

## Effects of inorganic ions on the photocatalytic degradation of carbamazepine

Xiaoya Gao, Qian Guo, Guangbei Tang, Wen Peng, Yongming Luo and Dedong He

### ABSTRACT

Carbamazepine (CBZ) is a typical class of pharmaceuticals and personal care products (PPCPs), and is a serious threat to the environment and human health. Photocatalytic degradation is an efficient technology to remove CBZ. However, the present work focused mainly on the improvement of photocatalytic degradation performance. The information about the effects of inorganic ions on the photocatalytic degradation activity of environmental pollutants is still scarce. This study systematically investigated the effects of inorganic ions on the photocatalytic degradation of CBZ in view of the practical applications. The addition of inorganic anions showed a negative effect on photocatalytic degradation of CBZ with the order of inhibition effects of  $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^-$ . This was due to the quenching effects of hydroxyl radicals or holes, which decreased the photocatalytic degradation of CBZ. The presence of  $\text{Al}^{3+}$  could adsorb on the surface of a photocatalyst to shield the active site, resulting in the decreased CBZ degradation, while coexistence of  $\text{Ca}^{2+}$  significantly promoted the photocatalytic degradation of CBZ owing to the enhanced CBZ adsorption.  $\text{Mg}^{2+}$  showed concentration and time-dependent effects (suppression or promotion) on the photocatalytic degradation of CBZ.

**Key words** | carbamazepine, inorganic anions, inorganic cations, photocatalysis degradation

Xiaoya Gao  
Qian Guo  
Guangbei Tang  
Wen Peng  
Yongming Luo  
Dedong He (corresponding author)  
Faculty of Environmental Science and Engineering,  
Kunming University of Science and Technology,  
Kunming 650500,  
China  
E-mail: [dedong.he@qq.com](mailto:dedong.he@qq.com)

### INTRODUCTION

Pharmaceuticals and personal care products (PPCPs), as emerging contaminants, are the subject of growing concern. Carbamazepine (CBZ) is a class of typical PPCPs which is mainly used to treat epilepsy, anti-central neuralgia, and prevent or treat manic depression. Its wide use has caused massive releases of CBZ into the environment (Yonetani *et al.* 2017; Ali *et al.* 2018). The presence of CBZ not only causes environmental pollution (Paz *et al.* 2016), but also poses a serious threat to human health. Therefore, an efficient technology must be developed to remove CBZ from the environment.

A variety of techniques have been applied to remove CBZ, such as adsorption, photocatalysis, and ozone oxidation (Hübner *et al.* 2014). Among them, photocatalytic technology can remove CBZ effectively. Our group has previously synthesized hierarchical BiOCl microspheres, and first demonstrated their excellent photocatalytic activity for CBZ degradation (Gao *et al.* 2015a, 2015b). To broaden the light absorption of BiOCl, we fabricated a visible-light-driven BiOCl photocatalyst via an ethylene glycol mediated solvothermal method (Gao *et al.* 2018). Our findings indicate that the BiOCl photocatalysis is a promising candidate for the efficient and cost-effective removal of recalcitrant pharmaceutical contaminants. Furthermore, the effectiveness of BiOCl photocatalysis in removing recalcitrant pharmaceutical contaminants

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (<http://creativecommons.org/licenses/by/4.0/>).

doi: 10.2166/wrd.2019.001

has also been demonstrated by another group (Zeng *et al.* 2018).

Unfortunately, photocatalytic technology is still limited in terms of practical applications due to the complicated effects of environmental coexistence (Rincon & Pulgarin 2004). For example, there are a variety of inorganic ions in water, including bicarbonate ions, nitrate ions, chloride ions, magnesium ions, calcium ions, and aluminum ions (Kanigaridou *et al.* 2017; Ramasamy *et al.* 2018). The presence of these ions can significantly affect photocatalytic degradation of organic pollutants (Bhatkhande *et al.* 2002). Research has shown that  $\text{Cl}^-$  and  $\text{NO}_3^-$  had an inhibiting effect on the degradation of methyl orange (Wang *et al.* 2013). Inorganic cations  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  had a suppressing effect on the photocatalytic degradation of bisphenol A (Wang *et al.* 2012). However, there are few reports about the effect of the presence of inorganic ions on the photocatalytic degradation activity of CBZ. Thus, there is a need to study inorganic ions to understand their influence on the degradation efficiency of CBZ. This will be beneficial to help govern the photocatalytic degradation of pollutants in real wastewater treatment, so as to effectively solve the problem of organic pollutants.

Therefore, in this study, the effects of inorganic ions on the photocatalytic degradation of CBZ over the visible-light-driven BiOCl photocatalyst were systematically explored. Batch experiments were performed to examine the effects of common inorganic anions ( $\text{HCO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ ) and cations ( $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) on the photocatalytic degradation efficiency and degradation kinetics of CBZ. Furthermore, the underlying mechanism was discussed, based on the experimental data.

## MATERIALS AND METHODS

### Materials

A visible-light-driven BiOCl photocatalyst was used throughout the whole experiment. The preparation details have been reported previously (Gao *et al.* 2018). Briefly,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (0.02 mol) and KCl (0.02 mol) were dissolved in ethylene glycol by stirring for 90 min to obtain a homogeneous solution. The solution was transferred to

a Teflon-lined autoclave and kept at 160 °C for 12 h. Then, the autoclave was cooled down to room temperature naturally. Finally, the product was centrifuged, washed thoroughly, and dried for photocatalytic activity testing.

Sodium chloride (NaCl), sodium nitrate ( $\text{NaNO}_3$ ), sodium hydrogencarbonate ( $\text{NaHCO}_3$ ), magnesium chloride ( $\text{MgCl}_2$ ), calcium chloride ( $\text{CaCl}_2$ ), and aluminum chloride ( $\text{AlCl}_3$ ) were obtained commercially from Sino-pharm Chemical Reagent Co., Ltd (Shanghai, China). Carbamazepine (CBZ, >98%) was provided by Aladdin (Beijing, China). Deionized water was used throughout the entire experiment.

