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## Efficient degradation of atrazine by BiOBr/UiO-66 composite photocatalyst under visible light irradiation: Environmental factors, mechanisms and degradation pathways



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#### HIGHLIGHTS

- BiOBr/UiO-66 exhibited high activity for atrazine degradation under
- visible light.The effects of water environmental factors on the degradation efficiency were investigated.
- A deductive degradation pathway of atrazine was proposed.

#### G R A P H I C A L A B S T R A C T



#### A R T I C L E I N F O

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#### ABSTRACT

Atrazine, a typical herbicide, has caused extensive concern due to its wide application and persistance. In this work, a visible light responsive photocatalyst BiOBr/UiO-66 was synthesized and applied to the degradation of atrazine. The BiOBr/UiO-66 materials exhibited significantly enhanced photocatalytic performance on the degradation of atrazine under visible light irradiation compared to pure BiOBr. Moreover, the effects of typical environment factors (i.e. pH, common anions, inorganic cations and water matrix) on the degradation of atrazine were investigated extensively. Results showed that atrazine was degraded with the fastest rate at the strong acidity conditions of pH = 3.1 in the investigated pH region (3.1–9.4). The photocatalytic degradation of atrazine was obviously inhibited by HCO<sub>3</sub> and SO<sub>4</sub><sup>2–</sup>. However, Cl<sup>-</sup> had negligible influence on the degradation of atrazine. Inorganic cations had little influence on the degradation of atrazine by BiOBr/UiO-66. In mineral water, tap water and river water, the removal efficiency of atrazine was evidently lower than that in pure water. The main active species that responsible for the degradation of atrazine by BiOBr/UiO-66 kere determined to be  $\cdot$ O<sub>2</sub> and h<sup>+</sup>. Ultimately, the degradation pathways of atrazine were proposed based on the intermediates detected by LC-MS/MS.

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#### 1. Introduction

Atrazine is a widely used highly toxic herbicide for crop production worldwide. It is structurally stable and has a long residual period. Atrazine remaining in the soil would enter into surface

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water and groundwater because of the leaching by rain, thus posing a threat to the ecological environment (Chen et al., 2009; Santacruz-Chávez et al., 2015; Guan et al., 2013; Xu et al., 2015; Souza et al., 2014). Therefore, more and more researchers are committed to the research on the treatment of atrazine. At present, traditional techniques include physical adsorption method (Wang et al., 2016a; Vanraes et al., 2015), advanced oxidation (Komtchou et al., 2017), microbial degradation (Wang et al., 2017a, 2017b) and electrochemical method are used to treat atrazine (Ding et al., 2017; Chen et al., 2014). Recent years, photocatalytic technique is widely used for atrazine degradation in virtue of its high efficiency, non-toxic, no secondary pollution (Chen et al., 2011; Wang et al., 2016b; Gupta et al., 2017; Cruz et al., 2017; Sudrajat and Sujaridworakun, 2017). In particular, photocatalytic degradation of atrazine activated by visible-light is a sustainable way because it is prospective to the utilization of solar energy.

Bismuth oxyhalides (BiOX, X = Br, Cl, I) is one type of effective, environmentally friendly photocatalytic material. They own unique layered structure and indirect transition mode, which are beneficial to the effective separation and transfer of electron-hole (Wang et al., 2017c; Li et al., 2017; Jing et al., 2016; Bhachu et al., 2016; Xu et al., 2017a). Among different bismuth oxyhalides, bismuth oxybromide (BiOBr) has aroused widespread concern due to the suitable bandgap and 2D lamellar structure. It possesses excellent photocatalytic performance for organic contaminants degradation under both UV and visible light irradiation (Han et al., 2017; Liu et al., 2017a; Zhu et al., 2017a; An et al., 2015; Gao et al., 2017; Ao et al., 2016). However, pure BiOBr is easily agglomerated and has high recombination rate of photoinduced electron-holes, which reduce the activity for the degradation of organic contaminant greatly. Therefore, researchers put forward a lot of ways to enhance its performance, such as element doping (Jiang et al., 2014; Wei et al., 2013), crystal regulation (Yu et al., 2017; Zhang et al., 2013), noble metal deposition (Lu et al., 2012; Guo et al., 2016) and semiconductor composite (Liu et al., 2017b; Wen et al., 2017). Compared with other methods, construction of semiconductor composite with heterojunctions is an efficient way to improve photocatalytic activity and has attracted more and more attention of researchers.

