1   **Attenuation of pharmaceutically active compounds in aqueous solution by**
2   **UV/CaO₂ process: Influencing factors, degradation mechanism and pathways**

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Abstract

As freshwater sources continue to be influenced by wastewater effluents, there is a dire need to develop advanced water treatment processes capable of treating the wastewater-derived contaminants, especially for pharmaceutically active compounds (PhACs). Ultraviolet light (UV) combined with calcium peroxide (CaO_2) as an advanced oxidation process (AOP) to attenuate five widespread PhACs (carbamazepine (CBZ), primidone (PMD), phenobarbital (PBB), thiamphenicol (TAP) and florfenicol (FF)) was investigated in this paper. The degradation of these compounds followed pseudo-first-order kinetics ($R^2 > 0.96$). The optimum CaO_2 dosage was 0.1 g L^{-1} and lower initial contaminants concentration was beneficial to their degradation. The UV/ CaO_2 treatment of test PhACs was attributed to the combination of UV/ H_2O_2 and UV-base-photolysis (UV/ $\text{Ca}(\text{OH})_2$), and the degradation mechanism was recognized as both UV direct photolysis and indirect photolysis caused by reactive radicals ($\bullet\text{OH}$, triplet states of dissolved organic matter ($^3\text{DOM}^*$), and $^1\text{O}_2$). Furthermore, the tentative transformation pathways of the five PhACs were proposed based on the detected intermediates and the degradation mechanisms. The final products of inorganic carbon and nitrogen indicate UV/ CaO_2 treatment can significantly mineralize test PhACs. Also, the CaO_2 addition significantly reduced the energy consumption of UV irradiation according to *electrical energy per order*. The effective removal of CBZ and PMD in a secondary wastewater effluent by UV/ CaO_2 treatment demonstrates the potential use of this

48 AOP technology in advanced treatment of wastewater-derived PhACs.

49 **Keywords:** UV/CaO₂; pharmaceutically active compounds (PhACs); reactive radicals;

50 degradation mechanism; wastewater effluent

51 **1 Introduction**

52 The persistence of trace organic contaminants (TOrcs), especially
53 pharmaceutically active compounds (PhACs), in effluents of wastewater treatment
54 plant (WWEs) has raised many concerns due to their potential harm to aquatic
55 ecosystems and human health (Liu and Wong 2013, Oulton et al. 2010). These PhACs
56 include antibiotics, antiepileptics, hormones, analgesics, blood lipid regulators, and
57 contrast agents (Pereira et al. 2007) which have been detected at high frequencies and
58 concentrations ranging from ng·L⁻¹ to µg·L⁻¹. Some PhACs such as carbamazepine
59 (CBZ) and primidone (PMD) can be used as tracers for aquatic environment pollution
60 caused by sewage effluents (Liu and Wong 2013, Tran et al. 2019). Previous
61 investigations showed that PhACs have been detected in WWEs in Asia, Europe,
62 America, and Oceania with maximum concentrations between 130–126000 ng L⁻¹
63 (Liu and Wong 2013, Tran et al. 2018). Accordingly, PhACs have been detected in
64 surface water with maximum concentration of 10000 ng L⁻¹ (Liu and Wong 2013,
65 Tran et al. 2019) , and in groundwater with maximum concentration of 3110 ng L⁻¹
66 (Lapworth et al. 2012, McCance et al. 2018). Antibiotics, one of the most concerning
67 pharmaceutical contaminants, can cause many problems for aquatic and terrestrial
68 organisms; e.g., thiamphenicol (TAP) and florfenicol (FF) has been shown to cause

inhibition of peptidyl transferase (Hayes et al. 2003) and the hematopoietic system (Festing et al. 2001). Another concern is that antibiotics may accelerate the emergence of antibiotic resistance genes (ARG), and even multiple antibiotic resistant (MAR) superintegrations under environmental exposure (Liu and Wong 2013, Yi et al. 2017). Antiepileptic drugs, like CBZ, PMD and phenobarbital (PBB) have also been highly studied in water. CBZ may cause oxidation stress in aquatic fish (Chen et al. 2012, Li et al. 2010) and affect the growth and morphology of human embryonic cells at environmentally relevant concentrations (Keen et al. 2012). PMD can have various effect on human, such as the feeling of intoxication or nausea (Sijak et al. 2015). PBB, a main active metabolite of primidone, can cause lethargy, dysarthria, and lack of coordination in humans (Mattson 1995). Moreover, when combined with other pharmaceuticals, the synergistic effects of these compounds can induce more severe harm to the ecosystems than expected from the measured impacts of any individual PhAC (Cleuvers 2003). Therefore, it is vital to investigate methods capable of adequately degrading these compounds and identify the relevant transformation mechanisms.

Calcium peroxide (CaO_2), one of the most frequently-used and safest solid inorganic peroxy compounds, is considered a “solid form” of H_2O_2 , and has been widely used in agriculture, aquaculture, and medicine (Lu et al. 2017, Ma et al. 2007). It is capable of producing H_2O_2 , O_2 and alkali compounds (Chen et al. 2016, Ma et al. 2007), as well as $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$ radicals in moist media (Ma et al. 2007, Zhang et al.

2015). Unlike liquid H_2O_2 , which is unstable and decomposes in the presence of a base or a catalyst, CaO_2 is relatively stable, making it convenient to transport and preserve. Meanwhile, the slow dissolution allows oxidants to be produced for longer periods, allowing more time for pollutants to be oxidized in aqueous solution (Zhang et al. 2016b). Several studies have demonstrated the ability of CaO_2 to degrade contaminants in aqueous solution. For example, CaO_2 can be used to remediate the MTBE-contaminated groundwater (Liu et al. 2006). CaO_2 nanoparticles can also be used for the recovery of valuable chemicals from aqueous waste streams and potentially for removal of toxic materials (Madan and Wasewar 2018). Additionally, trichloroethene (TCE) degradation could be significantly enhanced by CaO_2 activated with Fe(III) in the presence of citric acid solutions (Zhang et al. 2016a). Ozone combined with CaO_2 can effectively mineralize sulfolane in aqueous solution (Izadifard et al. 2018). Zhang et al. showed CaO_2 degraded greater than 50% of six endocrine-disrupting compounds in pure-water and waste active sludge under 7 days and was very effective in sludge solubilization (Zhang et al. 2015). Thus, CaO_2 could be a promising oxidant for the treatment of PhACs in wastewater effluents.

Most PhACs like CBZ and PMD are resistant to biodegradation (Roccaro 2018). Advanced oxidation processes (AOPs) are more efficacious for the attenuation of refractory contaminants, but challenges remain. UV and ozone are selective and have limited oxidation effect for certain classes of compounds including PMD (Roccaro 2018); and electron beam requires large space for machines, high-skilled technicians

for instrumental operations, and high energy consumption (Chmielewski and Han 2016). Although UV/H₂O₂ is considered as one of the most commonly used AOPs for control of refractory TOrC like CBZ and PMD (Yang et al. 2014), H₂O₂ is unstable and easily-decomposable, making it difficult to preserve (Lu et al. 2017). UV/CaO₂ possesses benefits over the aforementioned treatment technologies for TOrC abatement. The continuous generation of H₂O₂ from CaO₂ and its safe application in many industries (Lu et al. 2017) allow for its consideration in combination with other technologies to compose an AOP. Similarly to UV light being applied for photolytic decomposition of H₂O₂ to produce amounts of •OH in aqueous solution (Liao and Gurol 1995), UV has been combined with CaO₂ to produce •OH in aqueous solution (Kozak and Włodarczyk-Makula 2018). Therefore, UV/CaO₂ is a viable option for TOrC control. However, influencing factors and mechanisms to the degradation of refractory TOrCs in aqueous have still not been investigated. Furthermore, the increase of suspended solids (SS) or pH caused by CaO₂ dissolution should be discussed when it is applied in water treatment.

To explore the mechanism of UV/CaO₂ in the removal of refractory PhACs in aqueous solution, several PhACs including CBZ, PMD, PBB, TAP and FF degraded by UV/CaO₂ in aqueous solution were investigated in this paper. Altogether, this study evaluated: 1) effects of influencing factors (CaO₂ dosage, initial concentration of test PhACs and initial pH), 2) function of CaO₂ hydrolysates on the removal of test PhACs, 3) main reactive radicals and their respective contribution to the overall

removal, 4) main transformation products of selective contaminants under UV/CaO₂,
5) *electrical energy per order* for the degradation of test PhACs, and 6) application of
UV/CaO₂ on the removal of selective PhACs in WWE.