### Methods

A stock solution of CBZ ( $500 \text{ mg} \cdot \text{L}^{-1}$ ) was prepared and was diluted with deionized water to  $2.5 \text{ mg} \cdot \text{L}^{-1}$ . Batch experiments were carried out on a photocatalytic reactor irradiated by a 350-W xenon lamp. The beaker containing the reaction solution was placed in a thermostatic water bath and stirred by a magnetic stirrer. The vertical distance between the light source and the reactor was 20 cm. Typically, 0.04 g of photocatalyst and 1 mL of the investigated ions solution were added to the 50 mL CBZ solution. Then the solution was placed in the dark and stirred by a magnetic stirrer to achieve adsorption. After adsorption equilibrium, the light source was turned on, and the solution was placed in an irradiation state to undergo photocatalytic degradation reaction.

The effects of coexisting anions of  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$  on the photocatalytic degradation of CBZ were examined by adding various concentrations of  $\text{NaHCO}_3$ , NaCl, and  $\text{NaNO}_3$ , respectively. The influences of inorganic cations of  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were investigated by adding  $\text{AlCl}_3$ ,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$ , respectively.

### Photocatalytic efficiency

Upon irradiation, the concentration of CBZ solution was analyzed at intervals by a Varian Cary-50 UV-vis spectrophotometer. The photocatalytic efficiency was calculated

by the following formula (Equation (1)):

$$\text{Photocatalytic efficiency \%} = (C_0 - C)/C_0 \times 100/C_0 \quad (1)$$

where  $C_0$  and  $C$  are the CBZ concentration prior to irradiation and after irradiation in 5 min intervals, respectively.

### Photocatalytic kinetic

The photocatalytic degradation kinetic of CBZ was recorded as a function of irradiation time. The data were fitted to a second-order rate model (Equation (2)):

$$\ln(1/C - 1/C_0) = kt + \ln(1/C_1 - 1/C_0) \quad (2)$$

where  $k$  is the pseudo-second order rate constant,  $C_0$  is the initial concentration of CBZ,  $C_1$  is the concentration of CBZ after adsorption equilibrium, and  $C$  is the concentration of CBZ after irradiation in 5 min intervals.

## RESULTS AND DISCUSSION

### Specifications of BiOCl photocatalyst

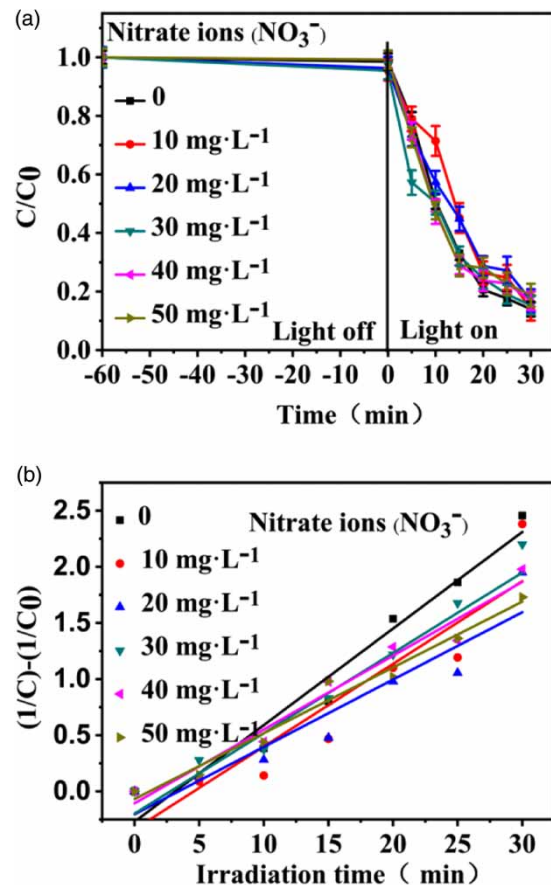
BiOCl photocatalyst with high purity was used in the present study. The BiOCl photocatalyst shows compact hierarchical structures. Calculated by Scherrer equation, the crystalline size of BiOCl is 14.3 nm. Moreover, hydroxyl groups appeared on the surface of BiOCl with highly exposed facets of (110) lattice plane.

### Effect of inorganic anions

Actual water samples contain a large amount of various inorganic ions, thus the process of research on CBZ photocatalytic degradation in deionized water is very different from the actual situation (Ravikumar *et al.* 2010). Therefore, we studied the effects on photocatalytic degradation of CBZ by adding three different anions in environmentally relevant concentrations to the photocatalytic reaction system.

### Effect of nitrate ions ( $\text{NO}_3^-$ )

The effect of  $\text{NO}_3^-$  on photocatalytic degradation of CBZ is provided in Figure 1. The added concentration of  $\text{NO}_3^-$  was 10, 20, 30, 40, and 50  $\text{mg}\cdot\text{L}^{-1}$ , respectively. The presence of  $\text{NO}_3^-$  slightly decreased the degradation efficiency of CBZ. The inhibition effects of  $\text{NO}_3^-$  can be explained by the fact that  $\text{NO}_3^-$  could act as a radical scavenger, which reacts with positive holes ( $h^+$ ) and hydroxyl radical ( $\cdot\text{OH}$ ) (Equations (3) and (4)) (Wang *et al.* 2012; Dugandžić *et al.* 2017). Although new radicals generate in the reaction, their activity was lower than  $h^+$  and  $\cdot\text{OH}$ . Therefore, there is a slight decrease in the photocatalytic degradation efficiency of CBZ in the presence of  $\text{NO}_3^-$ . The results were consistent with the previous report that  $\text{NO}_3^-$  decreased the photodegradation of pollutants (Wang *et al.* 2012).



