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1 **Mechanochemical destruction of decabromodiphenyl ether into**
2 **visible light photocatalyst BiOBr**

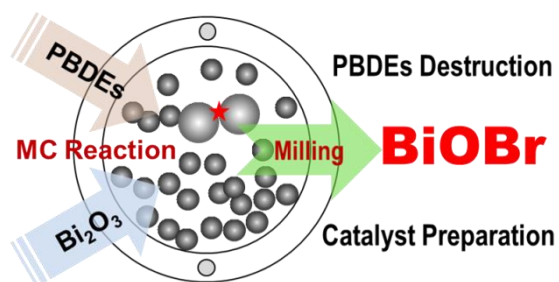
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Table of Contents Entry



By milling with Bi₂O₃, the destruction of polybrominated diphenyl ethers was achieved with the preparation of visible light photocatalyst.

Abstract

In the present study, mechanochemical (MC) treatment of polybrominated diphenyl ethers (PBDEs), a kind of emerging persistent organic pollutants (POPs), was performed using a high energy ball mill. With Bi_2O_3 as co-milling reagent, deca-BDE was effectively destroyed and no hazardous intermediates or organic products were observed in the MC reaction. Meanwhile, BiOBr, a promising visible light photocatalyst, was proved to be the final product which could be utilized in further steps. Neither excessive Bi_2O_3 nor unreacted deca-BDE was left after the reaction as they were originally added at stoichiometric ratio for BiOBr formation. FITR and Raman analyses demonstrate the collapse of deca-BDE skeleton and the cleavage of C-Br bonds with the generation of inorganic carbon, revealing the mechanism of carbonization and debromination. The gaseous products at different reaction atmosphere were also analyzed, showing that mostly CO_2 with a fraction of CO were released during the MC process. The reaction formula of deca-BDE and Bi_2O_3 was then proposed based on the identified final products. Besides, the photocatalytic activity of the generated BiOBr was evaluated using methyl orange as the model pollutant. A good degradation performance from BiOBr was achieved under both simulated sunlight and visible light irradiation, indicating the possibility for its further utilization.

1. Introduction

Over the last decades, polybrominated diphenyl ethers (PBDEs) have been widely used as non-reactive additives in polymers such as textiles, plastics and electronic products, to improve their flame resistance and prevent fire^{1,2}. There were three main formulations of commercially used PBDEs in the market, *i.e.*, penta-, octa- and deca-BDE. Due to substantial and long-term usage, PBDEs have been frequently detected in humans, wildlife, and abiotic environment around the world³⁻⁶. As a consequence of their toxic, bioaccumulative and persistent properties⁷⁻⁹, more and more concerns about this kind of chemicals have arisen. In 2009, the commercially used penta- and octa-BDE were listed as persistent organic pollutants (POPs) in the Annex A of the Stockholm Convention. In June 2013, deca-BDE was also proposed for the inclusion in the convention as it was considered to meet the screening criteria in Annex D for persistence, bioaccumulation, long-range transport and adverse effects¹⁰. Adding to this concern, deca-BDE can be degraded in biota or in the environment into lower brominated congeners, which themselves are POPs^{11,12}.

In terms of the sound disposal of PBDEs wastes, mechanochemical (MC) method has been proved to be an effective alternative instead of combustion technologies¹³. Via high energy ball milling, the MC reactions between pollutants and co-milling reagents are initiated by the mechanic force such as impact, friction, stress, deformation¹⁴, resulting in the destruction of pollutants into non-hazardous products. Compared with PBDEs wastes combustion which could possibly release toxic PBDD/Fs¹⁵, MC destruction happens at low temperature and normal pressure and can

67 avoid this kind of secondary pollution ¹⁶. Most previous MC studies focused on the
68 destruction of chlorinated POPs such as DDT ¹⁷, PCBs ¹⁸, PCDD/Fs ¹⁹ and few
69 attention was paid on non-chlorinated pollutants. Our recent studies has shown that
70 MC method was as well effective for the destruction of brominated and perfluorinated
71 pollutants ^{20, 21}. However in most cases, excessive co-milling reagents (represented by
72 CaO which is the mostly used) were required to ensure high reaction speed and
73 complete destruction ²². Additionally, the final products and the residual reagents after
74 reaction cannot be utilized and further treatment such as landfill is still needed.
75 Therefore, it is necessary to seek for new co-milling reagents that are used in the
76 required amount for reaction rather than excessive, and the final products are expected
77 to have proper utilization as well.

