the degradation rate was 96.4% when pH value was equal to 8.4. The photocatalytic activity enhancement may be due to increasing the OH<sup>-</sup> concentration, which would facilitate the formation of much more ·OH. However, with increasing pH value, the photocatalytic activity was decreased very quickly and degradation rate was only about 26% when the initial pH value was set to 12.6. The low photocatalytic activity may be caused by (1) the restraining of the reaction under high concentration of OH<sup>-</sup> (see Fig. 5) and (2)

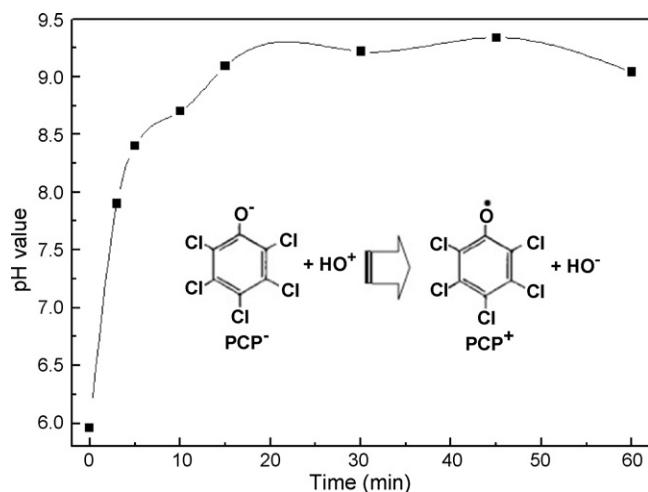


Fig. 5. Variation of pH value as a function of irradiation time.

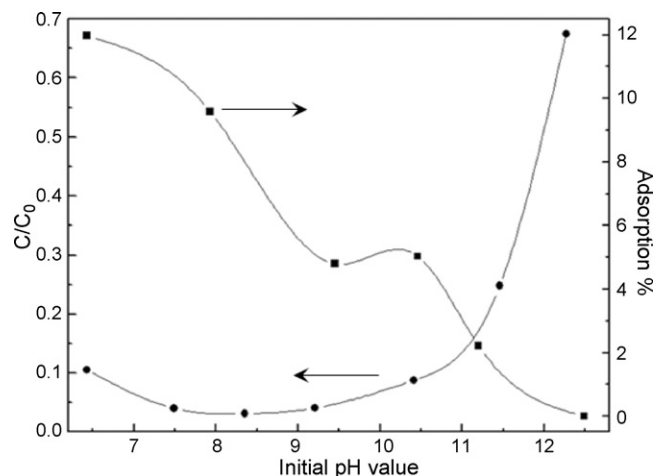


Fig. 6. Influence of initial pH value of PCP-Na solution on the photocatalytic degradation ( $C/C_0$ ) after 1 h and adsorption of PCP-Na on the surface of NaBiO<sub>3</sub>.

the weakening of the adsorption performance over NaBiO<sub>3</sub> powders when the initial pH value of PCP-Na solution was over 9. From Fig. 6 we can find easily that there was almost no adsorbed interaction when pH was 12.6.

### 3.4. Effect of initial concentration and catalyst content

Fig. 7 shows the linear relationship between  $\ln(C/C_0)$  and irradiation time during the photocatalytic reaction. The photocatalytic degradation of PCP-Na over NaBiO<sub>3</sub> was apparent first-order kinetics of the Langmuir–Hinshelwood model, and the influence of the initial PCP-Na concentration on the photocatalytic reaction rate was also discussed. The reaction rate was determined to be 0.04981 min<sup>-1</sup>, 0.04473 min<sup>-1</sup> and 0.03638 min<sup>-1</sup> for initial concentrations of PCP-Na of 50 ppm, 40 ppm and 26 ppm. Thus the initial concentration is critical to the photocatalytic reaction rate. The degradation rate was increased when decreasing the initial concentration of PCP-Na.

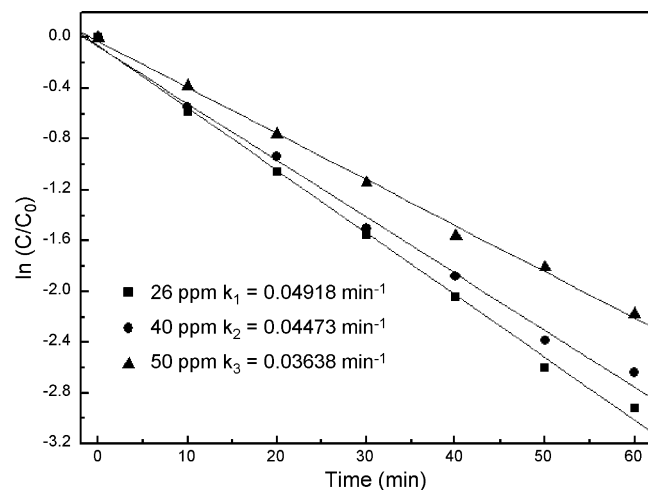


Fig. 7. The first order reaction kinetics of PCP-Na (26–50 ppm) degradation under visible light irradiation.