**Figure 1** | Effect of nitrate ions ( $\text{NO}_3^-$ ) on CBZ degradation under simulated solar light irradiation. Time-course variation of (a)  $C/C_0$  of CBZ solution and (b) pseudo-second order kinetics for the degradation of CBZ ( $[\text{CBZ}]_0 = 2.5 \text{ mg}\cdot\text{L}^{-1}$ ;  $[\text{BiOCl}] = 0.8 \text{ g}\cdot\text{L}^{-1}$ ).

The pseudo-second order model was applied to evaluate the CBZ degradation process in the presence of  $\text{NO}_3^-$ . As shown in Figure 1(b), all the CBZ degradation followed the pseudo-second order kinetic. The degradation rate constant of  $k$  decreased from 0.0860 to 0.0586  $\text{mg}^{-1}\cdot\text{L}\cdot\text{min}^{-1}$  at the  $\text{NO}_3^-$  concentration of 50  $\text{mg}\cdot\text{L}^{-1}$ . The half-life of CBZ during photocatalysis in the presence of inorganic anions is presented in Table 1. The half-life of CBZ during photocatalysis was longest at the  $\text{NO}_3^-$  concentration of 20  $\text{mg}\cdot\text{L}^{-1}$ .

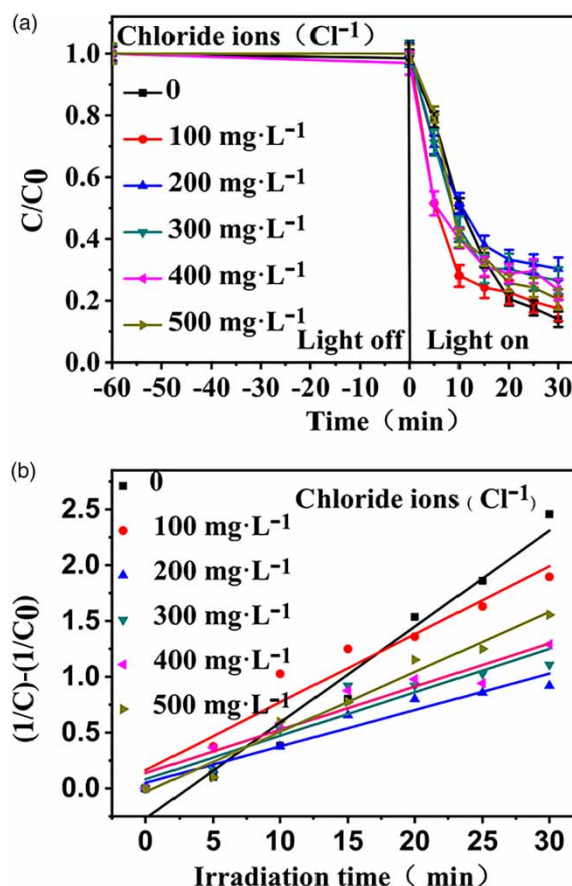


### Effect of chloride ions ( $\text{Cl}^-$ )

The effects of  $\text{Cl}^-$  on the photocatalytic degradation of CBZ were studied with various concentrations of 100, 200, 300, 400, and 500  $\text{mg}\cdot\text{L}^{-1}$ , respectively. As shown in Figure 2, it is interesting to find that almost all concentrations of  $\text{Cl}^-$  improve the photocatalytic degradation of CBZ in the first 15 min irradiation. However, inhibited photocatalytic degradation of CBZ was observed in all concentrations of  $\text{Cl}^-$  during the subsequent photocatalytic process. It was reported that the  $\text{Cl}^-$  could react with  $h^+$  and  $\bullet\text{OH}$  to form chlorine radicals ( $\text{Cl}^{\bullet}$ , Equations (5)–(7)) (Neppolian et al.

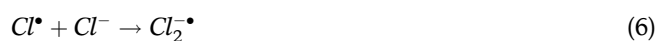
**Table 1** | The half-life of CBZ during photocatalysis in the presence of inorganic anions

| Inorganic anions | Concentration ( $\text{mg}\cdot\text{L}^{-1}$ ) | Half-life of CBZ (min) |
|------------------|---|------------------------|
| $\text{NO}_3^-$  | 10  | 9.41                   |
|                  | 20  | 11.55                  |
|                  | 30  | 9.69                   |
|                  | 40  | 10.54                  |
|                  | 50  | 11.83                  |
| $\text{Cl}^-$    | 100   | 6.57                   |
|                  | 200   | 12.28                  |
|                  | 300   | 10.27                  |
|                  | 400   | 10.33                  |
|                  | 500   | 7.44                   |
| $\text{HCO}_3^-$ | 50  | 136.05                 |
|                  | 100   | 154.44                 |
|                  | 150   | 51.88                  |
|                  | 200   | 152.67                 |



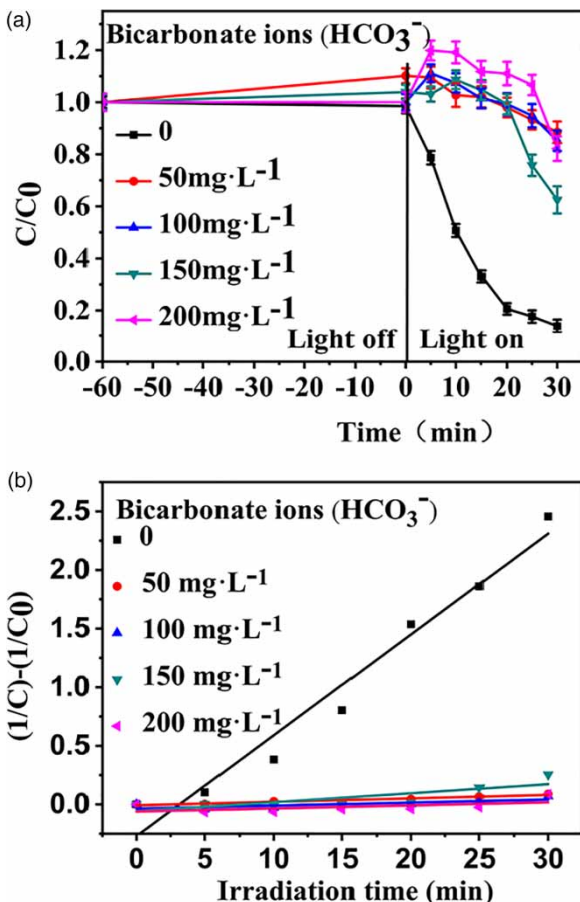
**Figure 2** | Effect of chloride ions ( $\text{Cl}^-$ ) on CBZ degradation under simulated solar light irradiation. Time-course variation of (a)  $C/C_0$  of CBZ solution and (b) pseudo-second order kinetics for the degradation of CBZ ( $[\text{CBZ}]_0 = 2.5 \text{ mg}\cdot\text{L}^{-1}$ ;  $[\text{BiOCl}] = 0.8 \text{ g}\cdot\text{L}^{-1}$ ).