2 Materials and methods

2.1 Chemicals

Of the five target PhACs, CBZ and PMD at > 98% purity were obtained from
Sigma-Aldrich. PBB was purchased from ICN pharmaceuticals with > 98% purity
and FF and TAP from Dr. E (Germany) with 99% and 98.5% purity, respectively.
Physicochemical information of the five test PhACs is shown in Table S1. Labeled
surrogate standards, carbamazepine-d₁₀ and primidone-d₆ were purchased from
Cambridge Isotope Laboratories (Andover, MA). CaO₂ (≥ 75%), and all solvents
(methanol, acetonitrile, isopropyl alcohol (IPA) and acetic acid) of a purity suitable
for chromatographic analysis were also obtained from Sigma-Aldrich. The superoxide
dismutase (SOD), catalase (CAT), 1,4-Diazabicyclo[2.2.2]octane (DABCO), isoprene
(IPE, > 98%), 5,5-dimethyl-1-pyrroline N-oxide (DMPO), dimethyl sulfoxide
(DMSO), thiourea, the short chain fatty acids (SCFAs) (formate, acetate, oxalate,
malonate, succinate, maleate, and fumarate), nitrate (NO₃⁻), nitrite (NO₂⁻), ammonia
(NH₄⁺), sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), sodium carbonate
(Na₂CO₃), sodium bicarbonate (NaHCO₃), sodium thiosulfate (Na₂S₂O₃) and 30 %
hydrogen peroxide (H₂O₂) at the highest available purity, were purchased from
Shanghai Chemical Reagent Co. Ltd unless otherwise stated. H₂SO₄ and NaOH were

used to adjust the pH of solutions. $\text{Na}_2\text{S}_2\text{O}_3$ was added to terminate the reaction.

Pure-water (PW, $> 18.2 \text{ M}\Omega\cdot\text{cm}$) used for stock solution preparation and instrument

analysis were prepared by a Milli-Q system (EMD Millipore, Billerica, MA, USA).

2.2 Secondary wastewater effluent

The secondary WWE prior to chlorination was collected from a WWTP in Arizona, USA which consists of primary clarifiers, a 5-stage bardenpho biological nutrient removal activated sludge process, secondary clarifiers, chlorination, and dechlorination (Anumol et al. 2015). The water was filtered using glass-fiber filters (Whatman GF/F, $0.7 \mu\text{m}$ nominal pore size) and stored at 4°C for up to 24 hours before analysis. The characteristics of the WWE samples are shown in Table 1.

2.3 Experimental Procedure

2.3.1 Photoirradiation set-up

A merry-go-round photochemical reactor (PhchemIII, NBeT Co. Ltd, Beijing, China) coupled with a max of 12 quartz tubes containing the reaction solution was used for the photodegradation experiments. The low-pressure mercury lamp was immersed in the circulated-water cooled quartz well. The light source irradiance spectra were measured by a spectroscope (USB2000+ UV-vis, Ocean Optics, USA) shown in Fig. S1. The UV lamp has a strong intensity at a 254 nm wavelength. After 50 mL of solution spiked with test PhACs were irradiated by UV, 2 mL was then collected from the tube at the preset sampling times with $\text{Na}_2\text{S}_2\text{O}_3$ as the terminator for the subsequent analysis.

2.3.2 Removal of test PhACs in PW by UV/CaO₂

The following influencing factors were evaluated for the degradation of test PhACs under UV/CaO₂: CaO₂ dosage (from 0 to 0.2 g L⁻¹), initial test compound concentration (from 0.5 to 20 mg L⁻¹) and initial pH (from 2.4 to 10.3). Furthermore, the degradation of test PhACs under pH from 2.4 to 11.3 irradiated by UV without CaO₂ was set as a comparison. CaO₂ can be hydrolyzed into Ca(OH)₂ and H₂O₂ upon adding to water (Chen et al. 2016, Ma et al. 2007), and the changes of H₂O₂ concentration in PW and WWE are shown in Fig. S2. The mechanism of UV/CaO₂ on test PhACs were evaluated with experiments using UV irradiation combined with different CaO₂ hydrolysates. The hydrolysates were set at theoretical equivalent concentrations of CaO₂: [75% CaO₂] = 0.100 g L⁻¹, [Ca(OH)₂] = 0.102 g L⁻¹, [H₂O₂] = 0.0354 g L⁻¹. UV/CaCl₂ ([CaCl₂] = 0.153 g L⁻¹) was used to evaluate the effect of Ca²⁺ on test PhACs removal. UV/NaCl ([NaCl] = 0.161 g L⁻¹) treatment was used to assess the effect of Cl⁻ in the UV/CaCl₂ treatment.

2.3.3 Identification of transformation products

Identification of transformation products of target PhACs was done in PW treated with UV/CaO₂. Each test PhAC was set at 10 mg L⁻¹ and separately treated by UV/CaO₂. Ion chromatography (IC) was used to detect the SCFAs and inorganic ions; liquid chromatography/quadrupole time-of-flight mass spectrometry (LC-QTOF-MS), liquid chromatography/triple quadrupole mass spectrometer (LC-QQQ-MS) and GC-MS techniques with NIST library were used to identify main intermediates

formed during UV/CaO₂.

2.3.4 Identification of reactive radicals

Removal of the target PhACs in aqueous solution under UV/CaO₂ might be due to both direct and indirect photolysis (Jasper and Sedlak 2013). To clarify contributions of different photolysis mechanisms to the overall removal of test PhACs in PW during UV/CaO₂, scavengers were used to isolate the contributions of different reactive species. All samples amended with test PhACs were treated with 0.1 g L⁻¹ CaO₂ (~1.0 mmol L⁻¹ (mM)) prior to UV irradiation. Scavengers were set as follows: IPA (~100 mM) was used to quench •OH reactions (Jasper and Sedlak 2013); IPE (~10 mM) was used to quench triplet states of dissolved organic matter (³DOM*) (Jasper and Sedlak 2013); SOD (~100 kU L⁻¹) was used to quench O₂^{•-} (Singh 1982); DABCO (~100 mM) was used to quench ¹O₂ (Zepp et al. 1977); ¹O₂ was primarily generated from the reaction between dissolved oxygen (DO) and ³DOM*, making other resources negligible (Haag and Hoigne 1986, Marchisio et al. 2015). The N₂-sparged condition (N₂, 99.999% purity) was used to evaluate effects of ¹O₂ and O₂ on test PhACs removal and high-purity air-sparged condition (99.999%) was used to quench ³DOM* (Jasper and Sedlak 2013).

Moreover, electron paramagnetic resonance (EPR, ESP300 (Bruker, Germany)) was used to further detect the main free radicals in the treatment of UV/CaO₂. EPR parameters and experimental settings were described in previous investigations (Li et al. 2015, Lipovsky et al. 2012). DMPO was used to trap the •OH, O₂^{•-} and alkyl

radicals ($\bullet$ C-R) forming DMPO-OH, DMPO-OOH and DMPO-C-R spin adduct, respectively (Li et al. 2015, Lipovsky et al. 2012). Thiourea (~1%, w/v) and DMSO (~10%, w/v) were used to quench $\bullet$ OH. DMSO reaction with $\bullet$ OH to produce $\bullet$ CH₃ can transform DMPO into DMPO-CH₃. Previous investigation shows the alkyl radical ($\bullet$ C-R) may be generated from the oxidation of contaminants to form DMPO-C-R which have similar EPR spectrum feature of DMPO-CH₃ (Zhang et al. 2015). Overall, the EPR spectrums under different treatments were compared: CaO₂, UV/CaO₂, thiourea + UV/CaO₂, DMSO + UV/CaO₂ and test PhACs + UV/CaO₂. The test steps were as follows: 5 μ L of phosphate buffered saline (PBS) (50 mM, pH 7.4), 5 μ L FeSO₄•(NH₄)₂SO₄ (1.0 mM), 5 μ L of DMPO (0.9 M), and 10 μ L of samples were mixed in sequence and the mixture was then put in a quartz capillary and measured by EPR immediately.

2.3.5 Removal of target PhACs in WWE by UV/CaO₂

Removal efficiencies of target PhACs from WWE were used to evaluate the treatment efficacy of UV/CaO₂ on PhACs in WWE. The CaO₂ dosage was set at 17, 50 and 100 μ M, which would not cause obvious pH change by CaO₂ addition. Meanwhile, UV and UV/H₂O₂ (100 μ M) treatments were set as comparisons. A collimated beam device (ITT Wedeco, Herford, Germany) with four low-pressure UV lamps (Type NLR2036) was used in this experiment. A UV absorbed dose (J cm⁻²) at 254 nm was the arithmetic product of UV irradiance (mW cm⁻²), correction factors and exposure time (s), which were determined by a previous research (Bolton and

Linden 2003).

