Degradation of Acetaminophen via UVA-induced advanced oxidation processes (AOPs). Involvement of different radical species: HO , SO4– and HO2/O2–

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Degradation of Acetaminophen via UVA-induced advanced oxidation processes (AOPs). Involvement of different radical species: $HO^{\bullet}$, $SO_4^{\bullet-}$ and $HO_2^{\bullet}/O_2^{\bullet-}$

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Abstract

In this work, UVA radiation that is part of solar light is taken as the irradiation source and radicals ($HO^{\bullet}$, $SO_4^{\bullet-}$ and $HO_2^{\bullet}/O_2^{\bullet-}$) are generated through activation of hydrogen peroxide (H_2O_2), sodium persulfate ($Na_2S_2O_8$) and Bismuth catalyst (BiOCl), respectively. The distinguished performance in removing acetaminophen (ACTP), a model pharmaceutical pollutant, by these three radicals was compared for the first time. Effect of pH, halide ions concentration and interfacial mechanism have been investigated in detail. Interestingly, results show that heterogeneous UVA/BiOCl process has higher degradation efficiency than homogeneous UVA/H_2O_2 and UVA/$Na_2S_2O_8$ systems whatever the solution's pH. To explain these results, second order reaction rate constant ($k_{radical,ACTP}$) have been determined with laser flash photolysis (LFP) or radical scavenging experiments. The strongly interfacial-depended $HO_2^{\bullet}/O_2^{\bullet-}$ radicals have the lowest second order rate constant with ACTP but highest steady state concentration. BiOCl was much easier activated by UVA, and outstanding ACTP mineralization can be achieved. Combination of BiOCl and $Na_2S_2O_8$ exhibits synergistic effects rather than antagonism effects with H_2O_2. This study highlights the relative effective utilization of solar light through interfacial directed BiOCl photocatalysis and its synergistic effects with traditional oxidants.

Key words: advanced oxidation process, photocatalysis, UVA, radicals, synergistic effects

1 Introduction

In recent years, advanced oxidation processes (AOPs) have been proposed as alternative methods to effectively remove persistent organic pollutants (POPs) in environment. Normally, AOPs have always proved to achieve the best yields in pollutant destruction when biological treatments are unfeasible, like for endocrine disrupting chemicals (EDCs) (Pera-Titus et al., 2004; Rosenfeldt and Linden, 2004), pharmaceuticals or personal care products (PPCPs) (Huber et al., 2003; Abdelmelek et al., 2011). The predominant oxidation processes are usually based on H_2O_2 or persulfate activation by *in situ* production of hydroxyl radical ($HO^{\bullet}$) or sulfate radical ($SO_4^{\bullet-}$), followed by reaction on the targets pollutants in aqueous solutions (Andreozzi et al., 1999; Esplugas et al., 2002). Especially, traditional Fenton reaction (Fe(II)/H_2O_2) (Neyens and Baeyens, 2003; Huang et al., 2013) and UV/H_2O_2 are predominant strategies to generate $HO^{\bullet}$. Similarly, $SO_4^{\bullet-}$ are always produced through activation of persulfate by heat (Nie et al., 2014), UV, alkalinity (Nie et al., 2019) and transition metals (Wu et al., 2015a). However, Fenton reactions always suffer from several limitations like strict acidic solution (pH < 4.0) and iron sludge disposal.

At the same time, interfacial based heterogeneous photocatalysis is also one of the most promising oxidation processes through producing electron (e^-) and hole (h^+) pairs under illumination. $HO^{\bullet}$ or hydroperoxyl radicals/superoxide radical anion ($HO_2^{\bullet}/O_2^{\bullet-}$, pKa 4.88) will be subsequently produced by reaction of photogenerated charge carriers with O_2 and H_2O (Shaban et al., 2013). Among these photocatalysts, TiO_2 and its doped products have received a great deal of attention due to its efficient