2002).  $\text{Cl}^-$  could participate in the CBZ degradation, thus improving the photocatalytic degradation of CBZ, while  $\text{Cl}^{\bullet}$  might form a chlorinated derivative of CBZ (Wang et al. 2017) which hinders the further degradation of CBZ with longer experimental durations. The most significant inhibited effect of  $\text{Cl}^-$  was observed in the concentration of 200  $\text{mg}\cdot\text{L}^{-1}$ . The pseudo-second order degradation rate was 0.0326  $\text{mg}^{-1}\cdot\text{L}\cdot\text{min}^{-1}$ . At the same concentration, the half-life of CBZ during photocatalysis reached the maximum, which is 12.28 min.



### Effect of bicarbonate ions ( $\text{HCO}_3^-$ )

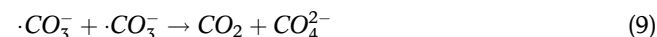
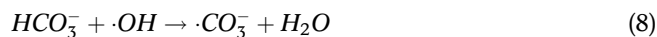
$\text{HCO}_3^-$  is an important substance in water. Here, we investigated the effect of the addition of  $\text{HCO}_3^-$  on photocatalytic degradation of CBZ. The added concentrations were 50, 100, 150, and 200  $\text{mg}\cdot\text{L}^{-1}$ , respectively. As can be seen from Figure 3,  $\text{HCO}_3^-$  had a significant negative effect on degradation of CBZ. After 60 min of adsorption process, the concentration of CBZ was determined to be increased compared to that prior to adsorption. This phenomenon was particularly remarkable at the concentration of 100  $\text{mg}\cdot\text{L}^{-1}$  of  $\text{HCO}_3^-$ . This was due to the varied pH in the solution in the presence of  $\text{HCO}_3^-$ , which changed the dissociation of CBZ. When the added concentration of  $\text{HCO}_3^-$  was 200  $\text{mg}\cdot\text{L}^{-1}$ , the degradation rate was decreased to 18%.



**Figure 3** | Effect of bicarbonate ions ( $\text{HCO}_3^-$ ) on CBZ degradation under simulated solar light irradiation. Time-course variation of (a)  $C/C_0$  of CBZ solution and (b) pseudo-second order kinetics for the degradation of CBZ ( $[\text{CBZ}]_0 = 2.5 \text{ mg}\cdot\text{L}^{-1}$ ;  $[\text{BiOCl}] = 0.8 \text{ g}\cdot\text{L}^{-1}$ ).

As shown in Figure 3(b), the CBZ degradation process abided by the pseudo-second order model at all  $\text{HCO}_3^-$  concentrations. However, the degradation rate constant of  $k$  decreased from 0.0860 to 0.0026  $\text{mg}^{-1}\cdot\text{L}\cdot\text{min}^{-1}$  due to the coexistence of  $\text{HCO}_3^-$  (200  $\text{mg}\cdot\text{L}^{-1}$ ). Additionally, due to the significant negative effect of  $\text{HCO}_3^-$ , the half-life of CBZ became longer. At the concentration of 100  $\text{mg}\cdot\text{L}^{-1}$ , the half-life of CBZ reached 154.44 min, which is 15.36 times longer than photocatalytic degradation of CBZ without adding  $\text{HCO}_3^-$ .

$\text{HCO}_3^-$  could act as a scavenger for hydroxyl radicals (Kanigaridou *et al.* 2017) (Equations (8) and (9)). Therefore, the degradation of contaminants will be inhibited in the presence of  $\text{HCO}_3^-$  (Pelaez *et al.* 2011). On the other hand, although  $\cdot\text{OH}$  is consumed, the degradation of some pollutants including cylindrospermopsin and ethylparaben is not greatly affected due to the formation of carbonate radicals ( $\text{CO}_3^{\cdot-}$ ) (Petala *et al.* 2015; Zhang *et al.* 2015). In addition,  $\text{CO}_3^{\cdot-}$  could play a leading role in some pollutant degradation processes and thus improve the degradation efficiency (Peralta-Zamora *et al.* 2001). Therefore, the effect of the addition of  $\text{HCO}_3^-$  on photocatalytic degradation is related to specific conditions such as the reaction system, the type of contaminant, the type of catalyst, and so on.