Samples were prepared according to a previous investigation (Anumol et al. 2015). Samples after treatments were spiked with a mixture of internal standards (200 ng L⁻¹) and allowed to equilibrate for ~30 min at room temperature. Then the samples were analyzed via direct injection by LC-QQQ-MS (Anumol et al. 2015). With respect to test PhACs, only CBZ and PMD were detected, and compound-specific parameters are given in Table S7.

2.4 Analytical Methods

CBZ, PMD, PBB, FF and TAP spiked in PW were detected using a high performance liquid chromatography (HPLC) system. Organic and inorganic ions were detected by IC. Major degradation intermediates of each PhAC were detected using LC-QTOF-MS, LC-QQQ-MS or GC-MS. Changes of CBZ and PMD in WWE were detected using LC-QQQ-MS. All details for the analytical methods are provided in supporting information (SI) text.

The analytical method for total organic carbon (TOC) was described in our previous investigation (Zhang et al. 2015). EPR parameters and experimental settings were also described in previous investigations (Li et al. 2015, Lipovsky et al. 2012). The H₂O₂ concentration was detected using Single Analyte Meters (SAMs, I-2016) with replacement kit (Hydrogen Peroxide — Vacu-vials® Instrumental Kit).

3 Results and Discussion

3.1 Removal of PhACs in PW by UV/CaO₂

3.1.1 Effect of CaO₂ dosage

The natural logarithmic values of normalized concentrations of test PhACs ($\ln(C/C_0)$) decreased linearly with the irradiation time (Fig. S3). The reaction kinetics of the test PhACs followed pseudo-first-order kinetics with $R^2 \geq 0.97$ for all the tested PhACs and their degradation rate constants (K , min⁻¹) at different CaO₂ dosages are shown in Fig. 1(a). The K escalated with increasing CaO₂ dosage, with the greatest K value at 0.1 g L⁻¹ of CaO₂. The increase of K may be attributed to the increased production of oxidative radicals ($\bullet$ OH) from the UV activating CaO₂ (reactions 1-3) (Chen et al. 2016, Ma et al. 2007). There are several possible reasons for the retarded increase of rate constants after the optimal CaO₂ dosage. First, the overdose of CaO₂ may cause an increase in turbidity (Fig. S4(a)) and UV-screening (Fig. S4(b)), which reduces the effective utilization of UV in the degradation of test PhACs. Secondly, a higher pH caused by excess CaO₂ can accelerate the disproportionation of H₂O₂ (reaction 4), which may decrease the effective concentration of $\bullet$ OH (reaction 3). Furthermore, the alkaline condition not only lowers the $\bullet$ OH concentration (reaction 5), but also lowers the $\bullet$ OH oxidation potential from 2.7 V in an acidic solution to 1.8 V in a neutral solution (Buxton et al. 1988). Additionally, Fig. 1(a) reveals that the increased K of CBZ, PMD, and PBB are significant more than that of TAP and FF when CaO₂ was added, indicating indirect photolysis (mainly by $\bullet$ OH) played an important role in the degradation of CBZ, PMD, and PBB, while direct photolysis played an important role in the degradation of TAP and FF during UV/CaO₂

treatment.

The change of TOC in Fig. 1(b) shows that the test PhACs could be gradually mineralized under UV/CaO₂ process. The addition of CaO₂ significantly enhanced the mineralization of test PhACs. However, the mineralization efficiencies were almost similar when the CaO₂ dosage was above 0.1 g L⁻¹. Comprehensively considering the cost of chemicals consumption and test PhACs removal, the optimum CaO₂ dosage recommend at 0.1 g L⁻¹.

3.1.2 Effect of initial concentration of the test PhACs

As shown in Fig. 2, the *K* of each PhAC decreased as their initial concentrations increased. This is because a higher concentration of test PhACs might increase UV-screen properties of the solution (Fig. S5) which could reduce the UV light activation to CaO₂ for generating reactive species and thus retarding the degradation of test PhACs. Furthermore, more complicated intermediates generated from higher initial concentration during the reaction may compete with test PhACs for the UV light and reactive radicals (Cater et al. 2000, Liu et al. 2015a). Additionally, the *K* of test PhACs were successfully fitted as an exponential function to their initial

concentration (Table S2) based on the high R^2 (> 0.98). Therefore, K of the test PhACs at different initial concentrations can be calculated based on the fitted formulas ($[\text{CaO}_2] = 0.1 \text{ g L}^{-1}$).

3.1.3 Effect of initial pH

The initial pH of the solution can influence the effective H_2O_2 and $\bullet\text{OH}$ concentration from CaO_2 hydrolysis (Buxton et al. 1988, Lu et al. 2017) and the forms of compounds due to protonation or deprotonation (Jasper and Sedlak 2013), and thus affects the degradation of test PhACs.

As shown in Fig. 3(a), during UV/ CaO_2 , the initial pH = 2.4, significantly promoted the removal of test PhACs with a final pH of 2.7, while the pH from 4.5 to 10.5 has little influence on the K , with a final pH at 11.1-11.2. The big increase of K with initial pH = 2.4 may be related to a final pH = 2.7, since the acidic solution promoted the H_2O_2 release rate and the final yield from CaO_2 (Wang et al. 2016), and facilitated the formation of $\bullet\text{OH}$ under UV irradiation to decay test PhACs (Liu et al. 2015a). The lower K with a final pH at 11.1-11.2 was because the alkaline solution may decrease the H_2O_2 release rate and final yield (Wang et al. 2016), and decrease the $\bullet\text{OH}$ concentration and its oxidation potential (Buxton et al. 1988). Meanwhile, the similar K with initial pH at 4.5-10.5 may be related to a similar final pH = 11.1-11.2.

Test PhACs under protonation and deprotonation may result in different direct and indirect photolysis (Boreen et al. 2004, Jasper and Sedlak 2013). 1) To assess the

forms of test PhACs on their direct photolysis, the effects of different pH conditions on the degradation of test PhACs under sole UV were evaluated. As shown in Fig. 3(b), at a pH from 2.4 to 11.3, the protonated CBZ and PMD ($pK_a > 11.5$, Table S1) was not influenced by pH; however, at a pH > 8.2 , K of the deprotonated PBB ($pK_a = 7.3/8.14$, Table S1) increased, and at a pH > 10 , K of the deprotonated TAP ($pK_a = 7.2/9.76$, Table S1) and FF ($pK_a = 9.03$, Table S1) increased. Considering the final pH was 11.1-11.2 during UV/ CaO_2 , PBB, TAP, and FF at deprotonation performed a higher direct photolysis. Actually, direct photolysis of PhACs containing amines may be affected by pH because of changes in molar absorption coefficients or quantum yields of different forms of the compounds (Jasper and Sedlak 2013), which was further proved in Fig. S6 that the UV absorbance of the mixed test PhACs increased upon pH > 8.2 , especially at 200-280 nm. 2) The indirect photolysis may be affected by pH because the protonated or deprotonated PhACs reacted with the reactive radicals ($^1O_2$ and $\bullet CO_3^-$) at second-order reaction rates that varied over more than 2 orders of magnitude (Jasper and Sedlak 2013). Additionally, Fig. S7 reveals PBB, TAP and FF underwent degradation through base-hydrolysis at pH > 8.2 . Previous investigations showed phenicols such as TAP and FF underwent base-hydrolysis via the breakage at the amide linkage (Glazko et al. 1950) and the chloro-group linkage (Mitchell et al. 2015).

3.2 Degradation mechanism of test PhACs under UV/ CaO_2

3.2.1 Effect of CaO_2 hydrolysates

Experiments using the combination of CaO_2 hydrolysates (Ca(OH)_2 or H_2O_2) with UV were conducted to explore the chemical mechanisms of PhACs degradation by UV/ CaO_2 in aqueous solution. As shown in Fig. 4(a), H_2O_2 played a vital role in the UV-photolysis of CBZ and PMD while Ca(OH)_2 had an insignificant influence. For PBB, TAP and FF, both H_2O_2 and Ca(OH)_2 improved their K values under UV. The significant improvement under UV/ H_2O_2 was due to the $\bullet\text{OH}$ generation during photolysis of H_2O_2 (Cater et al. 2000). As shown in Fig. 4(b), the pH of CaO_2 and Ca(OH)_2 were much higher than others. Results from the K under UV, UV/ CaCl_2 and UV/ NaCl showed that Ca^{2+} had no effect on the degradation of test PhACs. Therefore, the improvement of K under UV/ Ca(OH)_2 was attributed to the alkaline condition which was defined as base-catalytic UV-photolysis in this paper. According to 3.1.3, PBB, TAP and FF containing amines were deprotonated under Ca(OH)_2 , probably improving their hydrolysis and resulting in the increase in direct photolysis during UV irradiation. Therefore, the UV/ CaO_2 treatment of test PhACs can be considered as the combination of UV/ H_2O_2 and UV-base-photolysis.