and abundant production of $HO^{\bullet}$ (Yang et al., 2008a). Different to TiO_2, in bismuth-related photocatalytic process, especially layered BiOX (X = Cl, Br, I) (Zhang et al., 2008), quenching experiments and theoretical calculation have proved that they are featured with $HO_2^{\bullet}/O_2^{\bullet-}$ generation for organic compound degradation (Tian et al., 2019). Taking BiOCl as catalyst, the photocatalytic process can supply a simple route to produce $HO_2^{\bullet}/O_2^{\bullet-}$ effectively. In our last studies, a series of BiOCl related catalysts have been synthesized by precipitation method successfully followed with detailed characterization (Wang et al., 2014, 2016a, 2016b). BiOCl possesses great surface area and suitable valance/conduction band structures to produce $HO_2^{\bullet}/O_2^{\bullet-}$ active species, showing excellent performance in removing acetaminophen (ACTP) from water under irradiation (λ > 290 nm), although the band gap value of BiOCl (~ 3.2 eV) shows that it only can be activated by the ultraviolet light with the wavelength shorter than 387.5 nm. Similar to the previous literatures, $HO_2^{\bullet}/O_2^{\bullet-}$ species are the main radical determined by indirect scavenging experiments.

If UVA radiation (315–400 nm) is chosen as the irradiation source, H_2O_2 and persulfate as the oxidation sources, the quantum yield comparison between $HO^{\bullet}$ and $SO_4^{\bullet-}$ still stay unknown. Furthermore, nobody has compared these two radicals with $HO_2^{\bullet}/O_2^{\bullet-}$ under the same experimental conditions. The degradation rate of organic pollutant depends on the radical concentration, selectivity and oxidizing power. For these reasons, the distinguished and cumulated effects of these parameters need to be explored. ACTP was chosen as the model pollutant in this study, because of its heavy use all over the world. Most of the research on ACTP degradation are mainly based on

$HO^{\bullet}$ and $SO_4^{\bullet-}$ like UV/H_2O_2 (Andreozzi et al., 2003), Fenton (de Luna et al., 2013), TiO_2 photocatalyst (Yang et al., 2008b) and persulfate activation (Noorisepehr et al., 2019; Yun et al., 2019). Its degradation pathway by $HO^{\bullet}$ and $SO_4^{\bullet-}$ are almost clear, while its degradation and mineralization abilities by $HO_2^{\bullet}/O_2^{\bullet-}$ still stays largely unknown. Furthermore, the combination of TiO_2 with H_2O_2 (Li et al., 2001) or persulfate activation (Xu et al., 2019) has been widely investigated. However, rare studies focus on the synergistic effects between BiOCl with H_2O or persulfate (Zhang et al., 2017).

In brief, the main goal of this paper is to compare, for the first time, three different active species $HO^{\bullet}$, $SO_4^{\bullet-}$ and $HO_2^{\bullet}/O_2^{\bullet-}$ produced by UVA/H_2O_2, UVA/$Na_2S_2O_8$ and UVA/BiOCl respectively on the degradation of ACTP. pH and halide ions (Cl^- and I^-) concentration effects on ACTP's degradation have been investigated in this work. The combination of oxidants in the systems UVA/BiOCl/H_2O_2 and UVA/BiOCl/$Na_2S_2O_8$ are also studied to explore the potential synergistic effects. Interfacial mechanism, mineralization and efficiency of this process will be explained in detail. Furthermore, second order reaction rate constants between ACTP and $HO^{\bullet}$, $SO_4^{\bullet-}$ or $HO_2^{\bullet}/O_2^{\bullet-}$ radicals will be determined by laser flash photolysis (LFP) or competition experiments. The critical affecting parameters on ACTP's degradation rate will be determined.

2 Materials and methods

2.1 Chemicals

BiOCl catalyst was synthesized as in our previous papers (Wang et al., 2016a).

ACTP was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Bisphenol A (BPA), $NaH_2PO_4 \cdot H_2O$, NH_4SCN, ethanol (EtOH), tert-butanol (TBA), sodium persulfate ($Na_2S_2O_8$), benzoquinone (BQ) and potassium iodine (KI) were obtained from Sigma, France. Hydrogen peroxide (H_2O_2) solution (30% in water) and sodium chloride (NaCl) were purchased from Fluka, France. 5,5-Dimethyl-1-pyrroline N-Oxide (DMPO, 98%) was obtained from Adamas Reagent Co., Ltd. Perchloric acid ($HClO_4$) and sodium hydroxide (NaOH) were used to adjust the pH of the solutions. All chemicals were used without further purification, and milli-Q water was used throughout all the experiments.

