Chinese Chemical Letters 31 (2020) 2623–2626

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Communication

Enhanced removal of bisphenol A by cyclodextrin in photocatalytic systems: Degradation intermediates and toxicity evaluation

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ARTICLE INFO

Article history:
Received 6 January 2020
Received in revised form 1 February 2020
Accepted 6 February 2020
Available online 10 February 2020

Keywords:
Cyclodextrin
Bisphenol A
Photocatalysis
Toxicity
Carbon nitride

ABSTRACT

At present, the assessment of photooxidation system mainly focuses on the photodegradation efficiency of target pollutant, lacking of the toxicity assessment in the photocatalysis process. Here, photodecomposition of bisphenol A (BPA) was used to investigate the performance of several cyclodextrin modified photocatalysts. Moreover, the comprehensive toxicity changes of BPA under different photocatalytic oxidation conditions were conducted. The β-cyclodextrin (β-CD) modified photocatalyst, including titanium dioxide (CM-β-CD-TiO_2), carbon nitride (CM-β-CD-C_3N_4) and cadmium sulfide (SH-β-CD-AM/CdS) exhibit high degradation rate and mineralization efficiency of BPA. The highest total organic carbon (TOC) removal of BPA observed in the oxidation system of SH-β-CD-AM/CdS nanoreactor (73.4%). The main oxidation intermediates in these systems were detected, and the comprehension toxicity of BPA and its oxidation intermediates in different system were compared by toxicity estimation software tool (T.E.S.T.) based on quantitative structure-activity relationship (QSAR) prediction. The results show that β-CD can facilitate the photodecomposition of the target contaminant. However, many oxidation intermediates with high comprehensive toxicity, even in the oxidation system with high BPA removal, can still be detected. Therefore, not only decomposition of target contaminant but also the comprehensive toxicity of oxidation intermediates should be regarded as index to evaluate a photocatalysis technology.

Among the numerous of endocrine disrupting compounds we are exposed to, bisphenol A (BPA) stands out due to its widespread application, high environmental risk and refractory characterization [1]. Bisphenol A enters the environmental water body through different ways, such as effluent from sewage treatment plants or factory, landfill leachate and degradation by-product of plastic litter [2]. BPA can infiltrate into food and beverage through their containers and threaten human health. The widespread occurrence of BPA in our daily clothes and their relatively high exposure risk cannot be ignored [3]. BPA can be observed in human body, such as serum, urine, placental tissue and breast milk, and accumulation of BPA in human can lead to tumorigenic and birth defects [4]. In some epidemiological studies, BPA exposure is potentially associated with changes in hormone levels, impairment of ovarian and uterine functions as well as sperm quality decline [5]. Therefore, the development of efficient water treatment technology for BPA causes great concerns, such as adsorption [6], biodegradation [7] and advanced oxidation processes (AOPs) [8,9].

AOPs relied on the reactive oxygen species (ROS), such as hydroxyl radical ($\cdot$OH) and superoxide radical ($\cdot O_2^-$), effectively oxide the organic pollutants, including BPA. [10] Among the many advanced oxidation techniques, photocatalysis technology is an efficiency and eco-friendly mean for emerging organic contaminant removal [11]. In order to improve the photodegradation efficiency of target containment, many photocatalysts have been designed, which have the advantages of enhanced light absorption, high separation efficiency of photogenerated electron-hole pairs and prolonged life of ROS. For example, Fe-doped TiO_2/PSF composite could achieve 90.78% of BPA removal rate within 3 h visible-light irradiation [12]. Moreover, Yu *et al.* proposed a cobalt-to-oxygen doped graphitic carbon nitride (0.78% Co-OCN_{VN}), which could degrade 100% BPA within 3 h visible light illumination and total organic carbon (TOC) removal rate up to 66% [13]. Although those new materials can highly improve the removal rate of BPA,

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https://doi.org/10.1016/j.cclet.2020.02.008

BPA cannot be totally mineralized into inorganic small molecule during the photocatalysis oxidized process. Organic aromatic ring compounds, such as 4-hydroxybenzaldehyde, 4′-(methylmethylene) bisphenol, 4-(2-hydroxypropan-2-yl) phenol, benzoquinone can be detected in the photooxidation system [14,15]. Compared with BPA, those oxidization by-products may exhibit higher environmental risk due to its relative high toxicity, mutagenicity and bioaccumulation factors. However, no comprehensive study on these photooxidation byproducts especially their environmental risks has been reported so far [16]. Therefore, the toxicity intervention of photocatalytic oxidation process on BPA need to be furtherly investigated. According to the previous work [17], modification with cyclodextrin can facilitate the advanced degradation of BPA oxidation intermediates.