3.2.2 Effect of reactive radical scavengers

Fig. 5(a) shows the effects of radical scavengers on the removal of test PhACs, and Fig. 5(b) shows contributions of direct-photolysis and indirect-photolysis caused by different oxidative species ($\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, O_2^1 , $^3\text{DOM}^*$ and H_2O_2) for the removal of test PhACs. It appears the removal mechanism of each test PhAC was different during UV/ CaO_2 process. 1) UV direct-photolysis showed little contribution to CBZ and

363 PMD removal, and a minor contribution to PBB removal (~14%), while appreciable
364 contribution to TAP (~68%) and FF (~55%) removal. 2) IPA at the given
365 concentration (i.e., ~0.1 mol L⁻¹) can almost completely quench •OH (reaction 6),
366 whereas reactions of O₂^{•-} and ¹O₂ were unaffected (Singh 1982). With IPA addition,
367 CBZ and PMD degradations were almost completely inhibited (Fig. 5(a)), indicating
368 that •OH accounted for much of K of CBZ and PMD (with ~100% and ~99%
369 contribution, respectively (Fig. 5(b))). However, •OH accounted for 20-40% for K of
370 PBB, TAP and FF (Fig. 5(b)). 3) When comparing the UV/CaO₂ treatments with IPA
371 and IPA+DABCO additions, we can find only PBB and FF underwent obvious
372 indirect photolysis by ¹O₂ with ~18% and ~5%, respectively. The little observed
373 removal of CBZ by ¹O₂ is consistent with the investigation of Jasper and Sedlak
374 (2013). 4) Due to SOD, a O₂^{•-} scavenger, can react with •OH and ¹O₂ at 5.3×10¹⁰ M⁻¹
375 s⁻¹ and 2.5 ×10⁹ M⁻¹ s⁻¹, respectively (Singh 1982), IPA was added to remove •OH and
376 N₂-sparging was used to remove O₂ and ¹O₂ in advance. Comparison of K between
377 N₂+IPA and N₂+IPA+SOD showed O₂^{•-} had little contribution to the degradation of
378 all test PhACs (Fig. 5(b)). 5) During the UV/CaO₂ treatment of test PhACs, ³DOM*
379 may be introduced via the UV-excitation of test PhACs or their intermediates. As IPE
380 quenches both ³DOM* and •OH (Huang et al. 2011), IPA was used to exclude •OH
381 first. Meanwhile, N₂-sparged condition can remove O₂ from the CaO₂ decomposition,
382 and inhibit the reaction of ³DOM* with O₂ forming ¹O₂. The decrease of PBB and FF
383 under IPA+IPE compared to IPA and the increase under N₂-sparging, suggests a

contribution of $^3\text{DOM}^*$ to the degradation of PBB (~28%) and FF (~19%). However, $^3\text{DOM}^*$ had an insignificant influence on the removal of CBZ, PMD and TAP. Moreover, the attenuation of K upon sparging with air, a $^3\text{DOM}^*$ quencher, further revealed PBB and FF could be removed by $^3\text{DOM}^*$. However, the K of CBZ and PMD increased slightly under air-sparged condition and decreased slightly under N_2 -sparged condition (Fig. 5(a)). As CBZ and PMD were mainly removed by $\bullet\text{OH}$, this phenomenon may be explained as follows: When sparged with O_2 , extra reactive oxygen species (ROS) generating under UV irradiation may promote the removal of intermediates of test PhACs, thereby reducing their competition for $\bullet\text{OH}$ with CBZ and PMD; the sparged N_2 removed O_2 generated from CaO_2 (reaction 2) that might reduce the generation of ROS, resulting in a decrease in the overall removal of intermediates. 6) Although large amounts of H_2O_2 was produced from CaO_2 hydrolysis (Lu et al. 2017), sole H_2O_2 had an insignificant contribution to the removal of test PhACs compared with other degradation mechanisms. In summary, $\bullet\text{OH}$ played a vital role on CBZ (~100%) and PMD (~99%) degradation; direct photolysis (~14%), $\bullet\text{OH}$ (~36%), $^3\text{DOM}^*$ (~28%) and $^1\text{O}_2$ (~18%) mainly contributed to PBB removal; direct photolysis (~68%) and $\bullet\text{OH}$ (~35%) contributed to TAP removal; direct photolysis (~55%), $\bullet\text{OH}$ (~21%), and $^3\text{DOM}^*$ (~19%) contributed to FF removal.

3.2.3 Identification of the main reactive oxidative species by EPR.

The EPR was used to further ascertain main reactive radicals during UV/CaO₂. As shown in Fig. 6(a), the DMPO-OH signal (four split lines with 1:2:2:1 height ratio, the red solid diamonds) shows the probable existence of •OH during CaO₂ and UV/CaO₂, and •OH generation was significantly improved under UV/CaO₂ treatment compared to CaO₂ (Li et al. 2015). As DMPO-OOH is easily converted into DMPO-OH, DMSO and thiourea, •OH quenchers, were separately used in the trapping experiments (Li et al. 2015, Lipovsky et al. 2012). When DMSO was added, Fig. 6(b) shows the minor DMPO-OH signal and the primary spectral features of DMPO-CH₃ (six split lines with same height ration, the green open triangle), which confirmed the major existence of •OH radicals, because •OH radicals react with DMSO to produce •CH₃ radicals which convert DMPO into DMPO-CH₃. When thiourea was used to quench •OH, the major DMPO-OOH and minor DMPO-OH signals in Fig. 6(c) implies the generation of O₂^{•-} during UV/CaO₂. Meanwhile, a DMPO-CH₃-like signal appeared upon adding test PhACs under UV/CaO₂ in Fig. 6(b), indicating the probable formation of alkyl radicals (•C-R) (Zhang et al. 2015). Thus, •OH, O₂^{•-} and probable •C-R radicals are presented during the UV/CaO₂ treatment of test PhACs.

3.3 The transformation products of test PhACs under UV/CaO₂

3.3.1 IC analysis

Results for the main organic and inorganic ions analyzed by IC are shown in Table S3 and Fig. S8. Formate increased at the first 50 min, and then kept stable

during the degradation of CBZ, TAP and FF, but it continuously increased in the degradation of PMD and PBB. Acetate experienced a slow increase during CBZ, TAP and FF degradation, while a large increase in PMD and PBB degradation was observed. Oxalate was significantly generated after 2 h treatment of CBZ, TAP and FF, and after 3 h treatment of PMD and PBB. Maleate was detected in the treatment of all test PhACs, and fumarate was detected in the degradation of CBZ and PMD (Table S3), indicating that the central heterocyclic ring or aromatic rings were attacked and then opened, because of an *ipso*-attack on C-carrying chlorine, amino or carboxyl (Ozcan et al. 2008). Succinate was also detected in the degradation of CBZ, PMD and PBB. A previous study reported that organic nitrogen may be transformed into N_2 , NH_4^+ and NO_3^- during the oxidative degradation of CBZ (Vogna et al. 2004). As shown in Fig. S8, NH_4^+ was produced significantly, while production of NO_2^- and NO_3^- was insignificant during the treatment of test PhACs.

Cl^- and SO_4^{2-} were only detected in the degradation of TAP and FF, which increased quickly at the first 2 h, and then almost remained stable. The detachment of the Cl atom from TAP and FF was 57% and 63% respectively after 4 h reaction. The path of Cl^- generation can be inferred as Path 1 in Fig. 7 because of the oxidation (by $\bullet\text{OH}$) and hydrolysis. However, the detached S atom as SO_4^{2-} accounted for 16% and 15% of the total S from TAP and FF, respectively. A preliminary experiment showed the magenta solution faded upon pouring the gas collected from the UV/ CaO_2 (with 1 mM HCl) treatment while returned to red if heated (not shown here), indicating the

probable existence of $\text{SO}_3^{2-}/\text{SO}_2$. Therefore, the S atom was transformed into SO_4^{2-} and $\text{SO}_3^{2-}/\text{SO}_2$, and the tentative transformation pathway was proposed in Path 2 in Fig. 7. As shown in path 3 of Fig. 7, the detected F^- accounted for 72% of total F atom from FF. It is inferred that the F atom was detached from FF forming F^- .

