Study of the photodegradation of 2-chlorobenzoic acid by TiO₂ and the effects of eutrophicated water on the reaction

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1. Introduction

Recently chlorobenzoic acid (CBA) was widely used into every aspect of our life, such as industry, agriculture, pharmaceutical and so on (Cassani et al., 2013, Blackledge et al., 2000). CBA is an important organic compound with good water-soluble which may cause persistent pollution in the aquatic environment and it is harmful to human body and can also lead to macrocephaly, cancer and mutation (Gichner et al., 2008). In addition, it was difficult to achieve the effective degradation of CBA by conventional biological treatment. There were some reports about the degradation of the CBA. Li et al. researched the degradation of p-CBA using nickel modified activated carbon in ozone atmosphere and the removal rate of TOC (Total Organic Carbon) can reach to 60% (Li et al., 2009). B. Neppolian et al. used ultrasound/FeOOH-H₂O₂ to realize degradation of p-CBA. It was found to be substantially faster than that with ultrasound only (Neppolian et al., 2004). Milan Muziká et al. used ligninolytic fungal strains to degrade CBA, and the removal rate in the soil was almost 99% within 60 days (Muzikář et al., 2011). Asma Mhemdi et al. used electric-Fenton to degrade 2-CBA, in which the removal rate of TOC almost reaches to 80% 3 h later (Mhemdi et al., 2013).

A lot of literatures had described how to use advanced oxidation to degrade CBA, but there were much few articles to research the degradation of CBA with TiO₂ photocatalytic technology. It is well known that TiO₂ with cheapness, non-toxic, harmlessness, high chemical stability is widely used in the manufacture of products and the environment treatment such as surface cleaning products, air and water self-purification, photocatalysis, et al. (Nakata & Fujishima, 2012; Pelaez et al., 2012).

Elsevier B.V. et al. employed low temperature plasma combined with TiO₂ to eliminate isovaleraldehyde from the air at 364 nm, the results showed that isovaleraldehyde conversion reached 85% (Maciuca et al., 2012). L. Prieto-Rodriguez et al. use TiO₂ and H₂O₂ in the sun simulator as tertiary treatment for wastewater treatment plants in wastewater. The results showed that when dosing quantity of TiO₂ and H₂O₂ was 50 mg/L and 100 mg/L respectively, sulfamethoxazole in the waste water reduced from 100 mg/L to 65 mg/L (Ku et al. (1996). Yu et al. used 0.2 mg/mL S-doped-TiO₂ to remove the Gram positive bacterium (Micrococcus-lylae) in water with 100 W tungsten halogen lamp, the degradation rate as high as 96.7% after one hour (Yu et al., 2005).

Photocatalytic degradation of 2-CBA in pure water would be markedly different from that in contaminated water. Angelina-
Guiovana Rincón found that the bacterial inactivation rate had a meaningful decrease when various anions were introduced into the process of photocatalytic degradation bacteria with TiO2 (Rincon & Pulgarin, 2004). Liang et al. reported that the existence of Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}, and SO\textsubscript{4}\textsuperscript{2-} (0.05 M) had an obvious negative impact on the degradation of DCP (20 mg/L) when pH value was 5.3. The results showed that the removal rate of 2,3-DCP without anion was 93%, but it was only 77% when the concentration of Cl\textsuperscript{-} was 0.05 M (Liang et al., 2008). All of above showed that the existence of anion in water lead a great influence on photocatalysis of organic matter. It was found that human nutrient input was a major cause of eutrophication. Eutrophication can lead lack of oxygen of water and a large number of aerobic biological to die (Zhu et al., 2007). Inspired by the finding we will insight into the influence of 2-CBA photodegradation reaction with TiO2 (Lin & Lin, 2014). The oxidation degradation of organic matter by photogenerated hole was an important way for photodegradation reaction with TiO2 (Lin & Lin, 2014). In this work, the best initial concentration of TiO2 was chosen as 30 mg/L.

3.2. The dosing quantity of catalyst

To analyze the effect of dosing quantity of TiO2 on the efficiency of 2-CBA photodegradation, the account of TiO2 was carried out in the range from 0.005 to 0.025 g.