In this work, the photocatalytic degradation of BPA was employed to evaluate the performance of different cyclodextrin modified photocatalytic oxidation system. The photodegradation intermediates and products of different photocatalytic oxidation systems were detected. Moreover, the acute toxicity, bioaccumulation factor, developmental toxicity and mutagenicity of these oxidation products were analyzed in detail. And the comprehensive toxicity of different kinds of photoxodiation intermediates were proposed. Furthermore, the effects of different photooxidation system on the toxicity of BPA and its oxidation intermediates were also investigated. The considerate assessment system of water treatment technology was proposed.

Photocatalytic oxidation of BPA was employed to evaluate the photoactivity of different oxidation system (Fig. 1 and Table S1 in Supporting information). The photo-decomposition efficiency of BPA (20 mg/L) was 11% under ultraviolet light irradiation for 1 h. Under the same conditions, 74% and 92% of BPA were photodegraded by commercial titanium dioxide (P25) and carboxymethyl-β-cyclodextrin modified titanium dioxide, respectively. Only the 8.6% of BPA was photodegraded under the visible light irradiation for 2 h, which was lower than that of ultraviolet oxidation system. The enhanced photodegradation efficiency of BPA was obtained by the carbon nitride nanosheet (39%) and the hollow CdS nanoreactor (86%), owing to their high visible light absorption and high concentration of photogenerated electrons and holes. Moreover, the 33% and 100% of BPA were photocatalytic oxidized by CM-β-CD-C_3N_4 and SH-β-CD-AM/CdS, respectively, owing to the unique hydrophobic cavity of β-CD [18]. BPA and β-CD can easily form 1:1 inclusion complex with a high association constant (56,000 L/mol) [19], owing to the molecular sizes of BPA (1.24 nm × 0.54 nm × 0.44 nm) and β-CD cavity (0.60–0.65 nm × 0.79 nm, diameter × height) match each other best [20]. It facilitates the entrapment of target organic containment and promotes the transmission of electrons between the pollutant molecule and the photocatalyst [21].

Fig. 2 presents the *pseudo*-first-rate constants of BPA photodegradation over the different cyclodextrin photooxidation systems. The *pseudo*-first-order kinetic model could well interpret the experimental data ($R^2 > 0.9$). The apparent *pseudo*-first-order rate constant (k_1) of BPA photooxidation under the UV light and the visible light irradiation without any photocatalyst were 0.20×10^{-2} min^{-1} and 0.17×10^{-2} min^{-1}, respectively.

Compared with the pure TiO_2 (1.98×10^{-2} min^{-1}) and C_3N_4 nanosheet (0.22×10^{-2} min^{-1}), the CM-β-CD-TiO_2 and CM-β-CD-C_3N_4 exhibited a high photooxidation rate of BPA with 3.92×10^{-2} min^{-1} and 0.32×10^{-2} min^{-1}, respectively, owing to its accelerated transmission of photogenerated electrons by the covalent bond between semiconductor and CM-β-CD [22]. Moreover, the BPA photodecomposition rate of SH-β-CD-AM/CdS nanoreactor (9.04×10^{-2} min^{-1}) was more than 5 times higher than that of the hollow CdS nanoreactor (1.6×10^{-2} min^{-1}) [17]. The directional transfer of photogenerated charges induced by spatial separated co-catalysts and the enhanced adsorption of BPA over the SH-β-cyclodextrin should have significantly contributed to the high photooxidation rate [23].