2.2 Irradiation setup and experimental procedure

The photocatalytic degradation experiments were performed in a homemade photoreactor placed in a cylindrical stainless steel container. Four fluorescent lightbulb lamps (Philips TL D15W/05) were separately placed in the four different axes while the photoreactor, a water-jacketed Pyrex tube of 2.8 cm internal diameter, was placed in the center of the setup. The lamp emitting from 300 to 500 nm was used to simulate UVA solar light; their emission spectrum is shown in Fig. S1. 100 mL of solutions were magnetically stirred with a magnetic bar during irradiation and experiments were carried out at room temperature (293 ± 2 K) set by a circulating cooling water system. Samples were taken from the reaction tube at fixed interval times and the catalyst solid was removed by 0.22 μm PTFE filters before analysis. In the experiments, the initial concentrations used were: ACTP 50 μM, H_2O_2 and $Na_2S_2O_8$ 1 mM and BiOCl catalyst 0.3 g L^{-1} (approximately 1.1 mM). All experiments

were performed in duplicates, experimental points represent the averages of two values, and the error bars indicate the standard deviation.

2.3 Analytical method

The remaining ACTP concentration in the aqueous solution was determined by high performance liquid chromatography (HPLC) (Alliance, Waters, 2695, USA) equipped with a photodiode array detector (Waters 2998). A Nucleodur 100-3 C18 reverse column (150 × 2.0 mm, 3.0 μm) was used to separate the compound in the solution. The flow rate was 0.15 mL min^{-1} with a mobile phase mixture of methanol and water with 0.1% H_3PO_4 (30/70, v/v). The UV detection of ACTP was set at 244 nm wavelength, and the retention time was 4.9 min. Mineralization of ACTP solution was followed by total organic carbon (TOC) analysis (5050A, Shimadzu, Japan). UV−vis spectra were recorded with a Cary 300 UV−visible spectrophotometer. pH values of the solutions were measured using a Cyberscan 510 pH meter. The zeta potential of BiOCl was determined by the potentiometric titration method under N_2 atmosphere at 298 K in 1 mM NaCl solutions. X-ray photoelectron spectroscopy (XPS) spectra were collected by using a VG Scientific ESCALAB 250Xi spectrometer (Thermo Fisher Scientific) with C 1s as the calibration standard line. The optical properties of BiOCl samples were analyzed through the UV–vis diffuse reflectance (DRS) by Shimadzu UV-3600. The electron spin resonance (ESR) experiments were carried out on a JES-X320 spectrometer to detect the reactive radicals generated over the photocatalytic degradation process. As radical probe, DMPO (100 mM) was used for $SO_4^{\bullet-}$, $HO^{\bullet}$ and $HO_2^{\bullet}/O_2^{\bullet-}$. ESR spectrum was

recorded at room temperature under the following operating conditions: a modulation frequency of 100 kHz, a sweep width of 0.5 mT, a microwave power of 1 mW, a microwave frequency of 9.15 GHz and a centerfield of 326.0 ± 5 mT.

2.4 Determination of the second order rate constant

For the detection of second order rate constant between ACTP and $HO^{\bullet}$ ($k_{ACTP, HO\bullet}$), LFP method was adopted. Experiments were carried out using the fourth harmonic (λ_{exc} = 266 nm) of a Quanta Ray GCR 130-01 Nd: YAG laser system instrument and the energy was set as approximately 45 mJ/pulse. Other conditions were kept the same to those described in previous articles (Brigante et al., 2010; Huang et al., 2018). High concentrated stock solutions (ACTP, H_2O_2 and SCN^-) were mixed just before each experiment and diluted with Mili-Q water to obtain the desired mixtures and concentrations in a 3 mL quartz cuvette. The value of $k_{ACTP, HO\bullet}$ can be obtained through mixing SCN^- (0.1 mM), H_2O_2 (5.5 mM) with different concentrations of ACTP in the quartz cell. The detection wavelength was set at 475 nm to detect maximum absorbance of $SCN_2^{\bullet-}$. The specific detection calculation was shown in Scheme S1 and Equations S1-S4.

