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

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. 2014; 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
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. 2015). Research has shown that Cl⁻ and NO₃ had an inhibiting effect on the degradation of methyl orange (Wang et al. 2016). Inorganic cations Mg²⁺, Ca²⁺, Na⁺, and 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 (HCO₃⁻, Cl⁻, and NO₃⁻) and cations (Al³⁺, Ca²⁺, and Mg²⁺) 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, Bi(NO₃)₃·5H₂O (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 (NaNO₃), sodium hydrogen carbonate (NaHCO₃), magnesium chloride (MgCl₂), calcium chloride (CaCl₂), and aluminum chloride (AlCl₃) were obtained commercially from Sinopharm 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 mg·L⁻¹) was prepared and was diluted with deionized water to 2.5 mg·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 HCO₃⁻, Cl⁻, and NO₃⁻ on the photocatalytic degradation of CBZ were examined by adding various concentrations of NaHCO₃, NaCl, and NaNO₃, respectively. The influences of inorganic cations of Al³⁺, Ca²⁺, and Mg²⁺ were investigated by adding AlCl₃, CaCl₂, and MgCl₂, 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)):

\[
\text{Photocatalytic efficiency } \%_0 = \left(\frac{C_0 - C}{C_0}\right) \times 100/0_0
\]  

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)):

\[
\ln\left(\frac{1}{1 - C/C_0}\right) = kt + \ln\left(\frac{1}{1 - C_1/C_0}\right)
\]  

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 (NO\(_3^−\))**

The effect of NO\(_3^−\) on photocatalytic degradation of CBZ is provided in Figure 1. The added concentration of NO\(_3^−\) was 10, 20, 30, 40, and 50 mg·L\(^{-1}\), respectively. The presence of NO\(_3^−\) slightly decreased the degradation efficiency of CBZ. The inhibition effects of NO\(_3^−\) can be explained by the fact that NO\(_3^−\) could act as a radical scavenger, which reacts with positive holes (\(h^+\)) and hydroxyl radical (\(\cdot\)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 \(\cdot\)OH. Therefore, there is a slight decrease in the photocatalytic degradation efficiency of CBZ in the presence of NO\(_3^−\). The results were consistent with the previous report that NO\(_3^−\) decreased the photodegradation of pollutants (Wang et al. 2012).

![Figure 1: Effect of nitrate ions (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 ([CBZ]\(_0\) = 2.5 mg·L\(^{-1}\); [BiOCl] = 0.8 g·L\(^{-1}\)).](https://iwaponline.com/jwrd/article-pdf/9/3/301/599046/jwrd0090301.pdf)
The pseudo-second order model was applied to evaluate the CBZ degradation process in the presence of 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 mg L$^{-1}$·min$^{-1}$ at the NO$_3$ concentration of 50 mg 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 NO$_3$ concentration of 20 mg L$^{-1}$.

\begin{align*}
NO_3^- + h_{VB}^+ &\rightarrow NO_2^+ \tag{3} \\
NO_3^- + \cdot OH &\rightarrow NO_2^+ + OH^- \tag{4}
\end{align*}

**Effect of chloride ions (Cl$^-$)**

The effects of Cl$^-$ on the photocatalytic degradation of CBZ were studied with various concentrations of 100, 200, 300, 400, and 500 mg L$^{-1}$, respectively. As shown in Figure 2, it is interesting to find that almost all concentrations of 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 Cl$^-$ during the subsequent photocatalytic process. It was reported that the Cl$^-$ could react with $h^+$ and $\cdot$OH to form chlorine radicals (Cl, Equations (5)–(7)) (Neppolian et al. 2002). Cl$^-$ could participate in the CBZ degradation, thus improving the photocatalytic degradation of CBZ, while Cl$^-$ 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 Cl$^-$ was observed in the concentration of 200 mg L$^{-1}$. The pseudo-second order degradation rate was 0.0326 mg L$^{-1}$·min$^{-1}$. At the same concentration, the half-life of CBZ during photocatalysis reached the maximum, which is 12.28 min.

\begin{align*}
Cl^- + h_{VB}^+ &\rightarrow Cl^* \tag{5} \\
Cl^* + Cl^- &\rightarrow Cl_2^* \tag{6} \\
OH^* + Cl^- &\rightarrow Cl^* + OH^- \tag{7}
\end{align*}

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

<table>
<thead>
<tr>
<th>Inorganic anions</th>
<th>Concentration (mg L$^{-1}$)</th>
<th>Half-life of CBZ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$</td>
<td>10</td>
<td>9.41</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>11.55</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>9.69</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>10.54</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>11.83</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>100</td>
<td>6.57</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>12.28</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>10.27</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>10.33</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>7.44</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>50</td>
<td>136.05</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>154.44</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>51.88</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>152.67</td>
</tr>
</tbody>
</table>
Effect of bicarbonate ions (HCO$_3^-$)

HCO$_3^-$ is an important substance in water. Here, we investigated the effect of the addition of HCO$_3^-$ on photocatalytic degradation of CBZ. The added concentrations were 50, 100, 150, and 200 mg·L$^{-1}$, respectively. As can be seen from Figure 3, 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 mg·L$^{-1}$ of HCO$_3^-$, which changed the dissociation of CBZ. When the added concentration of HCO$_3^-$ was 200 mg·L$^{-1}$, the degradation rate was decreased to 18%.

