The effect of calcination temperature on the performance of Co$_3$O$_4$-Bi$_2$O$_3$ as a heterogeneous catalyst of peroxymonosulfate

Guangshan Zhang, Limin Hu, Peng Wang, Yixing Yuan

State Key Laboratory of Urban Water Resource and Environment, School of Environment, Harbin Institute of Technology, Harbin, 150090, China

E-mail: pwang73@vip.sina.com (P. Wang)

Abstract. In this work, a time-saving microwave-assisted method for synthesis of Co$_3$O$_4$-Bi$_2$O$_3$ was reported. The synthesized Co$_3$O$_4$-Bi$_2$O$_3$ samples were characterized with different techniques to probe their crystalline structures and morphologies. The catalytic performances of synthesized Co$_3$O$_4$-Bi$_2$O$_3$ as peroxymonosulfate activator were evaluated by the degradation of bisphenol A. The effect of calcination temperature on Co$_3$O$_4$-Bi$_2$O$_3$ products was explored and the result showed that the sample calcined at 400 °C possessing superior catalytic activity.

1. Introduction

Bisphenol A (BPA) has been widely used in the commercial and household products, such as thermal sensitive papers, medical equipment, feeding bottles, and food can linings and so on [1], which leading to BPA contamination of watery environment and organisms. As a refractory organic pollutant, an effective technique to remove it from wastewater is urgent.

Sulfate radical-based advanced oxidation processes (SR-AOPs) have attracted much attention owing to its high oxidation potential, long half-life, and high selective oxidation with electron transfer [2, 3]. Recent studies have focused on using heterogeneous cobalt-contained metal oxide as a peroxymonosulfate (PMS) activator for wastewater treatment [4, 5]. In this regard, it is necessary to seek for a time-saving and cost-free method for preparing the catalysts.

Since bismuth is an promising microwave-absorbing material [6], we report a Co$_3$O$_4$-Bi$_2$O$_3$ catalyst as the PMS activator prepared by microwave-assisted method. The crystallography and morphology were characterized. The catalytic activity of the Co$_3$O$_4$-Bi$_2$O$_3$/PMS system was evaluated by the degradation of BPA. Moreover, the effect of calcination temperature of Co$_3$O$_4$-Bi$_2$O$_3$ catalyst on the degradation performance was also explored in detail.

2. Experimental

2.1. Chemicals and reagents

BPA (Sinopharm, China), PMS (Oxone, KHSO$_5$·0.5KHSO$_4$·K$_2$SO$_4$, Aladdin, China), Bi(NO$_3$)$_3$·5H$_2$O (Sinopharm, China), Co(NO$_3$)$_2$·6H$_2$O (Sinopharm, China), HNO$_3$ (Sinopharm, China), NaOH (Sinopharm, China) and absolute ethyl alcohol (Sinopharm, China) were of analytical grade. Methanol (MeOH, Tianli, China) was of chromatographic grade. Deionized water (DI) was used throughout the study.

2.2. Preparation of Co$_3$O$_4$-Bi$_2$O$_3$ catalyst
In this work, a series of Co\textsubscript{3}O\textsubscript{4}-Bi\textsubscript{2}O\textsubscript{3} catalysts was prepared by microwave-assisted method. Briefly, 2.5 mmol of Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O and 2.5 mmol of Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O were dissolved in 20 mL of HNO\textsubscript{3} solution with concentration of 2 mol·L\textsuperscript{-1}. After the reagents were dissolved, the solution was added dropwise into the 100 mL of NaOH solution with 1.0 mol·L\textsuperscript{-1} under continuous stirring and then removed the mixture solution to microwave reactor (COOLPEX-E, Preekem Scientific Instruments Co., Ltd, China) immediately. The microwave temperature and microwave time were set as 75 °C and 30 min, respectively. After the microwave reaction and cooling down to room temperature, the precipitate was achieved by filtration and rinsed with DI water and absolute ethyl alcohol several times. The Co\textsubscript{3}O\textsubscript{4}-Bi\textsubscript{2}O\textsubscript{3} sample was obtained after dried at 70 °C in an oven overnight and labelled as CBO. The CBO particles calcined in a tube for 2 h at certain temperatures (200 °C-600 °C) were labelled as CBO-X (X=2, 3, 4, 5, 6).