78 As MC reactions can take place directly in solid state, besides the destruction of
79 POPs, it has also been used for the preparation of new materials and running chemical
80 reactions in absence of solvents ²³. Thus there should be a possibility to couple these
81 two processes together, in which not only pollutants were destroyed but also the final
82 products can be useful.

83 In the present study, Bi₂O₃ was selected as the co-milling reagents for the
84 destruction of PBDEs (represented by deca-BDE) since the element of bismuth has a
85 promising application in photocatalyst ^{24, 25}. With exactly the stoichiometric amount
86 of Bi₂O₃ and deca-BDE for reaction, deca-BDE was completely degraded and the
87 final product was proved to be a visible light photocatalyst BiOBr. The photocatalytic
88 activity of the generated BiOBr was also evaluated using methyl orange (MO) as

model pollutant in the irradiation of simulated sunlight and visible light.

2. Experimental

2.1. Materials

2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether (deca-BDE, $C_{12}Br_{10}O$ 98% in purity), Bismuth (III) oxide (Bi_2O_3 , 99% in purity), Calcium oxide (CaO, 99% in purity) were provided by Wako Pure Chemical Industries Ltd. The CaO and Bi_2O_3 were heated at 450 °C for 2 hours before use. Methyl orange (MO, 85% in purity) was purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used as model pollutant in photocatalytic experiments. All the solvents (*n*-hexane, acetone) used in the extraction and determination were of HPLC grade (J.T. Baker Inc., USA) and the ultrapure water was prepared by a Milli-Q system (Millipore, USA).

2.2. MC reaction

The MC experiments were performed using a planetary ball mill machine (Pulverisette-7, Fritsch, Germany). Two zirconia pots with the volume of 45 cm³ and seven zirconia balls with the diameter of 15 mm (approx. 10.5 g each) were employed in the ball milling. In each experiment, 0.875 g deca-BDE was milled with 2.125 g Bi_2O_3 (or CaO comparatively) as co-milling reagent, keeping the molar ratio Bi:Br=1:1. The rotary speed of machine disk was set as 700 rpm for 15-min intervals, after which there was a 15-min cooling period. The milled samples were collected and then preserved in a hermetic and dry apparatus for further use. For the 2 h milled sample of deca-BDE and Bi_2O_3 , the gas phase products at different reaction atmosphere were also collected for composition analysis.

2.3.Determination and characterization

For deca-BDE determination, 0.05 g of each milled sample was taken and extracted using 50 mL hexane/acetone (1:1, v/v) with 10-min ultrasonic treatment. The solution was firstly filtered by 0.45 μm polytetrafluoroethylene (PTFE) membrane and then subjected to instrumental analysis. A Shimadzu 2010 GC-MS equipped with a DB-5HT column (15 m \times 0.25 mm i.d., 0.10 μm film thickness) was used and operated in negative ion chemical ionization (NCI) mode. The collected gas phase products were analyzed using a micro gas chromatograph system (Micro-GC 3000A, Agilent, USA).

To identify the final products after MC reaction, X-ray diffraction (XRD) measurement were performed by an X-ray diffractometer (RINT-2200, Rigaku, Japan) equipped with a Cu K α radiation from $2\theta = 10^\circ \sim 60^\circ$ at a speed of 10°min^{-1} . The thermogravimetric (TG) analysis was carried out using a TG8120 analyzer (Rigaku, Japan) in nitrogen flow with 10 mg sample and $10^\circ \text{C}/\text{min}$ heating rate from 25°C to 600°C . To figure out the chemical changes during milling, the samples were characterized by a Fourier transform infrared (FTIR) spectrometer (FTS3000, Digilab, USA) with the KBr disk method. Raman spectra of the samples were also recorded using a LabSpec Raman spectrograph (HORIBA Jobin Yvon, France) with a He laser beam at the 632 nm line.

