Supporting Information

Efficient degradation of aqueous carbamazepine by bismuth oxybromide-activated peroxide oxidation

Tuqiao Zhang [1], Shipeng Chu [1], Jian Li [1], Lili Wang [3], Rong Chen [1], Yu Shao [1], Xiaowei Liu [1, 2, *], Miaomiao Ye [1, *]

[1] Institute of Municipal Engineering, College of Civil Engineering and Architecture, Zhejiang University, Hangzhou 310058, China; ztq@zju.edu.cn (T.Z.); chushipeng@zju.edu.cn (S.C.); xero@zju.edu.cn (J.L.); 21512060@zju.edu.cn (R.C.); shaoyu1979@zju.edu.cn (Y.S.); yemiao008@zju.edu.cn (M.Y.)

[2] Institute of Port, Coastal and Offshore Engineering, Ocean College, Zhejiang University, Hangzhou 310058, China

[3] Environmental Engineering, Jiyang College of Zhejiang A & F University, Zhuji 311800, China; liilive@163.com

* Correspondence: liuxiaowei@ zju.edu.cn; Tel.: +86-571-8820-8721

Summary：This file contains 7 pages, 5 texts, 9 figures and 1 tables.

Text S1. Chemicals

Anhydrous ethanol, $Bi(NO_3)_3{\cdot}5H_2O$, KCl, KBr, KI, H_2O_2 and ethylene glycol ($C_2H_6O_2$) were all provided by J&K Scientific Ltd. (Shanghai, China) CBZ, potassium persulfate (PS), PMS (available as Oxone®, manufactured by DuPont), humic acid (HA), *para*-chlorobenzoic acid (*p*CBA), acetonitrile (HPLC grade), 5,5-dimethyl-1-pyrroline N-oxide (DMPO), tert-butanol (TBA), and methanol (HPLC grade) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Ultrapure water was used to prepare the tested solutions.

Text S2. Parameters of analysis

For the determination of CBZ, a XDB-C18 column (4.6 mm×150 mm, 5 μm) was used. The mobile phase was a 70/30 (v/v) mixture of acetonitrile and 0.10% phosphoric acid. The flow rate was 1.0 $mL{\cdot}min^{-1}$. A 20 μL injection volume was adopted and the detection wavelength was set at 285 nm.

The parameter settings for the mass spectrometry were negative ion mode (ESI−) with a gas flow rate of 5 $L{\cdot}min^{-1}$ at 325 °C, a nebulizer pressure of 45 psi, sheath gas flowing at 11 $L{\cdot}min^{-1}$ at 350 °C, a nozzle voltage of 0 or 500 V(+), a capillary voltage of 3000 V(+)/3500 V(−), and a fragmentor voltage of 135 V. The mobile phase for the HPLC–MS analysis was a 70/30 (v/v) mixture of 10 mM ammonium acetate with acetonitrile, and it was run at 1.0 $mL{\cdot}min^{-1}$.

Text S3. Toxicity evaluation of samples

Freeze-dried bacteria, reconstitution solution, diluent (2% NaCl) and an adjustment solution (non-toxic 22% sodium chloride) were obtained from Beijing Hamamatsu (Beijing, China). Samples were examined in quartz tube containing 2% sodium chloride in three dilutions. A toxic-free control experiment in three repeats was conducted only containing 2% sodium chloride. The luminescence was recorded after 15 min of incubation at 15 ℃. The percentage of luminescence inhibition was calculated according to the procedure described by Calza et al. [1]. Sample solutions with 40 μM CBZ in the presence of 1 mM PMS and 0.5 $g{\cdot}L^{-1}$ BiOBr for 0, 10, 20, 30, 40, 50, and 60 min were tested and controlled blanks (using only freshwater or solution containing 4 mM sulfate and nitrite with designed concentration) were also tested. Analysis was conducted according to the standard Microtox® test procedures recommended by the manufacturer. Samples were concentrated by the freeze-drying method. The recovery for freeze-dried samples was 95~110%. The detoxification rate is defined as follow:

$$\text{Detoxification rate (\%)} = \frac{I_t - I_0}{I_0} \times 100\% \qquad (1)$$

where I_0 is the initial loss rate of light emission and I_t is loss rate of light emission at reaction time t (min).