2.3. Characterization of Co\textsubscript{3}O\textsubscript{4}-Bi\textsubscript{2}O\textsubscript{3} catalysts

The crystalline structures of the Co\textsubscript{3}O\textsubscript{4}-Bi\textsubscript{2}O\textsubscript{3} samples were analyzed by X-ray diffraction (XRD). The patterns were measured in the 2θ range of 10-90° with Cu Kα radiation using a Bruker D8 ADVANCE system. The morphology of the sample was observed using a FEI QUANTA 200 scanning electron microscope (SEM).

2.4. Experimental procedure

The catalytic activities of the Co\textsubscript{3}O\textsubscript{4}-Bi\textsubscript{2}O\textsubscript{3} catalysts for PMS activation were evaluated by BPA removal. The degradation experiments were implemented in a beaker with 250 mL volume. In each run, 0.01 g Co\textsubscript{3}O\textsubscript{4}-Bi\textsubscript{2}O\textsubscript{3} catalyst was dispersed in 100 mL of BPA solution with concentration of 20 mg·L\textsuperscript{-1}. During the whole process, the temperature was at room temperature and the pH was not adjusted. Prior to the degradation reaction, the suspension was continuous stirred for 30 min to reach an adsorption-desorption equilibrium between BPA molecules and Co\textsubscript{3}O\textsubscript{4}-Bi\textsubscript{2}O\textsubscript{3} particles. Through the test, 1.5 mL of the reaction solution was withdrawn at given time intervals and filtered into 2 mL autosampler vials. The samples were stored at 4 °C to interrupt the reaction.

2.5. Analysis

BPA concentration was monitored by HPLC equipment (LC-10A, Shimadzu) with a C18 column (5µm, 4.6×150 mm). The detection wavelength of the UV detector was set to 277 nm. The mobile phase was methanol and water and their volume ratio was 60:40. All measurements were carried out three times. Dates are presented as mean values with standard deviation as an error bar.

3. Results and discussion

3.1. Characterization

The XRD patterns of the Co\textsubscript{3}O\textsubscript{4}-Bi\textsubscript{2}O\textsubscript{3} catalysts with different calcination temperature were detected and the results are shown in Figure 1a. All the patterns of these six samples are well indexed to a monoclinic alpha-bismuth oxide (JCPDS 71-0465). This phenomenon indicated that calcination treatment has little effect on the phase structure of samples. However, increasing the calcination temperature of Co\textsubscript{3}O\textsubscript{4}-Bi\textsubscript{2}O\textsubscript{3} catalyst from 70 °C (drying temperature, CBO) to 400 °C (CBO-4), the crystallinity of the catalyst has improved gradually. Further increasing the calcination temperature to 600 °C, the samples exhibit poor crystallinity. It is interesting to find that the diffraction peak of cobalt oxide cannot be discovered in XRD pattern, this may be explanation by the fact that the cobalt oxide was amorphous state or the diffraction peak of it was too weak to detection. Moreover, the SEM images from Figure 1b provides a direct observation about the surface morphology of CBO-4 sample with ×10,000 magnification. Remarkably, CBO-4 sample shows rod-like shapes with many nanoparticles agglomerated on the surface of the rod. This result demonstrated that the formation of numerous nanoparticles will provide more active site and as a result of enhancing the catalytic activity of the CBO-4 catalyst.
3.2. Effect of calcination temperature on the performance of Co3O4-Bi2O3 catalysts