3.3.2 LC-MS analysis for CBZ, PMD and PBB

3.3.2.1 Carbamazepine

The intermediates from CBZ degradation under UV/ CaO_2 detected by LC-MS are shown in Table S4 and Fig. S9(a) and their changes are shown in Fig. S10(a). Based on intermediates and the aforementioned degradation mechanisms, the tentative degradation pathway of CBZ was proposed in Fig. 8. The $\bullet\text{OH}$ played a vital role in CBZ degradation. Firstly, the C10-C11 double bond in the central heterocyclic ring of CBZ may be hydroxylated into CBZ-10OH (Chiron et al. 2006), and then, it was oxidized into oxcarbamazepine (OXCBSZ) through breaking O-H bond at site *b*, C-H at *c* site and C-C at *d* site of CBZ-10OH (Hu et al. 2009). The second predominant pathway involves the heterocyclic ring contraction process. The reactive 10,11-double bond was attacked by $\bullet\text{OH}$ to yield 10,11-epoxycarbamazepine (CBZ-EP), which has been mentioned in other studies (Li et al. 2013, Miao et al. 2005). CBZ-EP subsequently evolved into diols, which may be identified as 10,11-dihydro-10,11-cis-dihydroxy-CBZ or 10,11-dihydro-10,11-trans-dihydroxy-CBZ (CBZ-DiOH) (De Laurentiis et al. 2012). The central heterocyclic ring of CBZ-EP and CBZ-DiOH underwent structural

alterations, leading to a heterocyclic ring contraction and cyclization reactions to form 4-formyl-9-carbamoyl-acridone (4-AOC) or acridine-9-carboxaldehyde (AIC) (Kosjek et al. 2009) via a pinacol-type rearrangement (Li et al. 2013). 4-AOC may further cleave the carboxyaldehyde and carbamoyl group to yield acridone (AO) (Hu et al. 2009). AIC may transform into acridine (AI) (Kosjek et al. 2009) or undergo a further hydroxylation to hydroxyacridine-9-carboxaldehyde (AIC-OH) (Calisto et al. 2011, Kosjek et al. 2009). AI can transform into AO via UV photolysis, as previously described (Kosjek et al. 2009). The third route is the hydroxylation of aromatic rings to form hydroxy-carbamazepine (CBZ-2(3)OH) and dihydroxycarbamazepine (CBZ-OH-OH) (De Laurentiis et al. 2012, Miao et al. 2005). CBZ-OH-OH was identified as 2,7-dihydroxycarbamazepine 2,8-dihydroxycarbamazepine and 3,8-dihydroxycarbamazepine with the hydroxyl function on the different carbon site of the outside aromatic ring (De Laurentiis et al. 2012). In addition, the CBZ underwent the cleavage of carbamoyl to form iminostilbene (IM), which was also observed in our study (Breton et al. 2005, Kosjek et al. 2009). Fig. S10(a) shows intermediates detected by LC-QQQ-MS increased and then decreased in 4 h, while Fig. S8(a) shows IC products increased or fluctuated during 4 h, indicating intermediates may be converted into SCFAs, and further mineralize into inorganic matters (Vogna et al. 2004).

3.3.2.2 *Primidone and Phenobarbital*

The transformation products of PMD and PBB were studied together because

PBB is the active metabolite of PMD. Major intermediates of PMD and PBB detected by LC-MS were shown in Table S5 and Fig. S9(b and c), and their changes are shown in Fig. S10(b and c). The tentative degradation pathway of PMD and PBB in water was proposed together in Fig. 9. During the reaction, PBB and hydroxyl-primidone (PMD-OH) were detected with $\bullet\text{OH}$ attacking the pyrimidine ring and aromatic ring of PMD, which was also found in previous investigations (Liu et al. 2015b, Sijak et al. 2015). Meanwhile, the cleavage of N[1]–C[2] bond and N[3]–C[2] bond of the pyrimidine ring in PMD and PBB led to phenylethylmalonamide (PEMA) (MacLeod et al. 2008). As the reaction continued, three new intermediates emerged: 4-hydroxyphenobarbital (PBB-4OH), 5-Ethyl-1,3-diazinane-4,6-dione (EDD), and benzoic acid (BZC). The oxidation of PBB or PMD-4OH produced PBB-4OH and the cleavage of C-C bond between the aromatic ring and pyrimidine ring of PMD-4OH led to EDD, which was also found in electron beam radiolysis of PMD in water (Liu et al. 2015b). The branch chain on the benzene ring of PEMA was easy to be transformed into carboxyl, producing a simple aromatic carboxyl molecule identified as BZC, which was further oxidized into small molecules like fumarate and maleate (Ozcan et al. 2008). PBB-OH, PEMA, and BZC were also detected in the degradation of PBB. The intermediates of PMD and PBB detected by LC-QQQ-MS were close to detection limits after 4 h (Fig. S10(b and c)), while the simple ions detected by IC increased or fluctuated in Fig. S8(b and c), indicating the intermediates may finally transform into SCFAs or inorganic matters (Sijak et al. 2015).

3.3.3 GC-MS analysis for TAP and FF

The intermediates of TAP and FF detected by GC-MS are shown in Table S6 and Fig. S9(d and e), and their changes in Fig. S10(d and e). The tentative transformation pathway of TAP and FF was proposed together in Fig. 10, since FF can be transformed into TAP, and some intermediates of FF and TAP are identical, which are in sequence-number from A to F in Table S6. The photolysis for the two phenicols are similar in three parts: the methylsulfonyl group, the benzene ring and the carbon branch chain containing amide and halogen group (Fig. 10). The reactions involve photo-induced hydrolysis, photo-oxidation, dehalogenation and $\bullet\text{OH}$ addition (Ge et al. 2009). (1) The $\bullet\text{OH}$ can attack the aromatic ring of TAP and FF to form product TAP-1 and FF-1, respectively. (2) The cleavage of the methylsulfonyl group underwent photo hydrolysis producing TAP-3 for TAP and FF-3 for FF. (3) The elimination, addition, substitution and oxidation reaction may happen on the branch chain. The defluorination reaction of FF or FF-intermediates led to the formation of double carbon covalent bonds ($\text{C}=\text{C}$) via the elimination reaction like product F or alcohol-compounds via hydrolysis (e.g. FF transformation into TAP) (Ge et al. 2009). The dechlorination reactions of TAP and FF led to products TAP-2 and FF-2 via photo-induced oxidation, respectively, which has also been found during photolysis of phenicols in water (Ge et al. 2009, Liu et al. 2015a). The cleavage of C-C bonds at b position led to products FF-4 and A, and the cleavage at c position led to B with further hydrolysis; FF-4 and B subsequently underwent the photooxidation reactions,

leading to an aromatic acid (product C) and aldehyde (product D), respectively. Product FF-4 may also undergo the elimination reaction, leading to product E which has two isomerides due to the different substituent position of the C=C groups, and their most likely structures are shown in Fig. 10. Finally, the C=C bonds and aromatic ring evolved into small molecular acids via •OH oxidation (Ozcan et al. 2008), which is similar to the previous investigation (Ge et al. 2009, Liu et al. 2015a). As shown in Fig. S10(d and e), the intermediates of TAP and FF detected by GC-MS disappeared in 4 h, while the simple matters detected by IC increased or fluctuated in Fig. S8(d and e), indicating TAP and FF and their intermediates finally evolved into SCFAs or inorganic matters under UV/CaO₂ treatment.

3.4 Electrical energy comparison

Electrical energy per order (E_{EO} , kWh m⁻³ order⁻¹) is used to better understand the electrical energy required to reduce the concentration of a pollutant by one order of magnitude (90%) under UV/CaO₂ systems (Cater et al. 2000). In the case of pollutant concentrations (≤ 100 mg L⁻¹), the efficiency of UV-based AOPs can be measured with the E_{EO} (Cater et al. 2000), which can be calculated from equation 7.

$$E_{EO} = \frac{Pt}{60V(\log(\frac{C_i}{C_f}))} \quad (7)$$

where P is the UV lamp power (0.01 kW); t is the irradiation time (min); V is the volume of the treated water (0.05 L); C_i and C_f are the initial and final test concentrations (mg L⁻¹).

According to equation (7), the calculated E_{EO} of test PhACs for UV and

UV/CaO₂ processes are summarized in Table 2. It is noted that a smaller E_{EO} value indicates a more efficient process. The addition of CaO₂ could greatly reduce E_{EO} , and therefore save energy consumption of UV irradiation. The E_{EO} of CBZ, PMD, and PBB exhibits more drastic decrease than that of TAP and FF upon adding CaO₂, because the UV photolabilities of TAP and FF were better than the other three (seeing in 3.1.1). Additionally, E_{EO} value of PMD not available because its degradation cannot be achieved by UV direct photolysis.