The TOC analysis was used to investigate the mineralization of BPA over the different photooxidation system (Fig. 3). 5.63% and 1.27% of BPA were mineralized within 1 h UV light irradiation and 2 h visible light irradiation, respectively. Compared with the pure titanium dioxide and carbon nitride, carboxymethyl-β-cyclodextrin modified photocatalysts showed a higher TOC removal of BPA, indicating that β-cyclodextrin promote the mineralization of BPA. TOC removal of BPA in CM-β-CD-TiO_2 (25.4%) and CM-β-CD-C_3N_4 (15.7%) photooxidation system were 1.4 times higher than that of bare titanium dioxide (18.6%) and C_3N_4 (10.9%), respectively. Moreover, 19.2% of BPA can be removed by hollow CdS nanoreactors. Furthermore, the relatively high TOC removal of BPA observed in the oxidation system of SH-β-CD-AM/CdS nanoreactor (73.4%) could be attributed to the synergistic effect of spatial separated co-catalysts and the SH-β-cyclodextrin. According to the results of TOC analysis over the different photooxidation system, modification with cyclodextrin can facilitate the mineralization of BPA in photocatalytic oxidation process. Although some oxidation intermediates may bind with the β-cyclodextrin, this kind of inclusion complexes will not cause catalyst poisoning, but is conducive to accelerated degradation.

The photocatalytic oxidation intermediates of BPA in different oxidation system are identified by the UPLC-MS analysis, as shown in Table S2 (Supporting information). The detail UPLC-MS data are

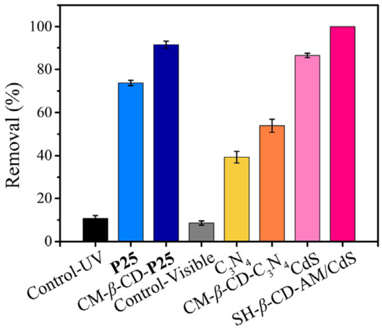

Fig. 1. The removal of bisphenol A by different photocatalytic oxidation systems. Reaction condition: $[BPA]_0 = 20$ mg/L. [photocatalyst] = 1 mg/mL, $pH_{ini} = 6.8$, $T = 298 \pm 1$ K.

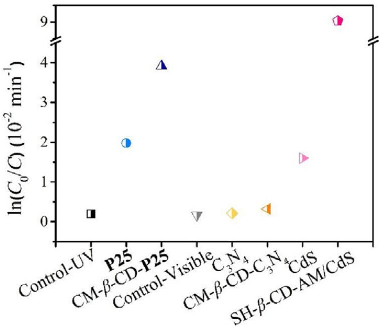

Fig. 2. The apparent rate constant (*K*a) of different cyclodextrin modified photooxidation systems for photocatalytic degradation of bisphenol A. Reaction condition: $[BPA]_0 = 20$ mg/L. [photocatalyst] = 1 mg/mL, $pH_{ini} = 6.8$, $T = 298 \pm 1$ K.

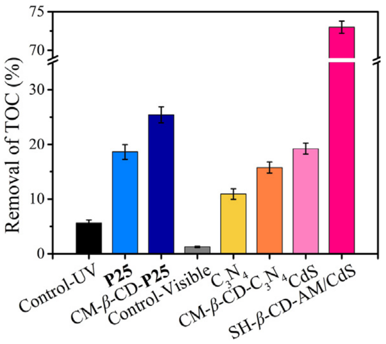

Fig. 3. TOC removal of different cyclodextrin modified photooxidation systems for photocatalytic degradation of bisphenol A. Reaction condition: $[BPA]_0 = 20$ mg/L. [photocatalyst] = 1 mg/mL, $pH_{ini} = 6.8$, $T = 298 \pm 1$ K.