Text S4. Effect of leaching bismuth ion

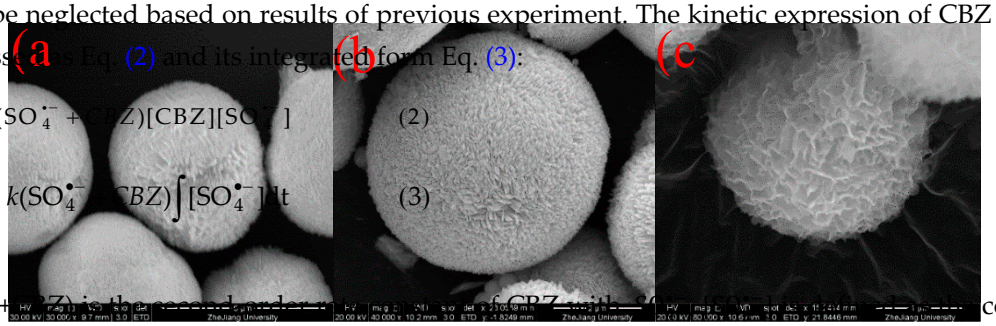
The bismuth ion leaching from BiOX during the degradation process could be Bi(III) or/and Bi(V). Bi(V) was identified as the main species in the bulk solution based on the color change when Mn(II) was dosed into 15-min reaction solution (BiOX particles were removed). Therefore, bismuth ion solution (0.2 mg·L^{-1}) prepared with $NaBiO_3$ was used to simulate the leaching bismuth ion. For comparison, the effect of Bi(III) (prepared with $Bi(NO_3)_3$ and EDTA) was also investigated. Designed amount Bi(III) or/and Bi(V) was added into a beaker containing calculated volume DI water. Then the solution pH was adjusted to be around 7.0 with borate buffer. After that CBZ and PMS were added in succession. It must also be mentioned that the bismuth ion leaching from BiOX would undergo rapid hydrolysis and react with other substrate in the solution. The results based on $NaBiO_3$ and $Bi(NO_3)_3$ can only qualitatively reflect the effect of leaching bismuth ion to a certain extent.

Text S5. Determination of $k(SO_4^{\bullet-}+CBZ)$

*p*CBA was chosen as a probe compound for determination of $k(SO_4^{\bullet-}+CBZ)$. $SO_4^{\bullet-}$ was generated by PMS activation using BiOBr, and HO• was quenched by 1 mM TBA. Both adsorption of *p*CBA by BiOBr and oxidation by PMS can be neglected based on results of previous experiment. The kinetic expression of CBZ degradation can be expressed as Eq. (2) and its integrated form Eq. (3):

$$-\frac{d[CBZ]}{dt} = k(SO_4^{\bullet-} + CBZ)[CBZ][SO_4^{\bullet-}] \qquad (2)$$

$$-\ln\frac{[CBZ]}{[CBZ]_0} = k(SO_4^{\bullet-} + CBZ)\int[SO_4^{\bullet-}]dt \qquad (3)$$



where $k(SO_4^{\bullet-}+CBZ)$ is the second-order rate constant of CBZ with $SO_4^{\bullet-}$, $[SO_4^{\bullet-}]$ is the concentration of $SO_4^{\bullet-}$, $[CBZ]_0$ and [CBZ] are the initial concentration of CBZ and concentration at time t, respectively.

Applying Eq. (3) to probe compound (*p*CBA) coexisting with CBZ in the system, Eq. (4) is obtained:

$$-\ln\frac{[pCBA]}{[pCBA]_0} = k(SO_4^{\bullet-} + pCBA)\int[SO_4^{\bullet-}]dt \qquad (4)$$

Dividing Eq. (3) with Eq. (4), leads to:

$$\frac{-\ln([CBZ]/[CBZ]_0)}{-\ln(pCBA[]/[pCBA]_0)} = \frac{k(SO_4^{\bullet-}+CBZ)}{k(SO_4^{\bullet-}+pCBA)} \qquad (5)$$

Based on the reported value of $k(SO_4^{\bullet-}+pCBA)$ (3.6×10^8 M^{-1}·s^{-1}, [2]) and slope of the plot of -ln ([CBZ]/[CBZ]$_0$) vs. -ln ([*p*CBA]/ln[*p*CBA]$_0$) (k = 4.50, Fig. SM-1), $k(SO_4^{\bullet-}+CBZ)$ was found to be 1.6×10^9 M^{-1}·s^{-1}.

Fig. S1. SEM images of BiOX microspheres: (a) BiOCl, (b) BiOBr, (c) BiOI.