2.4.Photocatalytic experiments

To evaluate the photocatalytic activity of the final products after MC reaction, a series of experiments were carried out using a projective photochemical reactor

(PLSSXE300UV, Beijing Trusttech Technology Co., China) with a 300 W Xenon lamp as simulated sunlight. The UV-CUT-400 filter was employed to remove the incoming wavelengths shorter than 400 nm and ensure visible light irradiation. A cooling device was equipped and the infrared irradiation of the light was cut off to avoid significant temperature increase of the reaction system.

In the experiments, 0.2 g of the 2 h milled sample was added into a cylindrical quartz reactor (160 mm length×32 mm inner diameter) with 100 mL MO solution at a concentration of 15 mg/L. A magnetic stirring apparatus was located at the bottom of the reactor to ensure thoroughly mixing of the aqueous system. The direct photolysis and control test in darkroom were also simultaneously carried out for comparison. At each sampling time, 2 mL of the suspension was taken and filtered by 0.45 µm nylon membrane, after which remaining MO in the filtrate was determined by a Hitachi U-3310 UV-visible spectrophotometer.

3. Results and discussion

3.1. Comparison of Bi_2O_3 with CaO as co-milling reagents

In order to investigate the performance of Bi_2O_3 in MC destruction of deca-BDE, the comparison experiment with CaO (as a representative of commonly used co-milling reagents) was carried out with the same weight ratio (2.125 g Bi_2O_3 or CaO with 0.875 g deca-BDE). The destruction efficiency of deca-BDE by Bi_2O_3 or CaO and the GC-MS spectra of Bi_2O_3 milled samples are shown in Fig.1.

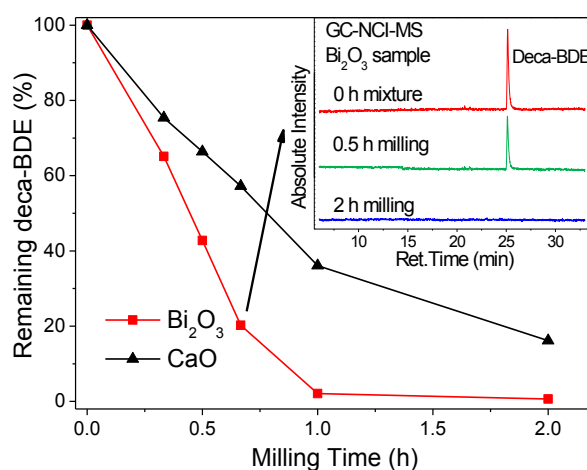


Fig.1. The destruction of deca-BDE together with GC-MS spectra of Bi₂O₃ milled samples

With the extension of milling time, the remaining deca-BDE quickly decreased roughly following a linear declination trend, showing that the MC method is effective for deca-BDE destruction. Nearly all the deca-BDE was destroyed after 1 h ball milling with Bi₂O₃ as co-milling reagent. Actually no peak could be found in the GC-MS spectra of the 2 h milled sample, indicating a complete degradation of deca-BDE after MC reaction. But when CaO was used as co-milling reagent, the performance was less effective and there was still more than 15% deca-BDE remaining in the solid even after 2 h ball milling. Obviously, as co-milling reagent, Bi₂O₃ showed better performance for PBDEs destruction.

It was expected that there should be some intermediates from the MC degradation of deca-BDE. However, unlike some other degradation reactions such as photolysis²⁶, no obvious intermediates or organic products of deca-BDE could be found in the Bi₂O₃ milled samples (as shown in the GC-MS spectra in Fig.1). This suggests that the MC reactions between deca-BDE and Bi₂O₃ should take place continuously and spontaneously, during which few intermediates could be detected.