The metal organic frameworks (MOFs) are reticular porous materials which are formed by the coordination between organic ligands and metal ions. Due to the high specific surface area, adjustable aperture and good stability, the MOFs are widely used for photocatalysis (Liang et al., 2017; Meyer et al., 2015; Xu et al., 2016). In recent years, many researches have shown that MOFs can also be used as the carrier of photocatalyst (Shen et al., 2013; Yin et al., 2015; Jiang et al., 2009). On one hand, this can increase the separation efficiency of photo-induced electron-holes. On the other hand, it is possible to control the growth of the photocatalyst on the MOFs' surface to decrease its size and reduce agglomeration, thus exposing more active sites. The combination of MOF and BiOBr has been proved to enhance the photocatalytic performance. For example, BiOBr/NH<sub>2</sub>-MIL 125(Ti) (Zhu et al., 2016),BiOBr/MOF-5 (Yang et al., 2012), and BiOBr/CAU-17 (Zhu et al., 2017b) have been synthesized for the degradation of dyes with higher performance. In 2008, a chain of Zr-based MOFs (such as UiO-66, UiO-67 and UiO-68) were first proposed to further enlarge the potential applications of MOFs (Cavka et al., 2008). Compared with other kinds of MOFs, Zr-based MOFs have higher thermal and chemical stability. In particular, UiO-66 (structural formula noted as Zr<sub>24</sub>O<sub>120</sub>C<sub>192</sub>H<sub>96</sub>) is one of most widely used Zr-based MOFs in the field of photocatalysis (Shen et al., 2015; Wang et al., 2015; Sha et al., 2015a). What's more, UiO-66 exhibits high structural stability in aqueous media (Decoste et al., 2013; Furukawa et al., 2014). This stability can still be maintained after the introduction of missing joint defects or the binding of active functional groups (Wu et al., 2013). Hence, combining UiO-66 with BiOBr would be a beneficial strategy for pollutants degradation. Sha et al. reported that the BiOBr/UiO-66 composite photocatalyst exhibited higher activity for the degradation of RhB than pure BiOBr under visible light irradiation. They proved that the combination of BiOBr and UiO-66 was an effective way to improve the photocatalytic performance of BiOBr for dye degradation. However, to the best of our knowledge, there is no work reported the utilization of MOF based composite photocatalysts for the photocatalytic degradation of atrazine under visible light irradiation.

Herein, we prepared the BiOBr/UiO-66 composite via a facile insitu growth method. Then, the as-prepared BiOBr/UiO-66 composites were applied to degrade atrazine under visible light irradiation. Besides, the effects of pH value, common anions, inorganic cations and water matrix on the degradation of atrazine were researched. Finally, the photocatalytic degradation mechanism of atrazine was analyzed, including active substances, intermediate products and degradation pathways.

#### 2. Materials and methods

The experimental section (reagent, materials preparation, characterization, photocatalytic experiments and analysis methods) are shown in supporting information.

#### 3. Results and discussion

#### 3.1. Characterization

The SEM photographs of different materials are shown in Fig. 1. Fig. 1 (a) shows the morphology of UiO-66 which presents relatively unified nanoparticles. The UiO-66 nanoparticles size in the region of 60–200 nm. The BiOBr sample is made up of smooth and irregular flakes as shown in Fig. 1(b). And the sizes of BiOBr sheets are from 200 to 600 nm. The morphology of BiOBr/UiO-66 composite is presented in Fig. 1(c) and (d). It can be observed that the BiOBr flakes are interspersed with UiO-66 particles. It can also be seen that the BiOBr nanoflakes in the composites are thinner than pure BiOBr. Because of the existence of UiO-66 nanoparticles, the agglomeration of these BiOBr flakes is reduced so that the surface area can be increased.

The crystal structure of the as-prepared materials was measured by XRD, and the obtained results are displayed in Fig. 2. The characteristic diffraction peaks of pure UiO-66 are consistent with the results reported in previous papers, which demonstrates the UiO-66 was successfully prepared in this research (Xu et al., 2017b). The XRD pattern shows that BiOBr exhibites main diffraction peaks at 20 of 10.9°, 21.9°, 25.2°, 31.8°, 32.3°, 33.2°, 39.4°, 44.8°, 46.3°, 50.8°, 53.5°, 57.3°, 62.1° and 67.6°, which correspond to (001), (002), (011), (012), (110), (003), (112), (004), (020), (014), (211), (212), (015) and (220) planes, respectively. These characteristic diffraction peaks are well conformed to the tetragonal phase of BiOBr (JCPDS: 73-2061) (Li et al., 2014). The XRD pattern of BU-3 also exists these peaks. However, the composite BU-3 emerges a new diffraction peak, which is accordant with the diffraction peaks of pure UiO-66. Thus, the above results confirm that the BU-3 materials were successfully obtained. Furthermore, the intensity ratio of (012) and (110) diffraction peaks in the BU-3 is different from that of pure BiOBr. It can be ascribed to the fact that the presence of UiO-66 would affect the growth preference of crystal planes of BiOBr.

Fig. 3a indicates the UV—vis diffuse reflection plots of asprepared materials. As illustrated in the figure, the optical absorption edge of pure UiO-66 is at 340 nm. Thus it can be concluded Download English Version:

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