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

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 HCO$_3^-$ (Pelaez et al. 2011). On the other hand, although ·OH is consumed, the degradation of some pollutants including cylindrospermopsin and ethylparaben is not greatly affected due to the formation of carbonate radicals (CO$_3^{2-}$) (Petala et al. 2015; Zhang et al. 2015). In addition, CO$_3^{2-}$ 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 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.

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$  \hspace{1cm} (8)

$$-CO_3^- + CO_3^{2-} \rightarrow CO_2 + CO_4^{2-}$$  \hspace{1cm} (9)

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 HCO$_3^-$ > Cl$^-$ > 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 (Al$^{3+}$)

It can be seen from Figure 4 that Al$^{3+}$ has a negative effect on the photocatalytic degradation of CBZ. The added...
concentrations of Al$^{3+}$ were 10, 20, 30, and 40 mg·L$^{-1}$, respectively. With the concentrations of Al$^{3+}$ increasing from 10 mg·L$^{-1}$ to 40 mg·L$^{-1}$, the inhibition on the photocatalytic degradation of CBZ was also enhanced. When the added concentration of Al$^{3+}$ was 40 mg·L$^{-1}$, the photocatalytic degradation efficiency was reduced about 16% compared to the solution without 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 mg·L$^{-1}$·min$^{-1}$ at the concentration of 40 mg·L$^{-1}$, confirming the inhibited degradation kinetics of CBZ in the presence of 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 Al$^{3+}$ was observed in the concentration of 20 mg·L$^{-1}$ with 12.16 min.

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

<table>
<thead>
<tr>
<th>Inorganic cations</th>
<th>Concentration (mg·L$^{-1}$)</th>
<th>Half-life of CBZ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$^{3+}$</td>
<td>10</td>
<td>8.87</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>9.27</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>9.43</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>12.16</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>20</td>
<td>2.46</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>6.42</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3.93</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>4.78</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>5</td>
<td>12.18</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>9.38</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>10.20</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>8.92</td>
</tr>
</tbody>
</table>

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. 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 (Ca$^{2+}$)**

The effect of Ca$^{2+}$ on photocatalytic degradation of CBZ is shown in Figure 5. As shown, the presence of Ca$^{2+}$ significantly promoted the photocatalytic degradation of CBZ. In particular, for Ca$^{2+}$ at a relatively low concentration of 40 mg·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 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 mg·L$^{-1}$ of Ca$^{2+}$ with a $k$ value of 0.1080 min$^{-1}$. The fastest degradation kinetics appeared in the concentration of 20 mg·L$^{-1}$ with a $k$ value of 0.2816 mg·L$^{-1}$·min$^{-1}$, which is 3.27 times greater than photocatalytic degradation of CBZ without adding Ca$^{2+}$. At the same concentration of Ca$^{2+}$, the half-life of CBZ was reduced to 2.46 min due to the positive effect of 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
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 V for (E°Ca²⁺/Ca) (Santiago et al. 2014). A comparison of the value with those from the band edge potentials of BiOCl implies that Ca²⁺ is not able to react with the photogenerated holes or electrons. From this point of view, Ca²⁺ 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 Ca²⁺. The adsorption is important for a photocatalytic degradation reaction to occur. In fact, the CBZ adsorption on BiOCl is negligible without the addition of Ca²⁺ due to negative charges on both CBZ and BiOCl. The positive Ca²⁺ 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 (Mg²⁺)**

Figure 6 shows the effect of Mg²⁺ on photocatalytic degradation of CBZ. The added concentration of Mg²⁺ was 5, 10, 15, and 20 mg·L⁻¹, respectively. The presence of Mg²⁺ increased the CBZ adsorption significantly (10%). Due to the increase of adsorption, the CBZ degradation improved slightly in the first 5 min at the Mg²⁺ concentrations of 10,
15, and 20 mg·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 mg·L\(^{-1}\)·min\(^{-1}\) due to the coexistence of Mg\(^{2+}\) (5 mg·L\(^{-1}\)). However, high concentrations of 10, 15, and 20 mg·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 mg·L\(^{-1}\)). However, the half-life of CBZ showed no significant difference at high concentrations of Mg\(^{2+}\).

\(\text{Al}^{3+}, \text{Ca}^{2+},\) 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.

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