This phenomenon also happened in many previous studies on MC destruction^{20, 27}.

3.2. Products identification

For the products identification of deca-BDE and Bi_2O_3 after MC reaction, XRD analysis of the milled samples was carried out and the results are shown in Fig.2, labeled with the patterns of the reagent and typical products.

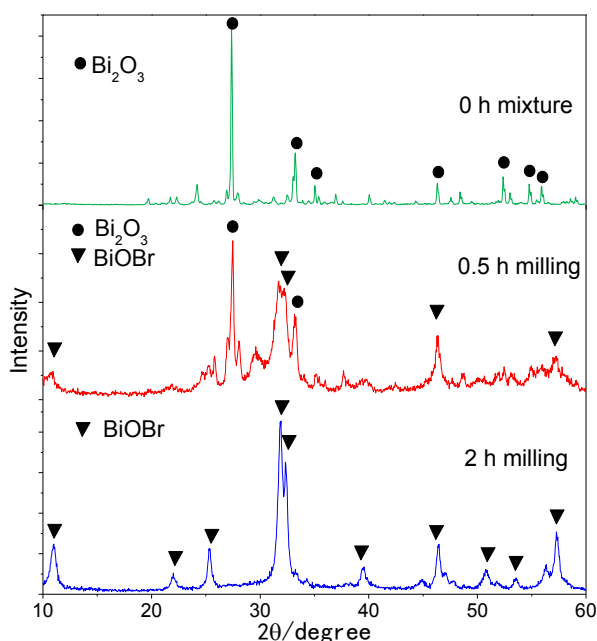


Fig.2. XRD spectra of the samples milled with Bi_2O_3 for different time

For 0 h mixture of deca-BDE and Bi_2O_3 , only the diffraction peaks of Bi_2O_3 (JCPDS Card No. 74-1373, labeled as ●) were shown clearly in the XRD spectra. While after 30 min milling, the pattern of Bi_2O_3 quickly receded and another new group of diffraction peaks with strong intensity started to appear. These new peaks were indexed to the hexagonal structure of bismuth oxybromide (BiOBr , JCPDS Card No. 73-2061, labeled as ▼) which was a promising visible light photocatalyst²⁸. After 2 h milling, there was no longer any peaks of Bi_2O_3 in the spectra, remaining only the pattern of BiOBr . This transformation from Bi_2O_3 to BiOBr illustrates that

deca-BDE was destroyed through the MC reaction and the organic bromine was changed into inorganic form as BiOBr, corresponding with the GC-MS results above.

It's worth mentioning that there was neither excessive Bi_2O_3 nor unreacted deca-BDE remaining in the samples after the MC process. Therefore as expected, deca-BDE was effectively destroyed with the stoichiometric amount of Bi_2O_3 rather than excessive. Meanwhile, a promising visible light photocatalyst BiOBr was prepared as the final product and can be utilized again. This process matches well with the concept of green chemistry in which pollutants were destroyed and useful products were generated.

To ensure the destruction of deca-BDE and the formation of BiOBr during MC treatment, thermogravimetric (TG) analysis of the samples was also conducted as shown in Fig.3.

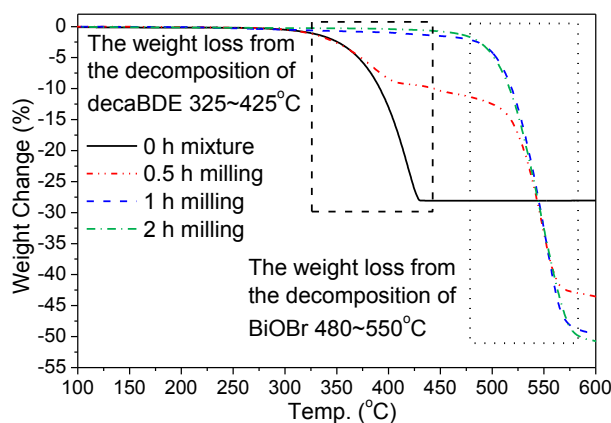
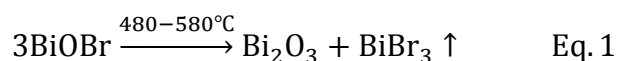