For the detection of second order rate constant of sulfate radical on ACTP ($k_{ACTP, SO4\bullet-}$), competition method was adopted by taking BPA as the competitor (Ji et al., 2013), because $k_{SO4\bullet-,BPA}=4.7\times10^9$ M^{-1} s^{-1} has been detected in previous studies by LFP (Huang et al., 2018). For this experiment, BPA (50 μM) and ACTP (50 μM) were undergoing competition reactions under $Na_2S_2O_8$ (1 mM)/UVA at pH 5.4 for 240 min. At this pH conditions, sulfate radical prevailed with negligible hydroxyl radical

existence (Fang et al., 2013a). The concentrations of BPA and ACTP were followed at different treatment time intervals and the rate constant of ACTP with $SO_4^{\bullet-}$ can be calculated through **Eq.1**.

$$k_{ACTP,SO_4^{\bullet-}} = k_{BPA,SO_4^{\bullet-}} \times \ln\left(\frac{[ACTP]_t}{[ACTP]_0}\right) \Big/ \ln\left(\frac{[BPA]_t}{[BPA]_0}\right) \quad (1)$$

3 Results and Discussion

3.1 ACTP degradation in UVA/H_2O_2 and UVA/$Na_2S_2O_8$ systems under different pH

To explore ACTP's degradation with H_2O_2 and $Na_2S_2O_8$ under UVA irradiation, blank experiments were firstly conducted in the dark to check its stability. ACTP alone in aqueous solution is stable between pH 3-9.5 within 40 hours (Fig.S2A). In addition, when ACTP was mixed with H_2O_2 and $Na_2S_2O_8$ (Fig.S2B, C), no detectable degradation can be observed until pH 9.0, while at higher pH a degradation was measured particularly with persulfate.

Degradation of ACTP with H_2O_2 and $Na_2S_2O_8$ under UVA during irradiation are shown in Fig.1, and all the reactions follow pseudo first order reaction kinetics (data are shown in Fig.4C). From the control experiment, direct photolysis of ACTP could be neglected (Fig.1A). Results of quenching experiments demonstrated that $HO^{\bullet}$ and $SO_4^{\bullet-}$ are the predominant radicals involved in the UVA/H_2O_2 and UVA/$Na_2S_2O_8$ system (**Eq.2-3**) at pH 5.4 respectively by taking IPA (10 mM) and EtOH (1 M) as $HO^{\bullet}$ ($k_{IPA,\ HO^{\bullet}}$=1.9×10^9 M^{-1} s^{-1}) (Wu et al., 2017) and $SO_4^{\bullet-}$ ($k_{EtOH,\ SO4^{\bullet-}}$=1.6-7.7×$10^7$ M^{-1} s^{-1}) (Tan et al., 2014) scavengers, respectively. No direct photolysis of ACTP was

observed under UVA radiation. With H_2O_2 or $Na_2S_2O_8$ addition to the solution, ACTP shows different degradation kinetics under various pH. In general, UVA/$Na_2S_2O_8$ shows a higher degradation efficiency than UVA/H_2O_2 system whatever the solution's pH. It has been reported that H_2O_2 only can be activated by the light at λ < 320 nm, which almost have been confirmed in this research for the weak degradation in UVA/H_2O_2 (Li et al., 2001). The obvious degradation of ACTP in UVA/$Na_2S_2O_8$ indicates that $Na_2S_2O_8$ is easier to be activated than H_2O_2 under UVA irradiation.

In UVA/H_2O_2 system, slightly acidic solution has the maximum removal percentage rather than acidic and alkaline solutions, although the maximum removal is only approximately 10%. In contrast, degradation rate is increasing with pH further increasing (Fig.1B) in UVA/$Na_2S_2O_8$ system, and about 57% ACTP can be removed at pH 10. At least two reasons are involved simultaneously to account for this phenomenon. Firstly, Fig.S2B has been taken into consideration, ACTP is easier to be oxidized in anionic form. Furthermore, alkaline solution favors more formation of $HO^{\bullet}$ radicals from $SO_4^{\bullet-}$ than neutral pH (**Eq.4-5**) (Fang et al., 2013a), and these two radicals have different second order reaction rate constants with ACTP, which will be explained in the following part.