Fig. 3 showed that removal rate coefficient of 2-CBA reduced along with the increase of catalyst when the catalyst dosing quantity was less than 0.01 g. And then the rate constant decreased with the addition of catalyst. This phenomenon was identified with report by Biljana et al., the degradation rate reached 82% under UV light irradiation for 4 h when dosing quantity of TiO2 was 0.01 g (Abramovic et al., 2013). The photodegradation reaction accords with the first order kinetics model and the catalyst dosing quantity had a great influence on reaction. Both larger and smaller dosing quantity of catalyst would inhibit the degradation, which could due to two reasons. While TiO2 was relatively less, the hydroxyl radicals produced in the reaction system would be little and were unfavorable to removing on organic matter. When the dosing quantity was excessive, TiO2 would agglomerate on the solution surface and hinder the photons from reaching the surface of the TiO2, that would lower photocatalytic degradation efficiency. It was observed in Fig. 4 that the optimum amount was 0.01 g.

3.3. pH

The initial pH was maintained at 3.5, 4.5, 5.5, 6.5, 7.5 or 8.5 in a suspension of TiO2 (0.01 g/L) and 2-CBA (30 mg/L). Fig. 5 showed the degradation rate of 2-CBA. The kinetic rate constant was summarized in Fig. 6.

A dramatically decreasing trend of degradation rate of 2-CBA was shown in Fig. 5. It was described in Fig. 6 that the pH value had little effect on the kinetic constants of 2-CBA between 5.5 and 8.5 while the constants declined gradually along with pH value from 3.5 to 5.5. The removal rate of 2-CBA had the maximum at 82.8% when pH value was 3.5. In addition, no matter how pH value changed, the degradation of 2-CBA was coincided with typical first-order kinetic reaction. This result accorded with the relevant report by Rincon (Maciuca et al., 2012).

The pH has significant impact on the zeta potential, which determines the charge characteristics on TiO2 particle surface. The charge turned from positive into negative when chemical condition changed from acidic to alkaline (Haque & Muneer, 2007). While pH of reaction system is greater than pKa value of 2-CBA (2.9), 2-CBA exists in ion state. Therefore, when pH value was lower than 6.5 more 2-CBA ion adsorption on the surface of TiO2, which was favorable to the oxidative degradation. On the contrary, the photodegradation was inhibited by electrostatic repulsion.
between 2-CBA ion and TiO₂ surface charge when pH value was higher than 6.5.

3.4. Anionic effect

3.4.1. Nitrogen

The excessive nutrients into water especially nitrogen and phosphorus would enhance phytoplankton development and destroy the ecological balance. We need to consider the effect of nitrogen and phosphorus on the photodegradation since a lot of rivers and lakes have presented a serious state of eutrophication. The influence of anions in water could be divided into inhibition, promotion and no influence. In Dunia's report, when Cl⁻/C₀ was in solution (300 mg/L), the removal rate of imazalil (50 mg/L) fell nearly 10% than that without Cl⁻. In Wang's report, H₂O₂ (0.06 mol/L) was introduced to evaluate the photodegradation of MO instead of TiO₂, and the result showed that 6% disappeared in 12 min. In this work, 0.5, 1, 2, 3, 4, 5 mL KNO₃ solution (100 mg/L) was added into reaction system respectively under the optimal conditions (initial concentration is 30 mg/L, pH3.5, catalyst dosing quantity is 0.01 g). In other word, the inorganic nitrogen concentration was set from 0.5 to 5 mg/L (Santiago et al., 2014; Wang et al., 2013). The result was showed in Fig. 7 and Fig. 8. Fig. 7 showed that the degradation rate reeclined with the increase of KNO₃. From the experiment result, NO₃⁻/C₀ had a negative influence on the photodegradation. The removal rate was only 39% in present of NO₃⁻/C₀ (5 mg/L) after 3 h, and the degradation efficiency had fallen by nearly 50% compared with the case without NO₃⁻. This result was consistent with the conclusion in other research. But Senthil et al. drawn a opposite conclusion. They used TiO₂ to take the photocatalytic degradation on dye in the present of NO₃⁻ and the result showed that NO₃⁻ had promoted the photocatalytic reaction (Barndök et al., 2012). Through the kinetics analysis (Fig. 8), it could be found that the removal rate of 2-CBA dropped significantly and then retained steady with the increase of NO₃⁻. The inhibition of photocatalytic activity could due to that NO₃⁻ acted as the scavenger of hydroxyl radicals or photogenerated hole. In theory, hydroxyl radicals or photogenerated hole can oxidize organic
matter in the reaction system (Antoine et al., 2001). So the presence of NO$_3$ inhibited the photocatalytic ability and had a negative impact on removing 2-CBA.