Fig.3. TG analysis of the samples milled with Bi_2O_3 for different time

For 0 h mixture, an obvious weight change could be observed during heating at the range of 325~425 °C, which was owing to the thermal decomposition of deca-BDE²⁹. The nearly 30% loss also agreed well with the weight ratio of deca-BDE in the mixture (0.875g deca-BDE/total 3.0 g = 29.2%). After 30 min ball milling, the weight

change around 325~425 °C became much smaller, indicating a large destruction of deca-BDE. Meanwhile there was another weight loss at the range of 480~580 °C starting to occur. Since most organics would be decomposed at the temperature above 450 °C, this new weight loss could be attributed the thermolysis of the final product. At above 500 °C, BiOBr would be easily decomposed into Bi₂O₃ (s) and BiBr₃ (g)³⁰, during which the evaporation of BiBr₃ at this temperature resulted in this large weight loss (shown in Eq.1).



For the samples after 2 h ball milling, there was no longer weight change at 325~425 °C, indicating that deca-BDE was completely destroyed and transformed into inorganic form. Correspondingly, there was a nearly 50% weight loss at 480~550 °C owing to the BiBr₃ evaporation from the BiOBr decomposition. This result again demonstrates that deca-BDE has just reacted with the Bi₂O₃ during ball milling with the formation of BiOBr.

3.3.Characterization of the samples milled with Bi₂O₃

To better understand the chemical change of deca-BDE during milling, Fourier transform infrared (FTIR) and Raman spectrometer were conducted on the milled samples. Fig.4 shows the FTIR spectra of the samples for different milling time.

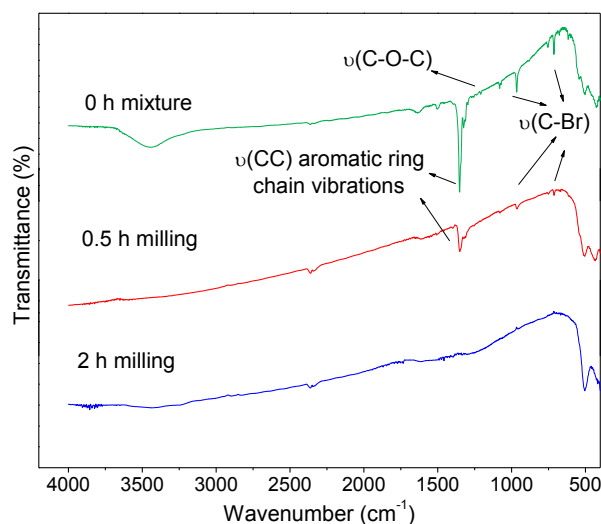


Fig.4. FTIR spectra of samples milled with Bi_2O_3 for different time

For 0 h mixture of deca-BDE and Bi_2O_3 , there was a strong peak centered at 1350 cm^{-1} in FTIR, which came from the $\nu(\text{CC})$ chain vibration of the aromatic ring and could be regarded as the indicator for deca-BDE molecule³¹. The peak band at 960 cm^{-1} , 761 cm^{-1} and 696 cm^{-1} were the $\nu(\text{C-Br})$ stretching vibrations, illustrating the existence of the organic bromine³². The weak stretching band around 1210 cm^{-1} was attributed to the $\nu(\text{C-O-C})$ asymmetric vibration. For the spectra of 30 min milled sample, these peaks quickly weakened, showing that the deca-BDE was greatly destroyed. Actually after 2 h ball milling with Bi_2O_3 , all the signal peaks of deca-BDE in FTIR were totally disappeared, illustrating that both the skeleton of deca-BDE was broken down and the organic bromine atoms were dissociated from the molecule.