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \quad (2)$$

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\bullet-} \quad (3)$$

$$SO_4^{\bullet-} + OH^- \rightarrow HO^{\bullet} + SO_4^{2-} \qquad k = (6.5\pm1.0)\times10^7\ M^{-1}\ s^{-1} \quad (4)$$

$$SO_4^{\bullet-} + H_2O \rightarrow HO^{\bullet} + HSO_4^- \qquad k = 11.9\ M^{-1}\ s^{-1} \quad (5)$$

3.2 Halide ions (chloride and iodide) effects on ACTP degradation in UVA/H_2O_2

and UVA/$Na_2S_2O_8$ systems

Effects of halide ions were widely studied in previous research works, especially chloride and bromide (Tamtam and Chiron, 2012; Li et al., 2015). In our study for the first time the comparison of Cl^- and I^-, which is also commonly detected in costal seawater, saline water or industrial wastewater discharges, were investigated in UVA/H_2O_2 and UVA/$Na_2S_2O_8$ systems. In the dark and whatever the systems, the addition of Cl^- has no impact on ACTP's concentration change (see Fig.S3). Under irradiation, the impact of Cl^- is also very weak. The only effect is observed in the UVA/H_2O_2 system, when NaCl is set as 10 mM, the pseudo first order reaction rate constant increase around 30% (see Fig.S4). In the presence of chloride ions, generated reactive species such as chlorine radical ($Cl^{\bullet}$) and dichlorine radical anion ($Cl_2^{\bullet-}$) could react more selectively with electron-rich organic compounds (Grebel et al., 2010).

On the contrary, when iodide ions at same concentrations were added to the solution, ACTP degradation rates are strongly affected as shown in Fig.2. In the dark, the addition of KI from 260 µM to 5 mM leads to an increase of the ACTP degradation with H_2O_2, which is much less the case with $Na_2S_2O_8$ at pH 5.4. In the presence of H_2O_2 or $Na_2S_2O_8$, iodide ions could be oxidized to iodine I_2 (**Eq.6**). Under UVA irradiation, KI alone in solution has no effect on ACTP (Fig.S5), indicating that iodide ions under UVA cannot transform or generate any active species. However, in the presence of H_2O_2 or $Na_2S_2O_8$ in the KI solution, the photo-degradation rate is highly enhanced (Fig. 2). In addition, $HOI^{\bullet-}/I^{\bullet}$ reactive halogenated species can be

generated from $HO^{\bullet}$ or $SO_4^{\bullet-}$ as shown in **Eq.7-8** (Elliot, 1992), indicating that iodide radicals ($I^{\bullet}$, $HOI^{\bullet-}$ and $I_2^{\bullet-}$) have higher reactivity with organic pollutants than chloride radicals (Yang et al., 2018a). Tamtam and Chiron (2012) and Li et al. (2015) have demonstrated that reactive halogenated species reacted more selectively than hydroxyl radicals with electron-rich organic pollutants. As ACTP contains hydroxyl and acetamido groups, which are electron donors to the aromatic rings, so it is hypothesized that these electron-rich moieties may selectively react with these iodide related radical reactive species. These selectivity properties of iodide based radicals are more emphasized than chloride ions. However, too much higher concentrated iodide ions (5 mM) will decrease the efficiency of ACTP degradation by self-quenching effects (**Eq.9**).

$$2I^- + H_2O_2/S_2O_8^{2-} \rightarrow 2HO\text{-}/SO_4^{2-} + I_2 \quad (6)$$

$$SO_4^{\bullet-}/HO^{\bullet} + I^- \rightarrow \rightarrow HOI^{\bullet-}/I^{\bullet} \quad \text{(Elliot, 1992)} \quad (7)$$

$$I^{\bullet} + I^- \rightarrow I_2^{\bullet-} \qquad k = 8.8\times10^9\ M^{-1}\ s^{-1} \quad \text{(Elliot, 1992)} \quad (8)$$

$$I^{\bullet} + I^{\bullet} \rightarrow I_2 \qquad k = 1.5\times10^{10}\ M^{-1}\ s^{-1} \quad \text{(Elliot, 1992)} \quad (9)$$