shown in Fig. S1 (Supporting information). During the photocatalytic oxidation process, the quaternary carbon atom of BPA is attacked by hydroxyl radical, phenoxyl (PhO) and isopropenylphenol (IPP) radicals are produced by the β-scission [24,25]. Subsequently, numerous of aromatic by-products were formed through addition, substitution, dehydration and oxidative skeletal rearrangement reaction [26]. After ring-opening reaction, different kinds of carboxylic acids were detected, such as **P17**-**19**, which were ultimately mineralized into carbon dioxide and water. Different oxidation intermediates were obtained from different oxidation systems. The **P11** and the polymers intermediate, such as **P12** and **P13**, have not been detected in the photooxidation system without any catalyst. However, it can be obtained in the oxidation system of TiO_2, CM-β-CD-TiO_2 and CdS. Compared with UV oxidation system (Control-UV), visible light oxidation system (Control-visible) has lower TOC removal rate, but the fewer intermediates were detected in this system. Typically, **P2**, **P5**, **P9**, **P10**, **P14** and **P15** have not been detected in the Control-visible oxidation system. Moreover, according to the comparison of oxidation intermediates of pure catalysts and the cyclodextrin modified catalysts, the modification of cyclodextrin can effectively promote advanced degradation of oxidation intermediates [17]. For example, compared with hollow CdS nanoreactor, SH-β-CD-AM/CdS can not only has higher TOC removal rate, but also avoid the generation of many polycyclic aromatic hydrocarbon (PAH) oxidation intermediates, such as **P12**-**P15**. These PAHs have huge potential environmental risk due to its high toxicity [27]. Interestingly, although the degradation rate and TOC removal of BPA in CM-β-CD-C_3N_4 oxidation system were lower than those of other catalysts, the number of intermediates detected in this system was the least. Therefore, the evaluation index of water treatment technology should not only consider the mineralization rate of target pollutant, but also the environmental risk of oxidation intermediates should be considered.

Toxicity estimation software tool (T.E.S.T.) based on quantitative structure-activity relationship (QSAR) prediction [28] was used to evaluate the corresponding toxicity of BPA and its photooxidation intermediates (Fig. S2 in Supporting information). QSAR model provides the corresponding toxicity data according to the quantitative relationship between the chemical structure and its toxicological activity [29]. The concentration of chemicals that cause 50% of blackhead fish to die after 96 h ($LC_{50-96\,h}$) is less than 1 mg/L, 1−10 mg/L and higher than 10 mg/L, which is defined as "very toxic", "toxic" and "harmful", respectively (Fig. S2a). Among the 21 detected oxidation intermediates, **P10**, **P12**, **P13** and **P16** are defined as "very toxic" oxidation products owing to its extremely high acute toxicity. These photooxidation intermediates pose a huge threat to aquatic organism and need attention because of their high environmental risks. Moreover, **P7**, **P9**, **P11**, **P14** and **P15** are defined as "toxic" compounds, which are more toxic than parent compound (BPA). In addition, the acute toxicity ($LC_{50-96\,h}$) of other oxidation intermediates are higher than 10 mg/L and lower than 100 mg/L, thus they are defined as "harmful" pollutants. So, the rest of other oxidation intermediates are defined as "harmful" compounds except **P18** and **P19**. Because **P18** and **P19** are defined as "low-toxic" compound, owing to its acute toxicity ($LC_{50-96\,h}$) are higher than 100 mg/L. Furthermore, Fig. 4 shows the number of oxidation intermediates with different acute toxicity produced in different photocatalytic oxidation systems. According to the statistical results, the number of the oxidation intermediates with high acute toxicity is in the following order, CM-β-CD-**P25** > **P25** > CdS > Control-UV > Control-visible > SH-β-CD-AM/CdS > C_3N_4 > CM-β-CD-C_3N_4. There is no significant positive correlation between the target pollutant removal and the acute-toxicity of the oxidation intermediates. Therefore, the removal rate of target pollutants cannot be the only factor to evaluate the oxidation system.