Raman spectra of the samples milled with Bi_2O_3 are shown in Fig.5. Correspondingly with FTIR, the $\nu(\text{CC})$ aromatic ring chain vibration of deca-BDE in Raman spectra was located at 1520 cm^{-1} with strong intensity and the asymmetric $\nu(\text{C-O-C})$ vibration showed around $1180\sim 1240\text{ cm}^{-1}$ ^{31, 33}. The peaks of C-Br bonds were observed over a wide range of $690\sim 1090\text{ cm}^{-1}$. With the ball milling ongoing,

the intensity of the peaks from deca-BDE largely decreased and two peak bands with the peak around 1312 cm^{-1} and 1582 cm^{-1} started to appear and strengthen. In Raman analysis, these two peak bands are usually classified as the “D-band” ($1330\text{-}1380\text{ cm}^{-1}$) and “G-band” ($1540\text{-}1580\text{ cm}^{-1}$) which are respectively the characteristic for sp^2 -bonded atoms of disordered carbon and crystal graphite³⁴. The appearance and intensification of “D-band” and “G-band” declare the generation of disordered and graphite carbon in the MC reaction.

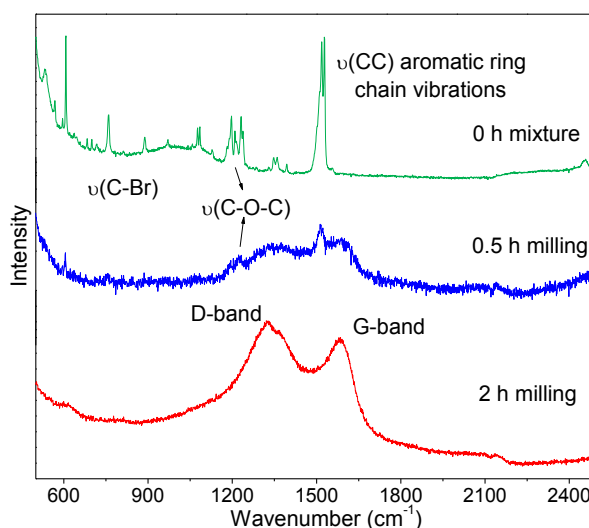


Fig.5. Raman analysis of samples milled with Bi_2O_3 for different time

Therefore, the collapse of deca-BDE skeleton and the cleavage of C-Br bonds, together with the generation of inorganic carbon, reveal that debromination and carbonization are the main mechanisms for deca-BDE destruction. In this way, the organic carbon and bromine in the molecule were transformed into inorganic forms, eliminating the POPs properties of deca-BDE.

3.4. Gas phase products identification

During the milling of deca-BDE with Bi_2O_3 , evident gas production could be observed after the experiment. As a result, the MC reactions in the atmosphere of air

or argon were performed for 2 h and the produced gases were collected for analysis. The results of the gaseous products from 2 h milled samples at different reaction atmosphere are shown in **Table 1**.

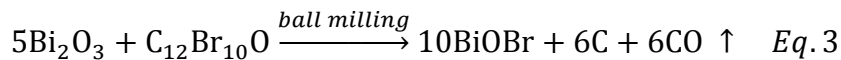
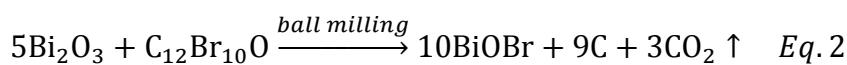
Table 1. Gas products analysis for 2 h milled samples at different reaction atmosphere

Components Atmosphere	CO ₂	CO	N ₂	O ₂	Ar
Air	56.5%	6.1%	29.3%	7.6%	-
Argon	54.7%	5.8%	-	-	39.5%

Through micro-GC analysis, CO₂ (roughly 90%) and CO were proved to be the gaseous products of the MC reaction. It should be pointed out that the atmosphere had few influence on the gas production. It is not difficult to understand because the MC reactions are usually initiated by mechanic force and take place in solid state at nearly room temperature, in which the gas phase is seldom involved in the reactions.