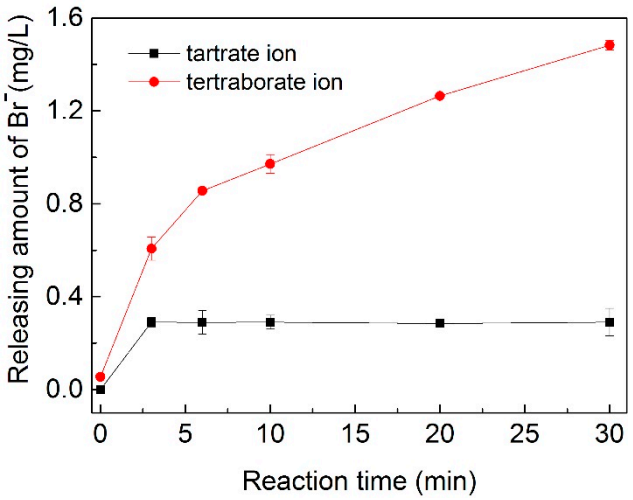


Fig. S2. Effect of anions in buffer on the releasing of bromide ion. ([CBZ]$_0$ = 5.0 μM, [PMS]$_0$ = 4.0 mM, [BiOBr]$_0$ = 1.0 g·L^{-1}, 10 mM tartrate ion/tetraborate ion, pH = 7.0, 24 ℃)

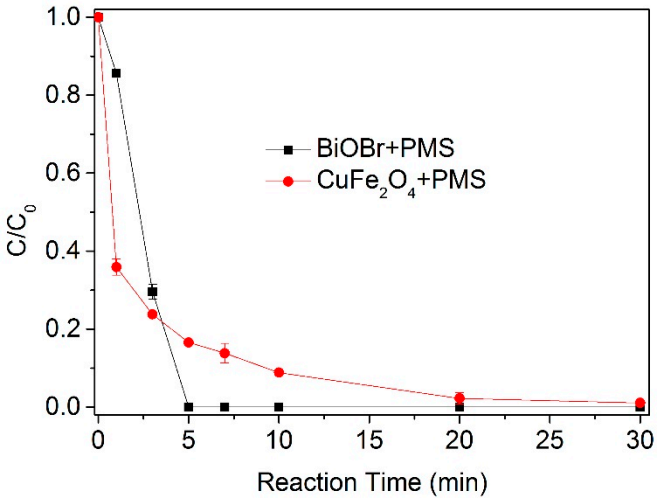


Fig. S3. Comparison of CBZ degradation by PMS/BiOBr and PMS/$CuFe_2O_4$. ([CBZ]$_0$ = 5.0 μM, [PMS]$_0$ = 4.0 mM, [BiOBr]$_0$ = [$CuFe_2O_4$]$_0$ = 1.0 g·L^{-1}, pH = 7.0, 24 ℃)

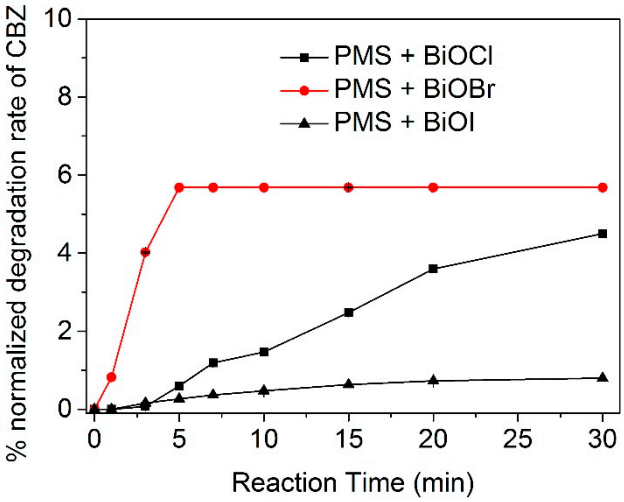


Fig. S4. Normalized degradation rate of CBZ based on specific surface area for PMS/BiOBr. ($[CBZ]_0$ = 5.0 μM, $[PMS]_0$ = 4.0 mM, $[BiOBr]_0$ = 1.0 g·L^{-1}, pH = 7.0, 24 ℃)