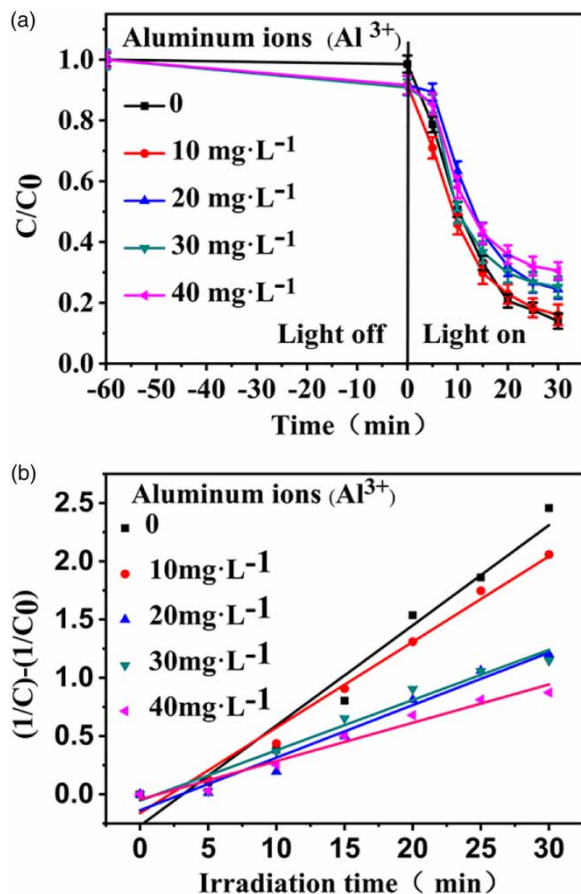
Based on the above analysis, it can be seen that the effects of the three anions on photocatalytic degradation of CBZ are different, and the order of inhibition of ions on the reaction is  $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^-$ .

### Effect of inorganic cations

There are a variety of cations in natural waters. Herein, the effects of three typical cations on photocatalytic degradation of CBZ were investigated.

### Effect of aluminum ions ( $\text{Al}^{3+}$ )

It can be seen from Figure 4 that  $\text{Al}^{3+}$  has a negative effect on the photocatalytic degradation of CBZ. The added



**Figure 4** | Effect of aluminum ions ( $\text{Al}^{3+}$ ) on CBZ degradation under simulated solar light irradiation. Time-course variation of (a)  $C/C_0$  of CBZ solution and (b) pseudo-second order kinetics for the degradation of CBZ ( $[\text{CBZ}]_0 = 2.5 \text{ mg}\cdot\text{L}^{-1}$ ;  $[\text{BiOC}] = 0.8 \text{ g}\cdot\text{L}^{-1}$ ).

concentrations of  $\text{Al}^{3+}$  were 10, 20, 30, and 40  $\text{mg}\cdot\text{L}^{-1}$ , respectively. With the concentrations of  $\text{Al}^{3+}$  increasing from 10  $\text{mg}\cdot\text{L}^{-1}$  to 40  $\text{mg}\cdot\text{L}^{-1}$ , the inhibition on the photocatalytic degradation of CBZ was also enhanced. When the added concentration of  $\text{Al}^{3+}$  was 40  $\text{mg}\cdot\text{L}^{-1}$ , the photocatalytic degradation efficiency was reduced about 16% compared to the solution without  $\text{Al}^{3+}$ . The degradation kinetics of CBZ was quantitatively calculated according to the pseudo-second order model, as shown in Figure 4(b). The  $k$  value of CBZ degradation decreased to  $0.0329 \text{ mg}^{-1}\cdot\text{L}\cdot\text{min}^{-1}$  at the concentration of 40  $\text{mg}\cdot\text{L}^{-1}$ , confirming the inhibited degradation kinetics of CBZ in the presence of  $\text{Al}^{3+}$ . Table 2 displays the half-life of CBZ during photocatalysis in the presence of inorganic cations. The longest half-life of CBZ during photocatalysis in the presence of  $\text{Al}^{3+}$  was observed in the concentration of 20  $\text{mg}\cdot\text{L}^{-1}$  with 12.16 min.

**Table 2** | The half-life of CBZ during photocatalysis in the presence of inorganic cations

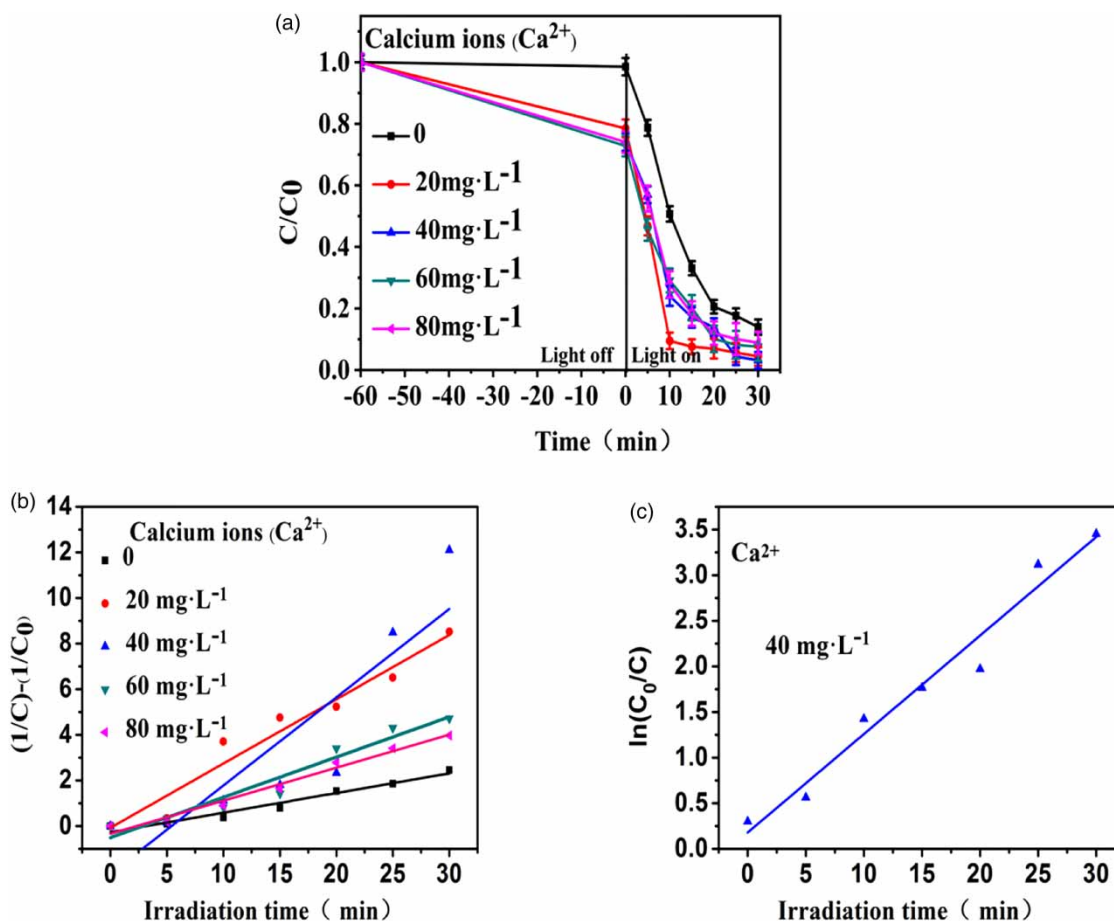
| Inorganic cations | Concentration ( $\text{mg}\cdot\text{L}^{-1}$ ) | Half-life of CBZ (min) |
|-------------------|---|------------------------|
| $\text{Al}^{3+}$  | 10  | 8.87                   |
|                   | 20  | 9.27                   |
|                   | 30  | 9.43                   |
|                   | 40  | 12.16                  |
| $\text{Ca}^{2+}$  | 20  | 2.46                   |
|                   | 40  | 6.42                   |
|                   | 60  | 3.93                   |
|                   | 80  | 4.78                   |
| $\text{Mg}^{2+}$  | 5   | 12.18                  |
|                   | 10  | 9.38                   |
|                   | 15  | 10.20                  |
|                   | 20  | 8.92                   |