3.5.MC reaction formula

In terms of the final products identified above (inorganic carbon, BiOBr, CO₂ or CO), the MC reaction between deca-BDE and Bi₂O₃ should follow either of the following equations:



Since the rough ratio between CO₂ and CO was 10:1, it can be inferred that the reaction mostly followed Eq.2 and fractionally went with Eq.3. Taking the experiment at air atmosphere for example, the final gas volume was about 108 mL (25 °C), in which there was 61.0 mL CO₂ and 6.6 mL CO. Then the generated CO₂ and CO could be calculated into 2.49 mmol and 0.27 mmol, corresponding to 0.798 g and 0.043 g

deca-BDE consumption following Eq.2 and Eq.3. As a result, the calculated total deca-BDE consumption (0.841 g) agreed well with the originally added amount (0.875 g), indicating that the gas production can be well balanced with the initial concentration of deca-BDE. Satisfyingly, there were no other gases or hazardous products generated and the secondary pollution was avoided.

3.6. Photocatalytic activity of BiOBr

In order to evaluate the photocatalytic activity of the generated BiOBr, the photocatalytic degradation of methyl orange (MO) in water was performed under direct Xenon lamp (simulated sunlight) and visible light ($\lambda > 400$ nm) irradiation. For comparison, the direct photolysis of MO and the control test with BiOBr in darkroom were also carried out. Fig.6 shows the variations of MO concentration (C/C_0) at different conditions.

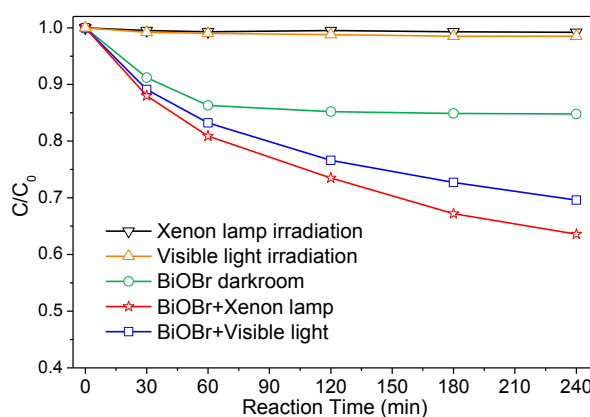


Fig.6. Variations of MO concentration at different conditions

It can be observed that the direct photolysis of MO was negligible under both Xenon lamp and visible light irradiation. Meanwhile in the control experiment, there was a nearly 15% decrease of MO concentration in the first 60 min and keep unchanged afterwards. Since no irradiation existed in the darkroom, this removal of

MO was ascribed to the absorption from the sample. Under Xenon lamp irradiation with BiOBr, there was a remarkable degradation of MO (20% after 4 h reaction) besides the absorption, indicating the occurrence of photocatalytic degradation³⁵. The visible light irradiation with BiOBr also showed a significant effect with 15% MO degradation after 4 h reaction, although the performance was not as good as simulated sunlight irradiation.

Therefore, it is demonstrated that the generated BiOBr after the MC reaction had good photocatalytic activity under both simulated sunlight and visible light irradiation. In this way, the final products after the MC destruction of deca-BDE could be utilized again as photocatalyst rather than discarded.

4. Conclusion

The present study successfully combined MC destruction of POPs with the preparation of catalyst. The main conclusions of the study are as follows:

1. MC reaction with Bi₂O₃ is shown to be an effective method for the destruction of deca-BDE, with no hazardous intermediates or organic products observed.
2. Besides the deca-BDE destruction, the final product after milling was a promising visible light photocatalyst BiOBr and could be utilized in further steps, matching well with the concept of green chemistry.
3. With stoichiometric ratio for BiOBr formation, deca-BDE had just reacted with Bi₂O₃, which economized the raw materials and saved the cost.
4. Carbonization and debromination were found to be the main reaction mechanisms for the destruction of deca-BDE.

5. The generated BiOBr showed good photocatalytic activity for MO degradation under both simulated sunlight and visible light irradiation.

Acknowledgement

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370