3.3 ACTP's degradation performance in BiOCl/UVA system

Heterogeneous photocatalytic degradation of ACTP has attracted numerous attentions recently, and various degradation pathways have been proposed for $SO_4^{\bullet-}$ and $HO^{\bullet}$ reactivity on ACTP. On the contrary, seldom studies have investigated the degradation of ACTP predominantly by superoxide radicals. In our previous studies (Wang et al., 2016a), BiOCl catalyst has been synthesized following with detailed characterization properties, as shown in Table 1. The XPS characterization is

presented in Fig.S6, the valance state of each element is in accordance with previous literatures, suggesting that BiOCl is well crystal organized with high purity. With a relatively wide band-gap (3.2 eV), BiOCl could hardly absorb the light wavelengths longer than 400 nm (Fig. S7A, B). The valance band of BiOCl determined from XPS spectra is 2.2 eV (Fig. S7C), which is not positive enough to oxidize H_2O to form hydroxyl radicals ($E^0(H_2O/HO^{\bullet})$ = 2.8 V *vs* NHE) (Wu et al., 2015b). Accordingly, the conduction band position can be calculated to be -1 eV, that is sufficiently negative enough to combine with dissolve oxygen to generate $HO_2^{\bullet}/O_2^{\bullet-}$ ($E^0(O_2/O_2^{\bullet-})$ = -0.28 V *vs* NHE) (Wu et al., 2015b). Consequently, UVA/BiOCl is adopted to produce $HO_2^{\bullet}/O_2^{\bullet-}$ radicals, which is further confirmed by quenching experiments (Fig.3A). In fact, no inhibition is obtained in the presence of TBA (1 mM) and KI (1 mM), which are traps of hydroxyl radicals and holes. Strong inhibition is noted with BQ (2 mM) which is able to trap also superoxide radicals. Furthermore, the obvious inhibition in N_2 purging condition further verifies that $HO_2^{\bullet}/O_2^{\bullet-}$ originate from the reaction between dissolved oxygen and electrons.

Before irradiation, adsorption capacity of the catalyst is tested and the results show that less than 10% of ACTP are adsorbed whatever the pH. Under irradiation, pH effects are investigated and strong increase of the ACTP degradation is observed at pH 3.0 if we compare with pH 5.8 and 7.5 (Fig.3B). These results are consistent with previous reports about BiOX used as photocatalyst (Gao et al., 2015; Liang et al., 2015) and the speciation of $HO_2^{\bullet}/O_2^{\bullet-}$ (pKa of 4.88) can explain the effect of pH (Li et al., 2017). Indeed, the second order rate constant between $O_2^{\bullet-}$ with phenol is 5.8×10^2

M^{-1} s^{-1} (Tsujimoto et al., 1993) and Kozmér et al. have demonstrated that in acidic solutions, $HO_2^{\bullet}$ shows a higher reactivity with phenol 2.7×10^3 M^{-1} s^{-1} (Kozmér et al., 2014), which is reasonably similar for phenolic compound ACTP. Furthermore, Zeta-potential of BiOCl is more negative with pH increasing (see Fig.3C), so less photo-induced electrons can transferred to the surface to combine with oxygen because electrostatic repulsion. While, as discussed above, electrons are crucial to form $HO_2^{\bullet}/O_2^{\bullet-}$. In terms of organic compounds mineralization, UVA/BiOCl shows excellent degradation and mineralization abilities compare to H_2O_2 or $Na_2S_2O_8$ whatever the solution's pH (Fig.3D).

3.4 Heterogeneous interfacial mechanism in UVA/BiOCl

For heterogeneous photocatalytic degradation, interfacial mechanism is essential to be investigated to confirm if the reaction is occurring in the solution or on the surface of catalyst. To clarify this question, NaH_2PO_4 has been proved to be a perfect desorbent in our experiment. Because NaH_2PO_4 could occupy almost all the adsorption sites on the surface of catalyst, and the surface was tightly surrounded by NaH_2PO_4 molecules instead of ACTP (Wang et al., 2018). With the addition of NaH_2PO_4, the degradation rate and removal percentage are both strongly suppressed (Fig.4A). As we discussed above, the main active species $HO_2^{\bullet}/O_2^{\bullet-}$ comes from the combination of dissolved oxygen in water and conduction band electrons. With a very short half-life time, $HO_2^{\bullet}/O_2^{\bullet-}$ would easily undergo disproportionation (Liang et al., 2015). Consequently, the fast and direct contact of pollutant and catalyst surface is crucial for the reaction. Furthermore, BiOCl nanosheets prepared in alkaline

conditions in this research were usually dominated with high [010] facets exposure. The [010] facets possessed open channels and abundant unsaturated Lewis/base sites, which was helpful for intimate contact between the interfacial surface and organic molecules (Jiang et al., 2012). So in this photocatalytic degradation system, degradation reactions must be occurred on the surface or very close to the surface of the catalyst.