3.5 Application to the treatment of test PhACs in secondary WWE

Of the 5 test PhACs, only CBZ and PMD were detected in the secondary WWE with concentrations of 309.6 ng L⁻¹ and 228.1 ng L⁻¹, respectively. As shown in Fig. 11, the removals of CBZ and PMD were significantly enhanced with the addition of CaO₂ and H₂O₂ under UV irradiation, and the degradation efficiencies of CBZ and PMD increased with increasing UV and CaO₂ dosage. Furthermore, UV/CaO₂ underwent a higher removal efficiency for CBZ and PMD compared to UV and UV/H₂O₂, suggesting the addition of CaO₂ is better than the addition of H₂O₂ for removal of PhACs during the UV irradiation of WWE. The degradation of CBZ and PMD in WWE followed the pseudo-first-order kinetic model very well with $R^2 > 0.96$, and 0.91, respectively (Table S8). According to K in Table S8, a UV dose at 3.8 and 4.6 J cm⁻² with 100 µM CaO₂ resulted in the removal of 90% CBZ and PMD, respectively.

The pH and turbidity may be the limiting factors for the application of UV/CaO₂

as an advanced treatment of secondary WwEs. Thus, the changes in pH, absorbance and turbidity were conducted for CaO₂ addition. As shown in Fig. S11(a), the pH fluctuated between 8.7 and 7.7 during the 7 days when 0.1 mM CaO₂ was added. Specifically, pH < 8 after 2 days indicated the pH of treated WwE may have little influence on the receiving water after UV/CaO₂ treatment. Moreover, the UV absorbance of WwE with 0.1 mM CaO₂ had little change (Fig. S11(b)). The WwE turbidity upon adding 0.1 mM CaO₂ decreased from 15 NTU to 4.7 NTU within 1 h, and the final turbidity was similar to the turbidity of WwE without adding CaO₂ (Fig. S11(c)). In all, the dosage of CaO₂ at 0.1 g L⁻¹ combined with UV can be used for the advanced treatment of PhACs in WwE. However, more detailed investigation should be conducted for the treatment of WwE by UV/CaO₂ for its reuse in the future.

4 Conclusion

UV/CaO₂ as a new and efficient AOP for the removal of PhACs was evaluated in this paper. The five test PhACs (CBZ, PMD, PBB, TAP, and FF) were effectively removed and mineralized, with the pseudo-first reaction kinetics. The greatest removal of these PhACs was observed with a CaO₂ dosage at 0.1 g L⁻¹. Lower initial concentrations of test PhACs yielded better reduction of the compounds, indicating that the extent of degradation depends on the initial concentration. UV/CaO₂ produces various reactive species that are beneficial for the attenuation of diverse compounds with various chemical structures. Direct photolysis and indirect photolysis caused by

•OH, $^3\text{DOM}^*$ and $^1\text{O}_2$ were involved in the removal mechanisms of test PhACs: •OH contributed the most to CBZ and PMD removal; PBB was removed via direct photolysis (~14%), •OH (~36%), $^3\text{DOM}^*$ (~28%) and $^1\text{O}_2$ (~18%); TAP was removed via direct photolysis (~68%) and •OH (~35%); FF was removed via direct photolysis (~55%), •OH (~21%), and $^3\text{DOM}^*$ (~19%). Based on the detected transformation products and the degradation mechanisms, the tentative degradation pathways of CBZ, PMD, PBB, TAP, and FF were proposed, respectively. According to the E_{EO} calculation, the addition of CaO_2 can significantly decrease the energy consumption of UV irradiation compared to solely using UV. When UV/ CaO_2 was applied to WWT treatment, the refractory indicator CBZ and PMD were better removed than using UV/ H_2O_2 . In summary, UV/ CaO_2 is a novel efficient and environmentally friendly AOP to remove wastewater-derived PhACs.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51578392). We thank Mauricius Marques dos Santos, PhD student of University of Arizona, USA, for the help with analysis of CBZ intermediates dissolved in purewater. We also thank the reviewers for valuable insights and suggestions.

Appendix A. Supplementary data

Supplementary data of this article can be found in the online version.

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**Attenuation of pharmaceutically active compounds in aqueous solution by
UV/CaO₂ process: Influencing factors, degradation mechanism and pathways**

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Abstract

As freshwater sources continue to be influenced by wastewater effluents, there is a dire need to develop advanced water treatment processes capable of treating the wastewater-derived contaminants, especially for pharmaceutically active compounds (PhACs). Ultraviolet light (UV) combined with calcium peroxide (CaO_2) as an advanced oxidation process (AOP) to attenuate five widespread PhACs (carbamazepine (CBZ), primidone (PMD), phenobarbital (PBB), thiamphenicol (TAP) and florfenicol (FF)) was investigated in this paper. The degradation of these compounds followed pseudo-first-order kinetics ($R^2 > 0.96$). The optimum CaO_2 dosage was 0.1 g L^{-1} and lower initial contaminants concentration was beneficial to their degradation. The UV/ CaO_2 treatment of test PhACs was attributed to the combination of UV/ H_2O_2 and UV-base-photolysis (UV/ $\text{Ca}(\text{OH})_2$), and the degradation mechanism was recognized as both UV direct photolysis and indirect photolysis caused by reactive radicals ($\bullet\text{OH}$, triplet states of dissolved organic matter ($^3\text{DOM}^*$), and $^1\text{O}_2$). Furthermore, the tentative transformation pathways of the five PhACs were proposed based on the detected intermediates and the degradation mechanisms. The final products of inorganic carbon and nitrogen indicate UV/ CaO_2 treatment can significantly mineralize test PhACs. Also, the CaO_2 addition significantly reduced the energy consumption of UV irradiation according to *electrical energy per order*. The effective removal of CBZ and PMD in a secondary wastewater effluent by UV/ CaO_2 treatment demonstrates the potential use of this

48 AOP technology in advanced treatment of wastewater-derived PhACs.

49 **Keywords:** UV/CaO₂; pharmaceutically active compounds (PhACs); reactive radicals;

50 degradation mechanism; wastewater effluent

51 **1 Introduction**

52 The persistence of trace organic contaminants (TOrcs), especially
53 pharmaceutically active compounds (PhACs), in effluents of wastewater treatment
54 plant (WWEs) has raised many concerns due to their potential harm to aquatic
55 ecosystems and human health (Liu and Wong 2013, Oulton et al. 2010). These PhACs
56 include antibiotics, antiepileptics, hormones, analgesics, blood lipid regulators, and
57 contrast agents (Pereira et al. 2007) which have been detected at high frequencies and
58 concentrations ranging from ng·L⁻¹ to µg·L⁻¹. Some PhACs such as carbamazepine
59 (CBZ) and primidone (PMD) can be used as tracers for aquatic environment pollution
60 caused by sewage effluents (Liu and Wong 2013, Tran et al. 2019). Previous
61 investigations showed that PhACs have been detected in WWEs in Asia, Europe,
62 America, and Oceania with maximum concentrations between 130–126000 ng L⁻¹
63 (Liu and Wong 2013, Tran et al. 2018). Accordingly, PhACs have been detected in
64 surface water with maximum concentration of 10000 ng L⁻¹ (Liu and Wong 2013,
65 Tran et al. 2019) , and in groundwater with maximum concentration of 3110 ng L⁻¹
66 (Lapworth et al. 2012, McCance et al. 2018). Antibiotics, one of the most concerning
67 pharmaceutical contaminants, can cause many problems for aquatic and terrestrial
68 organisms; e.g., thiamphenicol (TAP) and florfenicol (FF) has been shown to cause

inhibition of peptidyl transferase (Hayes et al. 2003) and the hematopoietic system (Festing et al. 2001). Another concern is that antibiotics may accelerate the emergence of antibiotic resistance genes (ARG), and even multiple antibiotic resistant (MAR) superintegrans under environmental exposure (Liu and Wong 2013, Yi et al. 2017). Antiepileptic drugs, like CBZ, PMD and phenobarbital (PBB) have also been highly studied in water. CBZ may cause oxidation stress in aquatic fish (Chen et al. 2012, Li et al. 2010) and affect the growth and morphology of human embryonic cells at environmentally relevant concentrations (Keen et al. 2012). PMD can have various effect on human, such as the feeling of intoxication or nausea (Sijak et al. 2015). PBB, a main active metabolite of primidone, can cause lethargy, dysarthria, and lack of coordination in humans (Mattson 1995). Moreover, when combined with other pharmaceuticals, the synergistic effects of these compounds can induce more severe harm to the ecosystems than expected from the measured impacts of any individual PhAC (Cleuvers 2003). Therefore, it is vital to investigate methods capable of adequately degrading these compounds and identify the relevant transformation mechanisms.