The photocatalyst used here was rich in surface hydroxyl. Surface hydroxyl was considered to be the most photoactive group for the photocatalytic degradation of organic pollutant.  $\text{Al}^{3+}$  was reported to be able to adsorb on the hydroxyl groups, reducing the photocatalytic activity (Santiago *et al.* 2014).

#### Effect of calcium ions ( $\text{Ca}^{2+}$ )

The effect of  $\text{Ca}^{2+}$  on photocatalytic degradation of CBZ is shown in Figure 5. As shown, the presence of  $\text{Ca}^{2+}$  significantly promoted the photocatalytic degradation of CBZ. In particular, for  $\text{Ca}^{2+}$  at a relatively low concentration of 40  $\text{mg}\cdot\text{L}^{-1}$ , the photocatalytic degradation efficiency of CBZ can reach 96.84%, which was an increase of 10.81% compared to the degradation solution without  $\text{Ca}^{2+}$ . Interestingly, it was found that the degradation kinetics of CBZ was changed from a pseudo-second order model to pseudo-first order model in the presence of 40  $\text{mg}\cdot\text{L}^{-1}$  of  $\text{Ca}^{2+}$  with a  $k$  value of  $0.1080 \text{ min}^{-1}$ . The fastest degradation kinetics appeared in the concentration of 20  $\text{mg}\cdot\text{L}^{-1}$  with a  $k$  value of  $0.2816 \text{ mg}^{-1}\cdot\text{L}\cdot\text{min}^{-1}$ , which is 3.27 times greater than photocatalytic degradation of CBZ without adding  $\text{Ca}^{2+}$ . At the same concentration of  $\text{Ca}^{2+}$ , the half-life of CBZ was reduced to 2.46 min due to the positive effect of  $\text{Ca}^{2+}$ .

The photocatalytic degradation was dominated by a serious active species, which originated from the photo-induced hole and electron transfer to the adsorbed species (acceptor) on the surface of photocatalysts. It is thermodynamically required that the redox potential of the acceptor is



**Figure 5** | Effect of calcium ions ( $\text{Ca}^{2+}$ ) on CBZ degradation under simulated solar light irradiation. Time-course variation of (a)  $C/C_0$  of CBZ solution, (b) pseudo-second order kinetics for the degradation of CBZ, and (c) pseudo-first order kinetics for the degradation of CBZ in the presence of 40  $\text{mg}\cdot\text{L}^{-1}$  of  $\text{Ca}^{2+}$  ( $[\text{CBZ}]_0 = 2.5 \text{ mg}\cdot\text{L}^{-1}$ ;  $[\text{BiOCl}] = 0.8 \text{ g}\cdot\text{L}^{-1}$ ).

more negative than the valence band potential (oxidation reaction) or more positive than the conduction band potential (reduction reaction). Therefore, the effect of cations on the photocatalytic degradation of pollutants is strongly dependent on the redox potential of the metal.

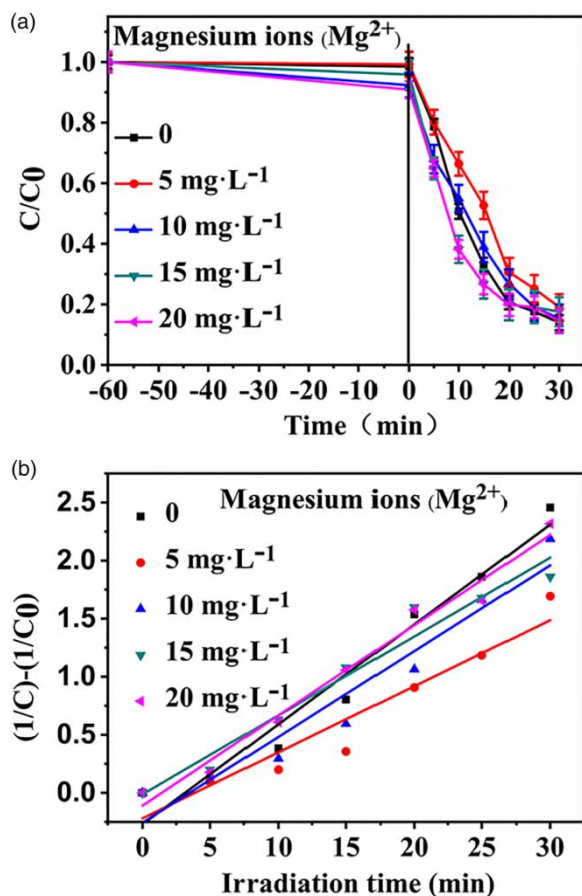
The potential for the valence band of BiOCl is about 3.55 eV and for the conduction band it is 0.11 eV (Ye *et al.* 2012). The standard redox potential is  $-2.87 \text{ V}$  for ( $E^\theta\text{Ca}^{2+}/\text{Ca}$ ) (Santiago *et al.* 2014). A comparison of the value with those from the band edge potentials of BiOCl implies that  $\text{Ca}^{2+}$  is not able to react with the photogenerated holes or electrons. From this point of view,  $\text{Ca}^{2+}$  could pose a negligible effect on the photocatalytic degradation of CBZ.