3.5 Combination effects between H_2O_2, $Na_2S_2O_8$ and BiOCl under UVA

Degradation of ACTP is investigated in H_2O_2/BiOCl/UVA and $Na_2S_2O_8$/BiOCl/UVA systems to explore the possible synergy effects between H_2O_2 or $Na_2S_2O_8$ and BiOCl, as shown in Fig.4B, C. It is obvious that UVA/BiOCl/$Na_2S_2O_8$ (k = 7.13 × 10^{-4} s^{-1}) exhibit strong synergy effects compared with UVA/$Na_2S_2O_8$ (k = 4.63 × 10^{-5} s^{-1}) and UVA/BiOCl (k = 1.42 × 10^{-4} s^{-1}) through accelerating ACTP's removal and mineralization rate (Fig.4B, 3D). The increased degradation can be ascribed to the following reasons. Firstly, the direct photolysis of $S_2O_8^{2-}$ generating $SO_4^{\bullet-}$ could contribute to the oxidation of ACTP. Secondly, $S_2O_8^{2-}$ also can trap the photogenerated conduction band electrons result in the formation of $SO_4^{\bullet-}$ (**Eq.10**) (Sarwan et al., 2012). For the third reason, previous research has demonstrated the reaction of $O_2^{\bullet-}$ with persulfate anion to generate $SO_4^{\bullet-}$ according to **Eq.11** (Fang et al., 2013b). However, addition of H_2O_2 slows down the degradation rate associated with TOC removal (Fig.4B, C and 3D). The higher O–O bond energy of H_2O_2 compared with the band in free persulfate ions under natural pH could explain why persulfate is easier to be activated than H_2O_2 by the same ROS (reactive oxygen

species) (Zhang et al., 2017).

$S_2O_8^{2-} + e^- \rightarrow SO_4^{\bullet-} + SO_4^{2-}$ $k = 1.2\times10^{10}$ M^{-1} s^{-1} (Buxton et al., 1988) (10)

$S_2O_8^{2-} + O_2^{\bullet-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + O_2$ (11)

ESR spectrum was performed to confirm the active species formed in this system (Fig.5). No signal was detected in UVA/BiOCl system even repeat for several times or with higher catalyst loading. This result is consistent with the results in paragraph 3.4, which indicates that $HO_2^{\bullet}/O_2^{\bullet-}$ species may mainly exist on the surface of catalyst, leaving trace amount dissolved in aqueous solutions, which is too low to be detected. With the addition of H_2O_2 to the photocatalytic process, very weak $HO^{\bullet}$ signals can be observed due to its trace concentrations. While, with the addition of $Na_2S_2O_8$, stronger $HO^{\bullet}$ signal associating with $HO_2^{\bullet}/O_2^{\bullet-}$ signal can be observed. It is well known that $SO_4^{\bullet-}$-DMPO is very hard to be detected because of its rapid transformation to $HO^{\bullet}$-DMPO (Yang et al., 2018b). $SO_4^{\bullet-}$ is indeed the main active species in natural and acidic solutions. Above all, the addition of $Na_2S_2O_8$ facilitates the formation of $SO_4^{\bullet-}$ and make full use of $HO_2^{\bullet}/O_2^{\bullet-}$ by driving them from surface to aqueous solutions, which all contribute to higher mineralization abilities as shown in Fig.3D.