Calcium peroxide (CaO_2), one of the most frequently-used and safest solid inorganic peroxy compounds, is considered a “solid form” of H_2O_2 , and has been widely used in agriculture, aquaculture, and medicine (Lu et al. 2017, Ma et al. 2007). It is capable of producing H_2O_2 , O_2 and alkali compounds (Chen et al. 2016, Ma et al. 2007), as well as $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$ radicals in moist media (Ma et al. 2007, Zhang et al.

2015). Unlike liquid H_2O_2 , which is unstable and decomposes in the presence of a base or a catalyst, CaO_2 is relatively stable, making it convenient to transport and preserve. Meanwhile, the slow dissolution allows oxidants to be produced for longer periods, allowing more time for pollutants to be oxidized in aqueous solution (Zhang et al. 2016b). Several studies have demonstrated the ability of CaO_2 to degrade contaminants in aqueous solution. For example, CaO_2 can be used to remediate the MTBE-contaminated groundwater (Liu et al. 2006). CaO_2 nanoparticles can also be used for the recovery of valuable chemicals from aqueous waste streams and potentially for removal of toxic materials (Madan and Wasewar 2018). Additionally, trichloroethene (TCE) degradation could be significantly enhanced by CaO_2 activated with Fe(III) in the presence of citric acid solutions (Zhang et al. 2016a). Ozone combined with CaO_2 can effectively mineralize sulfolane in aqueous solution (Izadifard et al. 2018). Zhang et al. showed CaO_2 degraded greater than 50% of six endocrine-disrupting compounds in pure-water and waste active sludge under 7 days and was very effective in sludge solubilization (Zhang et al. 2015). Thus, CaO_2 could be a promising oxidant for the treatment of PhACs in wastewater effluents.

Most PhACs like CBZ and PMD are resistant to biodegradation (Roccaro 2018). Advanced oxidation processes (AOPs) are more efficacious for the attenuation of refractory contaminants, but challenges remain. UV and ozone are selective and have limited oxidation effect for certain classes of compounds including PMD (Roccaro 2018); and electron beam requires large space for machines, high-skilled technicians

for instrumental operations, and high energy consumption (Chmielewski and Han 2016). Although UV/H₂O₂ is considered as one of the most commonly used AOPs for control of refractory TOrC like CBZ and PMD (Yang et al. 2014), H₂O₂ is unstable and easily-decomposable, making it difficult to preserve (Lu et al. 2017). UV/CaO₂ possesses benefits over the aforementioned treatment technologies for TOrC abatement. The continuous generation of H₂O₂ from CaO₂ and its safe application in many industries (Lu et al. 2017) allow for its consideration in combination with other technologies to compose an AOP. Similarly to UV light being applied for photolytic decomposition of H₂O₂ to produce amounts of •OH in aqueous solution (Liao and Gurol 1995), UV has been combined with CaO₂ to produce •OH in aqueous solution (Kozak and Włodarczyk-Makula 2018). Therefore, UV/CaO₂ is a viable option for TOrC control. However, influencing factors and mechanisms to the degradation of refractory TOrCs in aqueous have still not been investigated. Furthermore, the increase of suspended solids (SS) or pH caused by CaO₂ dissolution should be discussed when it is applied in water treatment.

To explore the mechanism of UV/CaO₂ in the removal of refractory PhACs in aqueous solution, several PhACs including CBZ, PMD, PBB, TAP and FF degraded by UV/CaO₂ in aqueous solution were investigated in this paper. Altogether, this study evaluated: 1) effects of influencing factors (CaO₂ dosage, initial concentration of test PhACs and initial pH), 2) function of CaO₂ hydrolysates on the removal of test PhACs, 3) main reactive radicals and their respective contribution to the overall

removal, 4) main transformation products of selective contaminants under UV/CaO₂,
5) *electrical energy per order* for the degradation of test PhACs, and 6) application of
UV/CaO₂ on the removal of selective PhACs in WWE.

2 Materials and methods

2.1 Chemicals

Of the five target PhACs, CBZ and PMD at > 98% purity were obtained from
Sigma-Aldrich. PBB was purchased from ICN pharmaceuticals with > 98% purity
and FF and TAP from Dr. E (Germany) with 99% and 98.5% purity, respectively.
Physicochemical information of the five test PhACs is shown in Table S1. Labeled
surrogate standards, carbamazepine-d₁₀ and primidone-d₆ were purchased from
Cambridge Isotope Laboratories (Andover, MA). CaO₂ (≥ 75%), and all solvents
(methanol, acetonitrile, isopropyl alcohol (IPA) and acetic acid) of a purity suitable
for chromatographic analysis were also obtained from Sigma-Aldrich. The superoxide
dismutase (SOD), catalase (CAT), 1,4-Diazabicyclo[2.2.2]octane (DABCO), isoprene
(IPE, > 98%), 5,5-dimethyl-1-pyrroline N-oxide (DMPO), dimethyl sulfoxide
(DMSO), thiourea, the short chain fatty acids (SCFAs) (formate, acetate, oxalate,
malonate, succinate, maleate, and fumarate), nitrate (NO₃⁻), nitrite (NO₂⁻), ammonia
(NH₄⁺), sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), sodium carbonate
(Na₂CO₃), sodium bicarbonate (NaHCO₃), sodium thiosulfate (Na₂S₂O₃) and 30 %
hydrogen peroxide (H₂O₂) at the highest available purity, were purchased from
Shanghai Chemical Reagent Co. Ltd unless otherwise stated. H₂SO₄ and NaOH were

used to adjust the pH of solutions. $\text{Na}_2\text{S}_2\text{O}_3$ was added to terminate the reaction.

Pure-water (PW, $> 18.2 \text{ M}\Omega\cdot\text{cm}$) used for stock solution preparation and instrument

analysis were prepared by a Milli-Q system (EMD Millipore, Billerica, MA, USA).

2.2 Secondary wastewater effluent

The secondary WWE prior to chlorination was collected from a WWTP in Arizona, USA which consists of primary clarifiers, a 5-stage bardenpho biological nutrient removal activated sludge process, secondary clarifiers, chlorination, and dechlorination (Anumol et al. 2015). The water was filtered using glass-fiber filters (Whatman GF/F, $0.7 \mu\text{m}$ nominal pore size) and stored at 4°C for up to 24 hours before analysis. The characteristics of the WWE samples are shown in Table 1.

2.3 Experimental Procedure

2.3.1 Photoirradiation set-up

A merry-go-round photochemical reactor (PhchemIII, NBeT Co. Ltd, Beijing, China) coupled with a max of 12 quartz tubes containing the reaction solution was used for the photodegradation experiments. The low-pressure mercury lamp was immersed in the circulated-water cooled quartz well. The light source irradiance spectra were measured by a spectroscope (USB2000+ UV-vis, Ocean Optics, USA) shown in Fig. S1. The UV lamp has a strong intensity at a 254 nm wavelength. After 50 mL of solution spiked with test PhACs were irradiated by UV, 2 mL was then collected from the tube at the preset sampling times with $\text{Na}_2\text{S}_2\text{O}_3$ as the terminator for the subsequent analysis.

2.3.2 Removal of test PhACs in PW by UV/CaO₂

The following influencing factors were evaluated for the degradation of test PhACs under UV/CaO₂: CaO₂ dosage (from 0 to 0.2 g L⁻¹), initial test compound concentration (from 0.5 to 20 mg L⁻¹) and initial pH (from 2.4 to 10.3). Furthermore, the degradation of test PhACs under pH from 2.4 to 11.3 irradiated by UV without CaO₂ was set as a comparison. CaO₂ can be hydrolyzed into Ca(OH)₂ and H₂O₂ upon adding to water (Chen et al. 2016, Ma et al. 2007), and the changes of H₂O₂ concentration in PW and WWE are shown in Fig. S2. The mechanism of UV/CaO₂ on test PhACs were evaluated with experiments using UV irradiation combined with different CaO₂ hydrolysates. The hydrolysates were set at theoretical equivalent concentrations of CaO₂: [75% CaO₂] = 0.100 g L⁻¹, [Ca(OH)₂] = 0.102 g L⁻¹, [H₂O₂] = 0.0354 g L⁻¹. UV/CaCl₂ ([CaCl₂] = 0.153 g L⁻¹) was used to evaluate the effect of Ca²⁺ on test PhACs removal. UV/NaCl ([NaCl] = 0.161 g L⁻¹) treatment was used to assess the effect of Cl⁻ in the UV/CaCl₂ treatment.