It was found that the adsorption of CBZ on the BiOCl photocatalysts was enhanced with the addition of  $\text{Ca}^{2+}$ .

The adsorption is important for a photocatalytic degradation reaction to occur. In fact, the CBZ adsorption on BiOCl is negligible without the addition of  $\text{Ca}^{2+}$  due to negative charges on both CBZ and BiOCl. The positive  $\text{Ca}^{2+}$  could bridge between BiOCl and CBZ to facilitate the adsorption (about 22–27% increases), which was beneficial for the photocatalytic degradation of CBZ.

#### Effect of magnesium ions ( $\text{Mg}^{2+}$ )

Figure 6 shows the effect of  $\text{Mg}^{2+}$  on photocatalytic degradation of CBZ. The added concentration of  $\text{Mg}^{2+}$  was 5, 10, 15, and 20  $\text{mg}\cdot\text{L}^{-1}$ , respectively. The presence of  $\text{Mg}^{2+}$  increased the CBZ adsorption significantly (10%). Due to the increase of adsorption, the CBZ degradation improved slightly in the first 5 min at the  $\text{Mg}^{2+}$  concentrations of 10,



**Figure 6** | Effect of magnesium ions ( $Mg^{2+}$ ) on CBZ degradation under simulated solar light irradiation. Time-course variation of (a)  $C/C_0$  of CBZ solution and (b) pseudo-second order kinetics for the degradation of CBZ ( $[CBZ]_0 = 2.5 \text{ mg}\cdot\text{L}^{-1}$ ;  $[BiOCl] = 0.8 \text{ g}\cdot\text{L}^{-1}$ ).

15, and  $20 \text{ mg}\cdot\text{L}^{-1}$ . As a whole, the influence of all the concentrations of  $Mg^{2+}$  was not obvious with longer experimental durations of 30 min. As shown in Figure 6(b), the CBZ degradation process abided by pseudo-second order model at all  $Mg^{2+}$  concentrations. The degradation rate constant of  $k$  decreased from  $0.0860$  to  $0.0569 \text{ mg}^{-1}\cdot\text{L}\cdot\text{min}^{-1}$  due to the coexistence of  $Mg^{2+}$  ( $5 \text{ mg}\cdot\text{L}^{-1}$ ). However, high concentrations of 10, 15, and  $20 \text{ mg}\cdot\text{L}^{-1}$  did show significant changes in the degradation rate constant. Consistently, the half-life of CBZ changed from 8.06 to 12.18 min in the presence of  $Mg^{2+}$  ( $5 \text{ mg}\cdot\text{L}^{-1}$ ). However, the half-life of CBZ showed no significant difference at high concentrations of  $Mg^{2+}$ .

$Al^{3+}$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  ions are the common inorganic cations in the aquatic environment. All these metal ions are in the highest and most stable oxidation state, which

cannot capture photo-induced holes or electrons in solution (Wang *et al.* 2012). In some reports, cations were hypothesized to show no significant impacts on the photodegradation of pollutants. However, we found that these cations could adsorb on the surface of photocatalysts, thereby influencing the photocatalytic degradation of CBZ.

## CONCLUSIONS

The effect of various ions on the photocatalytic degradation of CBZ was investigated in the presence of the BiOCl photocatalyst. The addition of inorganic anions showed a negative effect on photocatalytic degradation of CBZ with the order of inhibition effects of  $HCO_3^- > Cl^- > NO_3^-$ , which was due to the quenching effects of hydroxyl radicals or holes. The coexistence of inorganic cations influences the photocatalytic degradation of CBZ based on a different mechanism: cations could adsorb on the surface of the photocatalyst, thereby affecting the photocatalytic degradation of CBZ.  $Al^{3+}$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  exhibited suppression, promotion, and concentration-dependent effects on the photocatalytic degradation of CBZ. Considering the varied effect of inorganic ions on CBZ degradation, complicated effects of environmental coexistence must be considered in the practical application of photocatalytic technology.

## ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (U1402233) and the High-level Scientific Research Foundation for Talent Introduction of Kunming University of Science and Technology (10978172).

## REFERENCES

- Ali, F., Khan, J. A., Shah, N. S., Sayed, M. & Khan, H. M. 2018 Carbamazepine degradation by UV and UV-assisted AOPs: kinetics, mechanism and toxicity investigations. *Process Safety and Environmental Protection* **117**, 307–314.
- Bhatkhande, D. S., Pangarkar, V. G. & Beenackers, A. A. C. M. 2002 Photocatalytic degradation for environmental