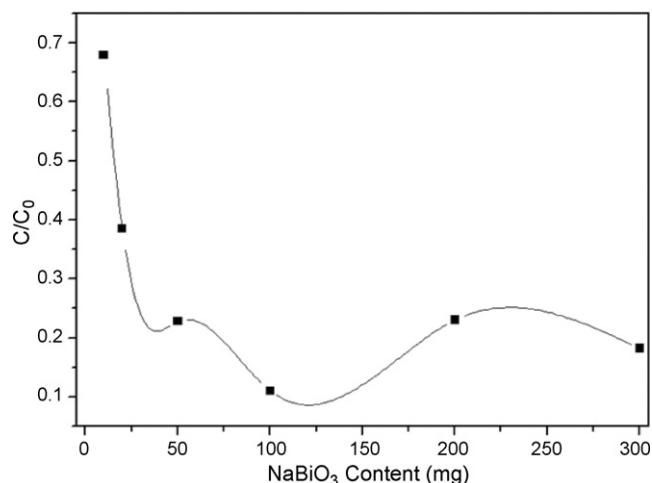


Fig. 8. Influence of catalyst content on the photocatalytic degradation ( $C/C_0$ ) after 1 h.

The catalyst content can also affect the photocatalytic performance (Fig. 8). It is considered that there was a suitable amount of  $\text{NaBiO}_3$  powder during the photocatalysis. When 100 mg of  $\text{NaBiO}_3$  was used, the photocatalytic degradation rate could reach to 90.5% after 1 h irradiation. However, the smaller amount of  $\text{NaBiO}_3$  powders exhibited lower catalytic activity because not enough catalytic active sites were supplied during the photocatalytic process, and it is not difficult to understand. If more amount of catalyst was adopted, the photocatalytic degradation rate would not increase and the light utility efficiency from the Xenon lamp would be decreased because  $\text{NaBiO}_3$  powder could absorb parts of the light from the lamp.

### 3.5. Comparison of several photocatalytic systems

Compared to several common photocatalysis systems (P25,  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  heterojunction),  $\text{NaBiO}_3$  exhibited highest photocatalytic activity under visible light irradiation. For  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  (m/m=2:8) and  $\text{TiO}_2\text{-Bi}_2\text{O}_3$  (m/m=5:5) heterojunction photocatalysts, their photocatalytic degradation for PCP-Na was only about ~11%, 32.5% and ~53.8% after 1 h irradiation (Fig. 9). And the nanosized  $\text{TiO}_2$  (P25) shows little photocatalytic activity (photocatalytic degradation less than 5%) under the visible light

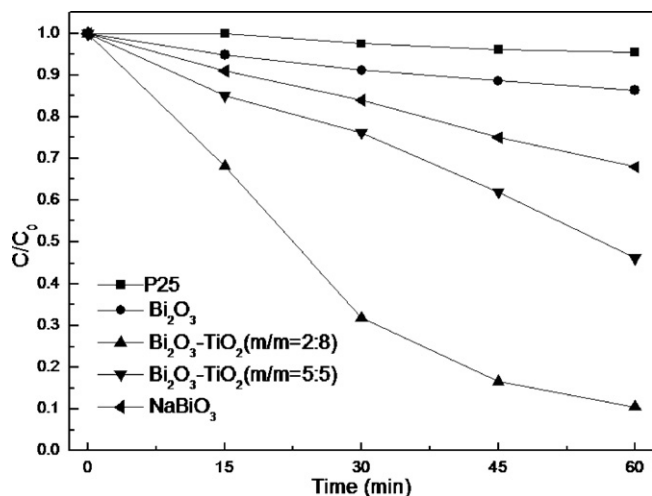


Fig. 9. Photocatalytic degradation of PCP-Na by catalysts driven by visible light irradiation.

irradiation because of its only UV sensitive property. Furthermore,  $\text{NaBiO}_3$  has a very interesting energy band structure [15]. The hybridized sp orbital in the CB of  $\text{NaBiO}_3$  support a high mobility on the sp bands for the photoexcited electrons, which may lead to suppression of the recombination of electron-hole pair and a relatively higher photocatalytic activity of the material than that of other photocatalysts.

## 4. Conclusions

In this work, the photocatalytic performance of PCP-Na over  $\text{NaBiO}_3$  under visible light irradiation was studied systematically and  $\text{NaBiO}_3$  photocatalyst exhibited excellent performance towards the degradation of PCP-Na. In a typical experiment, the photocatalytic degradation rate and dechlorination rate for 1 h were 90.5% and 87.3%, respectively.  $\cdot\text{OH}$  was the dominant photooxidant during the photocatalytic process. The photocatalytic procedure over  $\text{NaBiO}_3$  followed the rule of first-order reaction. The initial concentration of the PCP-Na, the initial pH value of PCP-Na aqueous solution and the amount of  $\text{NaBiO}_3$  used were critical factors on the degradation performance of  $\text{NaBiO}_3$  catalytic process.

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