Moreover, the bioaccumulation factor (BAF) of **P7**, **P9**, **P10**, **P12**, **P13** and **P16** are larger than that of BPA (Fig. S2b). Among all of them, **P7**, **P9** and **P10** can be classified as potential bioaccumulative compounds due to those BAF higher than 500 [30]. Its worth noting that these oxidation intermediates are easy to threaten the ecological security through the food chain. The rest of oxidation intermediates have lower BAF than BPA owing to their low lipophilicity, indicating that they are difficult to accumulate in organisms than BPA [31]. After photodecomposition process, oxidation products without developmental toxicity can be detected in oxidation system, including **P4**, **P5**, **P8**-**10**, **P14**-**16**, **P19** and **P22** (Fig. S2c). It demonstrates that photooxidation can reduce the developmental toxicity of pollutants. However, the photooxidation process still produces oxidation products with higher developmental toxicity, such as **P11** and **P19**. These intermediates interfere with the translation and expression of nucleic acids and thus affect the growth and development of individuals [32]. Furthermore, BPA and its oxidation products except **P20** have negative mutagenicity [33], indicating that photooxidation hardly effect on the mutagenicity of BPA (Fig. S2d). Acute toxicity, bioaccumulation factor, developmental toxicity and mutagenicity were considered as the determinants of comprehensive toxicity. Some oxidation products, such as **P10**, **P12**, **P13**, **P7** and **P9**, have high environmental risk due to their higher comprehensive toxicity.

According to the results of identification of photooxidation intermediates in different oxidation system, modification of β-cyclodextrin effectively inhibit the production of high-risk intermediates. Interestingly, although the degradation rate and TOC removal of BPA in the CM-β-CD-C_3N_4 oxidation system is lower than that of CM-β-CD-TiO_2, no high-risk oxidation intermediates

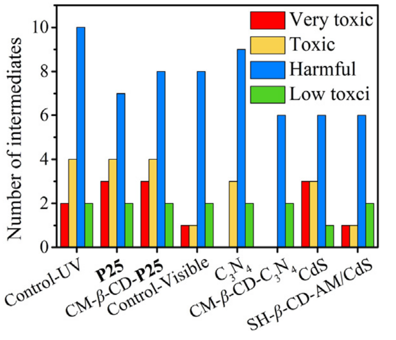

Fig. 4. The number of intermediates with different acute toxicity in different photocatalytic oxidation system.

have been detected in this system. Therefore, decomposition of parent BPA cannot be regarded as the only factor to evaluate photooxidation treatment technology, but neglected the high-risk intermediates produced in the photooxidation process.

In summary, β-cyclodextrin in several cyclodextrin oxidation systems can facilitate the entrapment of target organic containment and accelerate the transmission of electrons between the semiconductors and target organic pollutants. Thus, the CM-β-CD-TiO_2, CM-β-CD-C_3N_4 and SH-β-CD-AM/CdS exhibit higher photodecomposition efficiency and photo-degradation rate of BPA than that of bare catalysts. TOC removal of BPA in CM-β-CD-TiO_2 (25.4%) and CM-β-CD-C_3N_4 (15.7%) photooxidation system were 1.4 times higher than that of bare titanium dioxide (18.6%) and C_3N_4 (10.9%), respectively. Among all oxidation systems, the highest TOC removal of BPA observed in the oxidation system of SH-β-CD-AM/CdS nanoreactor (73.4%), owing to the synergistic effect of spatial separated co-catalysts and the SH-β-cyclodextrin. Different kinds of oxidation intermediates were detected in these oxidation systems. And T.E.S.T. based on QSAR prediction revealed that some photooxidation intermediates, such as **P10**, **P12**, **P13**, **P7** and **P9**, have high environmental risk due to their higher comprehensive toxicity. It worth noting that even in the oxidation system with high mineralization rate of BPA, many oxidation intermediates with high comprehensive toxicity can be detected. On the contrary, almost no high-risk oxidation intermediates were detected in the CM-β-CD-C_3N_4 oxidation system with low TOC removal rate. In conclusion, decomposition of target contaminant cannot be regarded as the only factor to evaluate oxidation treatment technology, the high-risk intermediates produced in the oxidation process shall also be considered.

Declaration of competing interest

The authors declare that there are no conflicts of interest.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 51778230, 21906056), Shanghai Rising-Star Program (No. 17QA1401000), China Postdoctoral Science Foundation (No. 2018M641943), Shanghai Sailing Program (No. 19YF1411900) and the Fundamental Research Funds for the Central Universities (No. 222201718003).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2020.02.008.

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