3.6 Determination of second order reaction rate constant between ACTP and $HO^{\bullet}$, $SO_4^{\bullet-}$ and $HO_2^{\bullet}/O_2^{\bullet-}$ radicals

From the results discussed above, conclusions can be drawn that under same illuminations, the degradation rate of ACTP follows: UVA/BiOCl > UVA/$Na_2S_2O_8$ > UVA/H_2O_2, which mainly depends on the second order reaction rate constant ($k_{ACTP,\ radical}$) and radical's concentrations. $k_{ACTP,HO^{\bullet}}$ was determined from Eq.S1-S4 and

Scheme S1, by following the absorbance of $SCN_2^{\bullet-}$ at 475 nm using different ACTP concentrations. The absorbance decreased from 0.021 to 0.006 when concentration of ACTP increases from 0 to 2.33×10^{-4} M (Fig.S8A), because ACTP compete with SCN^- to react with $HO^\bullet$. The slope "a" can be obtained from the linear regression of Abs_0/Abs versus different ACTP concentrations, and it was equal to 11276. Thus the second order constant $k_{ACTP,HO\bullet}$ can be evaluated from the product of "a", concentration of SCN^- (1×10^{-4} M) and $k_{HO\bullet,SCN-}=1.2\times10^{10}$ M^{-1} s^{-1} (Motohashi and Saito, 1993), finally it was calculated to be 1.35×10^{10} M^{-1} s^{-1}.

From competition method (Fig.S8B), $k_{SO4\bullet-,ACTP}=6.44\times10^9$ M^{-1} s^{-1} was determined. For $k_{HO2\bullet/O2\bullet-,ACTP}$, reference's results, already mentioned in part 3.3 (5.8×10^2 M^{-1} s^{-1} for $O_2^{\bullet-}$ and 2.7×10^3 M^{-1} s^{-1} for $HO_2^\bullet$) are took into account and because it has similar oxidation abilities towards phenolic compounds.

The steady state concentration of each radical ($[Radical]_{SS}$) can be estimated from the pseudo first degradation constant of ACTP in three systems determined in Fig.S8C. Considering that the pseudo first-order kinetic constant (k', s^{-1}) is equal to $k_{radical,\ ACTP}\times[Radical]_{SS}$, we can estimate the steady state concentration of each radical as $[Radical]_{SS}=k_{radical,\ ACTP}/k'$, where $k_{radical,\ ACTP}$ is the second order rate constant between ACTP and selected radical. Under adopted experimental conditions, a steady state concentration of $HO^\bullet$ and $SO_4^{\bullet-}$ was determined to be 1.0×10^{-15} and 7.2×10^{-15} M respectively while for $HO_2^\bullet/O_2^{\bullet-}$ was in the range 10^{-8}-10^{-7} M (Table 2). Although $HO_2^\bullet/O_2^{\bullet-}$ radical has the weakest oxidation capacities, its concentration is 7-8 orders of magnitude higher than $HO^\bullet$ and $SO_4^{\bullet-}$ radicals, thus directing the fast

degradation and mineralization efficiency of ACTP. From the view of economic, H_2O_2 and $Na_2S_2O_8$ are cheaper than the as-prepared BiOCl. But, it's essential to note that, H_2O_2 and $Na_2S_2O_8$ are gradually consumed in solution under irradiation and as a contrary, BiOCl catalyst, which is stable and can be preserved after catalytic reaction, has the advantage of easy recovery and so to be recyclable.

Conclusion

In summary, heterogeneous photocatalytic process UVA/BiOCl was always more efficient than the homogeneous UVA/H_2O_2 and UVA/$Na_2S_2O_8$ processes to degrade ACTP whatever the solution's pH. Halide ions such Cl^- plays a negligible role in UVA/H_2O_2 and UVA/$Na_2S_2O_8$ systems, while I^- could significantly improve the degradation performance due to the reactive species formation. BiOCl catalyst can be efficiently activated by solar light than traditional oxidant such as H_2O_2 and $Na_2S_2O_8$. With the same amount of oxidant or catalyst loading, UVA/BiOCl system could produce higher concentration of $HO_2^{\bullet}/O_2^{\bullet-}$ radicals, compared to $HO^{\bullet}$ and $SO_4^{\bullet-}$. This surface-depended $HO_2^{\bullet}/O_2^{\bullet-}$ oxidation process could induce significant mineralization abilities. Addition of $Na_2S_2O_8$ shows synergistic effects in UVA/BiOCl compared to the addition of H_2O_2. This research could provide implications in heterogeneous photocatalyst utilization, and shed light on capable combinations between photocatalyst and oxidants in future wastewater treatment under solar light irradiation.

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