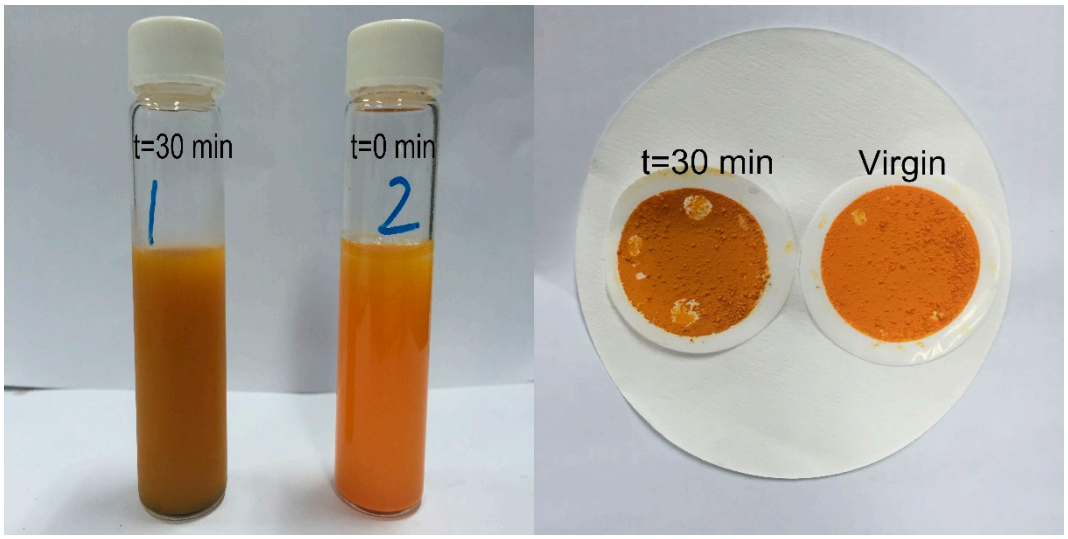


Fig. S5. Color change of BiOI suspension during the degradation process. ($[CBZ]_0$ = 5.0 μM, $[PMS]_0$ = 4.0 mM, $[BiOI]_0$ = 1.0 g·L^{-1}, pH = 7.0, 24 ℃)

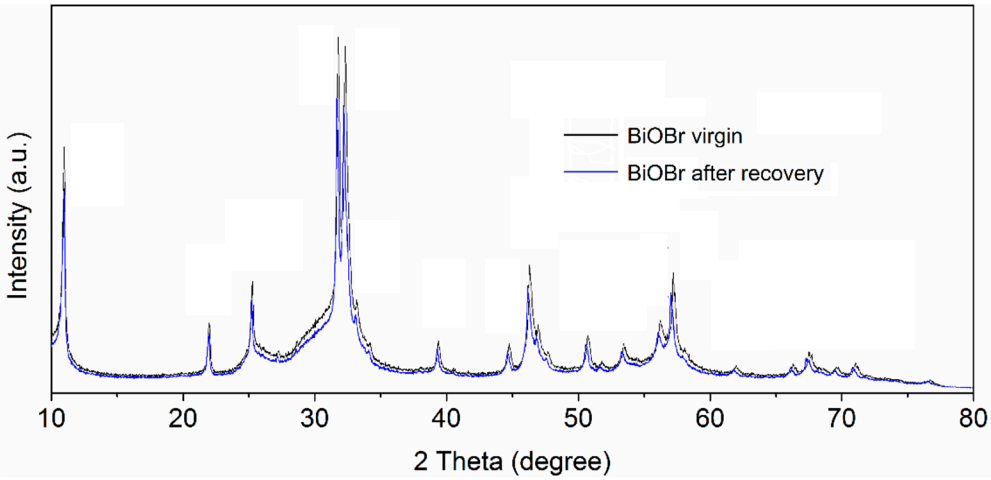


Fig. S6. XRD spectra of BiOBr particles before and after the repeated catalytic PMS oxidation (7 cycles). (BiOBr dose 0.5 g·L^{-1}, $[CBZ]_0$ = 5 μM, $[PMS]_0$ = 1.0 mM, pH = 7.0, 24 ℃, reaction for 30 min)