- applications – a review. *Journal of Chemical Technology and Biotechnology* **77** (1), 102–116.
- Dugandžić, A. M., Tomašević, A. V., Radišić, M. M., Šekuljica, N. Ž., Mijin, D. Ž. & Petrović, S. D. 2017 Effect of inorganic ions, photosensitisers and scavengers on the photocatalytic degradation of nicosulfuron. *Journal of Photochemistry and Photobiology A: Chemistry* **336**, 146–155.
- Gao, X., Zhang, X., Wang, Y., Peng, S., Yue, B. & Fan, C. 2015a Rapid synthesis of hierarchical BiOCl microspheres for efficient photocatalytic degradation of carbamazepine under simulated solar irradiation. *Chemical Engineering Journal* **263**, 419–426.
- Gao, X., Zhang, X., Wang, Y., Peng, S., Yue, B. & Fan, C. 2015b Photocatalytic degradation of carbamazepine using hierarchical BiOCl microspheres: some key operating parameters, degradation intermediates and reaction pathway. *Chemical Engineering Journal* **273**, 156–165.
- Gao, X., Peng, W., Tang, G., Guo, Q. & Luo, Y. 2018 Highly efficient and visible-light-driven BiOCl for photocatalytic degradation of carbamazepine. *Journal of Alloys and Compounds* **757**, 455–465.
- Hübner, U., Seiwert, B., Reemtsma, T. & Jekel, M. 2014 Ozonation products of carbamazepine and their removal from secondary effluents by soil aquifer treatment—indications from column experiments. *Water Research* **49**, 34–43.
- Kanigaridou, Y., Petala, A., Frontistis, Z., Antonopoulou, M., Solakidou, M., Konstantinou, I., Deligiannakis, Y., Mantzavunis, D. & Kondarides, D. I. 2017 Solar photocatalytic degradation of bisphenol A with CuO<sub>x</sub>/BiVO<sub>4</sub>: insights into the unexpectedly favorable effect of bicarbonates. *Chemical Engineering Journal* **318**, 39–49.
- Neppolian, B., Choi, H. C., Sakthivel, S., Arabindoo, B. & Murugesan, V. 2002 Solar light induced and TiO<sub>2</sub> assisted degradation of textile dye reactive blue. *Chemosphere* **46** (8), 1173–1181.
- Paz, A., Tadmor, G., Malchi, T., Blotvogel, J., Borch, T., Polubesova, T. & Chefetz, B. 2016 Fate of carbamazepine, its metabolites, and lamotrigine in soils irrigated with reclaimed wastewater: sorption, leaching and plant uptake. *Chemosphere* **160**, 22–29.
- Pelaez, M., Armah, A., O'Shea, K., Falaras, P. & Dionysiou, D. D. 2011 Effects of water parameters on the degradation of microcystin-LR under visible light-activated TiO<sub>2</sub> photocatalyst. *Water Research* **45** (12), 3787–3796.
- Peralta-Zamora, P., Gouvêa, C. A., Wypych, F. & Durán, N. 2001 Effect of Na<sub>2</sub>CO<sub>3</sub> on the photocatalytic degradation of remazol brilliant blue R. *Toxicological and Environmental Chemistry* **80** (1–2), 83–93.
- Petala, A., Frontistis, Z., Antonopoulou, M., Konstantinou, I., Kondarides, D. I. & Mantzavinos, D. 2015 Kinetics of ethyl paraben degradation by simulated solar radiation in the presence of N-doped TiO<sub>2</sub> catalysts. *Water Research* **81**, 157–166.
- Ramasamy, V., Mohana, V. & Rajendran, V. 2018 Characterization of Ca doped CeO quantum dots and their applications in photocatalytic degradation. *OpenNano* **3**, 38–47.
- Ravikumar, P., Venkatesharaju, K. & Somashekar, R. K. 2010 Major ion chemistry and hydrochemical studies of groundwater of Bangalore South Taluk, India. *Environmental Monitoring and Assessment* **163** (1–4), 643–653.
- Rincon, A. G. & Pulgarin, C. 2004 Inorganic ions, organic matter and H<sub>2</sub>O<sub>2</sub> on *E. coli* K12 photocatalytic inactivation by TiO<sub>2</sub> implications in solar water disinfection. *Applied Catalysis B: Environmental* **51** (4), 283–302.
- Santiago, D. E., Araña, J., González-Díaz, O., Al Mán-Dominguez, M. E., Acosta-Dacal, A. C., Fernandez-Rodríguez, C., Pérez-Peña, J. & Doña-Rodríguez, J. M. 2014 Effect of inorganic ions on the photocatalytic treatment of agro-industrial wastewaters containing imazalil. *Applied Catalysis B: Environmental* **156**, 284–292.
- Wang, C., Zhu, L., Wei, M., Chen, P. & Shan, G. 2012 Photolytic reaction mechanism and impacts of coexisting substances on photodegradation of bisphenol A by Bi<sub>2</sub>WO<sub>6</sub> in water. *Water Research* **46** (3), 845–853.
- Wang, Y., Lu, K. & Feng, C. 2013 Influence of inorganic anions and organic additives on photocatalytic degradation of methyl orange with supported polyoxometalates as photocatalyst. *Journal of Rare Earths* **31** (4), 360–365.
- Wang, W. L., Wu, Q. Y., Li, Z. M., Lu, Y., Du, Y., Wang, T., Huang, N. & Hu, H. Y. 2017 Light-emitting diodes as an emerging UV source for UV/chlorine oxidation: carbamazepine degradation and toxicity changes. *Chemical Engineering Journal* **310**, 148–156.
- Ye, L., Liu, J., Gong, C., Tian, L., Peng, T. & Zan, L. 2012 Two different roles of metallic Ag on Ag/AgX/BiOX (X = Cl, Br) visible light photocatalysts: surface plasmon resonance and Z-scheme bridge. *ACS Catalysis* **2** (8), 1677–1683.
- Yonetani, T., Echigo, S. & Itoh, S. 2017 Fate of selected pharmaceuticals and their metabolites in soil aquifer treatment. *Journal of Water Reuse and Desalination* **7** (2), 142–151.
- Zeng, X., Gong, X., Wan, Y., He, R. & Xu, Z. 2018 Formation of oxygen vacancies on the {010} facets of BiOCl and visible light activity for degradation of ciprofloxacin. *Chemical Research in Chinese Universities* **34** (5), 711–718.
- Zhang, G., He, X., Nadagouda, M. N., O'Shea, K. E. & Dionysiou, D. D. 2015 The effect of basic pH and carbonate ion on the mechanism of photocatalytic destruction of cylindrospermopsin. *Water Research* **73**, 353–361.

First received 25 January 2019; accepted in revised form 1 April 2019. Available online 30 April 2019