3.4.2. Effect of phosphorus

Under the best condition of mineralize 2-CBA, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 mL KH$_2$PO$_4$ (10 mg/L) were added into the solution
respectively, and phosphorus concentrations in the solution were 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mg/L.

Fig. 9 indicated that the performance of phosphorus in the solution was consistent with above mentioned nitrogen. Both ions had negative effect on the photodegradation of 2-CBA. With increase of phosphorus concentration, the removal rate of 2-CBA reduced gradually. The photolysis rate constant also showed the same trend in Fig. 10. The removal rate of 2-CBA (30 mg/L) with TiO₂ under the presence of phosphorus (0.5 mg/L) had fallen by 50% compared to that containing no phosphorus. Yoshiyuki came to the similar conclusion in the research about inactive MS₂ with TiO₂, in which the photocatalytic activity declined in presence of phosphorus (Yoshiyuki & Masahito, 2002). Especially the KH₂PO₄ added into the solution would dissociate into H⁺ and H₂PO₄⁻/CO. The competitive adsorption between anion and 2-CBA reduced the efficiency of photocatalytic. Besides, H₂PO₄⁻/CO had been used as scavenger for the hydroxyl radical, and it would also have inhibited the photodegradation of 2-CBA (Prieto-Rodriguez and Miralles-Cuevas, 2012).

3.5. Effect of alcohol

In Fig. 11, it could be found that ethanol had a remarkable inhibition on the photodegradation of 2-CBA. With increase of the ethanol concentration, the inhibition rate raised to 51% after 4 h photodegradation, which showed that OH⁻ played a critical fact in photodegradation process. Isopropanol was also introduced to confirm this result and then we get the same conclusion as before. It was noteworthy that under the same condition the photodegradation rate of 2-CBA was only 31% in presence of isopropanol.

3.6. The photolysis pathway of 2-CBA

LC-MS analysis was used to evaluate the photodegradation reaction of 2-CBA. The samples showed the peaks with different retention time after separation by chromatographic column.
the sample’s fragment ions were recorded according to the ratio of $m/z$ under the comprehensive effect of electric field and magnetic field by mass spectrometry. Test result was shown in Fig. 12.

In Fig. 12, there are two obvious peaks appearing at 3.19 and 2.85 min. The peak appearing at 2.85 min was preliminarily identified as intermediate product by comparing with the full scan spectrum. The nuclear ratio of peak appearing at 3.19 min was 155/157 by mass spectrometry (Fig. 13), which was attributed to 2-CBA. Fig. 14 shows that the peak at 2.85 with $m/z$ 127 tested under negative ion mode can be speculated as o-chlorophenol. This was due to that first the decarboxylation reaction of 2-CBA carried out easily and then the hydroxylation reaction of aromatic took place.

It can satisfy the basic degradation pathway which we are concluded. The similar results had been bring out by Brett, Helene, Asma, Young, et al. (Faber et al., 2014; Ku et al., 1996; Vanderford et al., 2007; Wang et al., 2017, 2018; Zhang et al., 2019a, 2019b).

4. Conclusion

The optimal dosing quantity of TiO$_2$ was 0.01 g for photocatalytic degradation 2-CBA(30 mg/L), and the removal rate reached as high as 82.9% after 4 h irradiation under UV light in pH3.5. Both NO$_3$ and H$_2$PO$_4$ can make negative affect on the photodegradation of 2-CBA. It could be caused by the reduce of hydroxyl radicals or
photogenerated hole which was produced by anionic in solution. By using alcohol as scavenger, hydroxyl radicals had been verified primarily that played an key role in the process of photocatalytic degradation towards organic matter with TiO2. By determining the intermediate product of 2-CBA, we found that photocatalysis pathways is first decarboxylation and then hydroxylation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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