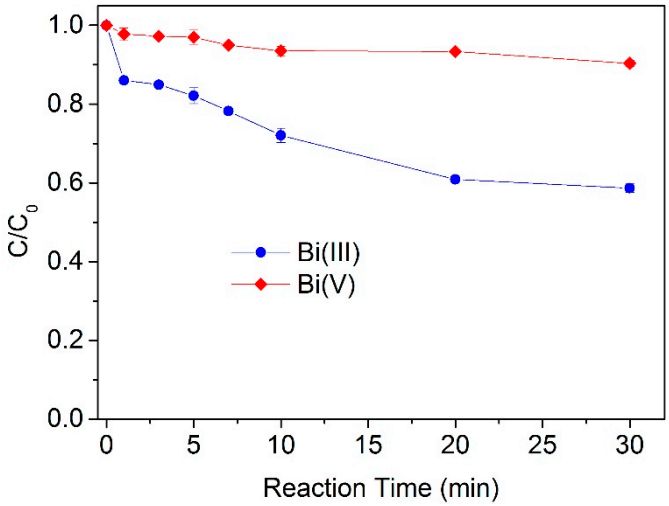


Fig. S7. Effect of leaching bismuth ion on the degradation of CBZ. (Bi(III) = Bi(V) = 0.2 mg·L^{-1}, [CBZ]$_0$ = 5 μM, [PMS]$_0$ = 4.0 mM, pH = 7.0, 24 ℃)

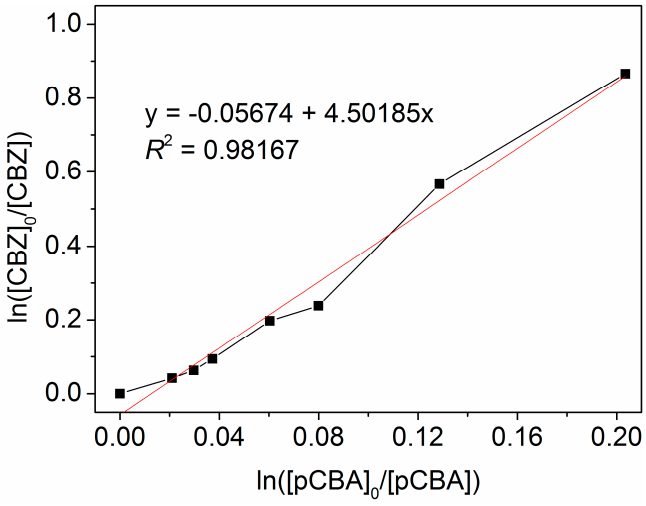


Fig. S8. -ln ([CBZ]/[CBZ]$_0$) vs -ln ([*p*CBA]/[*p*CBA]$_0$) ([CBZ]$_0$ = 5 μM, [*p*CBA]$_0$ = 50 μM, pH = 7.0, 24 ℃, BiOBr dose 0.5 g·L^{-1})

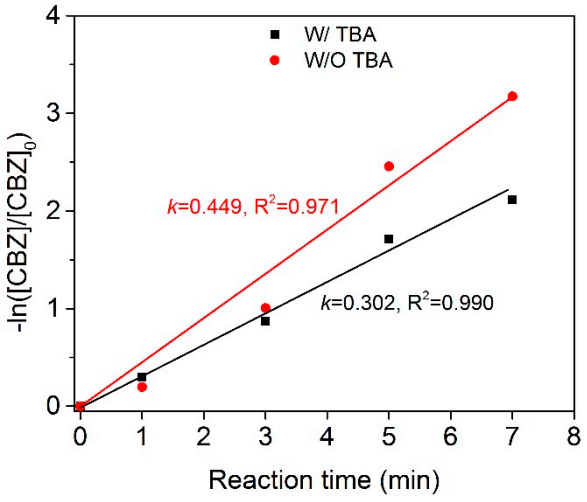


Fig. S9. CBZ degradation in the presence or absence of TBA. ([CBZ]$_0$ = 5 μM, [*p*CBA]$_0$ = 50 μM, [TBA]$_0$ = 1 mM, [PMS]$_0$ = 4 mM, pH = 7.0, 24 ℃, dosage of BiOBr 0.5 g·L^{-1})

Table S1. BET surface area, average pore and particle size, and pH_{pzc} of BiOX (X=Cl, Br, I)

BiOX	BET surface area ($m^2 \cdot g^{-1}$)	Average pore size (μm)	Particle size (nm)	pH_{pzc}
BiOCl	16.1	114.0	3.7	2.2
BiOBr	17.7	81.7	3.5	3.5
BiOI	64.9	163.0	0.9	2.5

References:

[1] Calza P., Marchisio S., Medana C., Baiocchi C. Fate of antibacterial spiramycin in river waters. *Anal. Bioanal. Chem.* **2010**, *396* 1539-1550.

[2] Freedman L.D., Doak G.O., Preparation, reactions, and physical-properties of organobismuth compounds. *Chem. Rev.* **1982**, *82*, 15-57.