It is well known that the calcination treatment is an efficient way to modify the catalytic activities of the catalysts in AOPs system [7]. In order to seek for the optimal catalyst in our present work, the BPA degradation efficiencies using Co3O4-Bi2O3 catalysts at different calcination temperatures were explored and the results are shown in Figure 2. Regarding to Figure 2a, the calcination temperature of the catalyst has significant influence on the catalytic activity of Co3O4-Bi2O3/PMS system. When the catalysts without calcination treatment (CBO) or calcined at 200 °C (CBO-2), both of them are exhibited almost 100% degradation efficiencies of BPA during 30 min reaction times. Moreover, it is observed that the catalysts calcined at 300 °C (CBO-3) and 400 °C (CBO-4) possess outstanding catalytic activities that BPA can be totally removed within 15 min. However, further increasing the calcination temperatures to 500 °C (CBO-5) and 600 °C (CBO-6), it shows blocking effect on the degradation performances in Co3O4-Bi2O3/PMS systems.

Furthermore, the catalytic degradations of BPA by Co3O4-Bi2O3 at different calcination treatment in Co3O4-Bi2O3/PMS systems follow the pseudo-first-order kinetics, and it can be described by Eq. (1):

\[
\ln\left(\frac{C_0}{C}\right) = kt
\]

where \(k\) presents the pseudo-first-order rate constant (min\(^{-1}\)), \(C_0\) and \(C\) stand for the concentration of BPA at reaction time 0 min and \(t\) min, respectively. Then the reaction rate constants of catalytic degradation of BPA in Co3O4-Bi2O3/PMS systems were calculated and the results are shown in Figure 2b. It can be seen that the reaction rate constant augments from 0.136 min\(^{-1}\) to 0.380 min\(^{-1}\) with the increase of the calcination temperature of catalysts from 70 °C (drying temperature, CBO) to 400 °C (CBO-4). However, further increasing the calcination temperatures lead to adverse impact for the reaction rates. Therefore, 400 °C was considered as the optimal calcination temperature for Co3O4-Bi2O3 catalyst in our present work.

Figure 1. (a) The XRD patterns of the Co3O4-Bi2O3 catalysts with different calcination temperature, and (b) SEM image of CBO-4 catalyst.
4. Conclusions
In summary, a facile and time-saving microwave-assisted method is offered to obtain a Co₃O₄-Bi₂O₃ catalyst for PMS activation. We found that the calcination treatment had a considerable effect on the crystallinity, morphology and catalytic performances of the Co₃O₄-Bi₂O₃ catalysts. The result demonstrated that catalyst calcined at 400 °C (CBO-4) exhibited an excellent performance for BPA removal in Co₃O₄-Bi₂O₃/PMS system.

Acknowledgments
The work was supported by the National Natural Science Foundation of China (51678185), the 9th Special Financial Grant from the China Postdoctoral Science Foundation (2016T90304) and Technological Innovation Talent Special fund of Harbin, China (2016RAQXJ175).

References
[1] H. Sambe, K. Hoshina, K. Hosoya, J. Haginaka, J Chromatogr A, 1134 (2006) 16-23.
[2] F. Ghanbari, M. Moradi, Chem Eng J, 310 (2017) 41-62.
[3] A. Tsitonaki, B. Petri, M. Crimi, H. MosbÆK, R.L. Siegrist, P.L. Bjerg, Crit Rev Env Sci Tec, 40 (2010) 55-91.
[4] T. Chaoqun, G. Naiyun, F. Dafang, D. Jing, D. Lin, Sep Purif Technol, 175 (2017) 47-57.
[5] Y. Feng, J. Liu, D. Wu, Z. Zhou, Y. Deng, T. Zhang, K. Shih, Chem Eng J, 280 (2015) 514-524.
[6] Y. Qiu, J. Zhou, J. Cai, W. Xu, Z. You, C. Yin, Chem Eng J, 306 (2016) 667-675.
[7] E. Saputra, H. Zhang, Q. Liu, H. Sun, S. Wang, Chemosphere, 159 (2016) 351-358.