2.3.3 Identification of transformation products

Identification of transformation products of target PhACs was done in PW treated with UV/CaO₂. Each test PhAC was set at 10 mg L⁻¹ and separately treated by UV/CaO₂. Ion chromatography (IC) was used to detect the SCFAs and inorganic ions; liquid chromatography/quadrupole time-of-flight mass spectrometry (LC-QTOF-MS), liquid chromatography/triple quadrupole mass spectrometer (LC-QQQ-MS) and GC-MS techniques with NIST library were used to identify main intermediates

formed during UV/CaO₂.

2.3.4 Identification of reactive radicals

Removal of the target PhACs in aqueous solution under UV/CaO₂ might be due to both direct and indirect photolysis (Jasper and Sedlak 2013). To clarify contributions of different photolysis mechanisms to the overall removal of test PhACs in PW during UV/CaO₂, scavengers were used to isolate the contributions of different reactive species. All samples amended with test PhACs were treated with 0.1 g L⁻¹ CaO₂ (~1.0 mmol L⁻¹ (mM)) prior to UV irradiation. Scavengers were set as follows: IPA (~100 mM) was used to quench •OH reactions (Jasper and Sedlak 2013); IPE (~10 mM) was used to quench triplet states of dissolved organic matter (³DOM*) (Jasper and Sedlak 2013); SOD (~100 kU L⁻¹) was used to quench O₂^{•-} (Singh 1982); DABCO (~100 mM) was used to quench ¹O₂ (Zepp et al. 1977); ¹O₂ was primarily generated from the reaction between dissolved oxygen (DO) and ³DOM*, making other resources negligible (Haag and Hoigne 1986, Marchisio et al. 2015). The N₂-sparged condition (N₂, 99.999% purity) was used to evaluate effects of ¹O₂ and O₂ on test PhACs removal and high-purity air-sparged condition (99.999%) was used to quench ³DOM* (Jasper and Sedlak 2013).

Moreover, electron paramagnetic resonance (EPR, ESP300 (Bruker, Germany)) was used to further detect the main free radicals in the treatment of UV/CaO₂. EPR parameters and experimental settings were described in previous investigations (Li et al. 2015, Lipovsky et al. 2012). DMPO was used to trap the •OH, O₂^{•-} and alkyl

radicals ($\bullet$ C-R) forming DMPO-OH, DMPO-OOH and DMPO-C-R spin adduct, respectively (Li et al. 2015, Lipovsky et al. 2012). Thiourea (~1%, w/v) and DMSO (~10%, w/v) were used to quench $\bullet$ OH. DMSO reaction with $\bullet$ OH to produce $\bullet$ CH₃ can transform DMPO into DMPO-CH₃. Previous investigation shows the alkyl radical ($\bullet$ C-R) may be generated from the oxidation of contaminants to form DMPO-C-R which have similar EPR spectrum feature of DMPO-CH₃ (Zhang et al. 2015). Overall, the EPR spectrums under different treatments were compared: CaO₂, UV/CaO₂, thiourea + UV/CaO₂, DMSO + UV/CaO₂ and test PhACs + UV/CaO₂. The test steps were as follows: 5 μ L of phosphate buffered saline (PBS) (50 mM, pH 7.4), 5 μ L FeSO₄•(NH₄)₂SO₄ (1.0 mM), 5 μ L of DMPO (0.9 M), and 10 μ L of samples were mixed in sequence and the mixture was then put in a quartz capillary and measured by EPR immediately.

2.3.5 Removal of target PhACs in WWE by UV/CaO₂

Removal efficiencies of target PhACs from WWE were used to evaluate the treatment efficacy of UV/CaO₂ on PhACs in WWE. The CaO₂ dosage was set at 17, 50 and 100 μ M, which would not cause obvious pH change by CaO₂ addition. Meanwhile, UV and UV/H₂O₂ (100 μ M) treatments were set as comparisons. A collimated beam device (ITT Wedeco, Herford, Germany) with four low-pressure UV lamps (Type NLR2036) was used in this experiment. A UV absorbed dose (J cm⁻²) at 254 nm was the arithmetic product of UV irradiance (mW cm⁻²), correction factors and exposure time (s), which were determined by a previous research (Bolton and

Linden 2003).

Samples were prepared according to a previous investigation (Anumol et al. 2015). Samples after treatments were spiked with a mixture of internal standards (200 ng L⁻¹) and allowed to equilibrate for ~30 min at room temperature. Then the samples were analyzed via direct injection by LC-QQQ-MS (Anumol et al. 2015). With respect to test PhACs, only CBZ and PMD were detected, and compound-specific parameters are given in Table S7.

2.4 Analytical Methods

CBZ, PMD, PBB, FF and TAP spiked in PW were detected using a high performance liquid chromatography (HPLC) system. Organic and inorganic ions were detected by IC. Major degradation intermediates of each PhAC were detected using LC-QTOF-MS, LC-QQQ-MS or GC-MS. Changes of CBZ and PMD in WWE were detected using LC-QQQ-MS. All details for the analytical methods are provided in supporting information (SI) text.

The analytical method for total organic carbon (TOC) was described in our previous investigation (Zhang et al. 2015). EPR parameters and experimental settings were also described in previous investigations (Li et al. 2015, Lipovsky et al. 2012). The H₂O₂ concentration was detected using Single Analyte Meters (SAMs, I-2016) with replacement kit (Hydrogen Peroxide — Vacu-vials® Instrumental Kit).

3 Results and Discussion

3.1 Removal of PhACs in PW by UV/CaO₂

3.1.1 Effect of CaO_2 dosage

The natural logarithmic values of normalized concentrations of test PhACs ($\ln(C/C_0)$) decreased linearly with the irradiation time (Fig. S3). The reaction kinetics of the test PhACs followed pseudo-first-order kinetics with $R^2 \geq 0.97$ for all the tested PhACs and their degradation rate constants (K , min^{-1}) at different CaO_2 dosages are shown in Fig. 1(a). The K escalated with increasing CaO_2 dosage, with the greatest K value at 0.1 g L^{-1} of CaO_2 . The increase of K may be attributed to the increased production of oxidative radicals ($\bullet\text{OH}$) from the UV activating CaO_2 (reactions 1-3) (Chen et al. 2016, Ma et al. 2007). There are several possible reasons for the retarded increase of rate constants after the optimal CaO_2 dosage. First, the overdose of CaO_2 may cause an increase in turbidity (Fig. S4(a)) and UV-screening (Fig. S4(b)), which reduces the effective utilization of UV in the degradation of test PhACs. Secondly, a higher pH caused by excess CaO_2 can accelerate the disproportionation of H_2O_2 (reaction 4), which may decrease the effective concentration of $\bullet\text{OH}$ (reaction 3). Furthermore, the alkaline condition not only lowers the $\bullet\text{OH}$ concentration (reaction 5), but also lowers the $\bullet\text{OH}$ oxidation potential from 2.7 V in an acidic solution to 1.8 V in a neutral solution (Buxton et al. 1988). Additionally, Fig. 1(a) reveals that the increased K of CBZ, PMD, and PBB are significant more than that of TAP and FF when CaO_2 was added, indicating indirect photolysis (mainly by $\bullet\text{OH}$) played an important role in the degradation of CBZ, PMD, and PBB, while direct photolysis played an important role in the degradation of TAP and FF during UV/ CaO_2

treatment.

The change of TOC in Fig. 1(b) shows that the test PhACs could be gradually mineralized under UV/CaO₂ process. The addition of CaO₂ significantly enhanced the mineralization of test PhACs. However, the mineralization efficiencies were almost similar when the CaO₂ dosage was above 0.1 g L⁻¹. Comprehensively considering the cost of chemicals consumption and test PhACs removal, the optimum CaO₂ dosage recommend at 0.1 g L⁻¹.

3.1.2 Effect of initial concentration of the test PhACs

As shown in Fig. 2, the *K* of each PhAC decreased as their initial concentrations increased. This is because a higher concentration of test PhACs might increase UV-screen properties of the solution (Fig. S5) which could reduce the UV light activation to CaO₂ for generating reactive species and thus retarding the degradation of test PhACs. Furthermore, more complicated intermediates generated from higher initial concentration during the reaction may compete with test PhACs for the UV light and reactive radicals (Cater et al. 2000, Liu et al. 2015a). Additionally, the *K* of test PhACs were successfully fitted as an exponential function to their initial

concentration (Table S2) based on the high R^2 (> 0.98). Therefore, K of the test PhACs at different initial concentrations can be calculated based on the fitted formulas ($[\text{CaO}_2] = 0.1 \text{ g L}^{-1}$).

3.1.3 Effect of initial pH

The initial pH of the solution can influence the effective H_2O_2 and $\bullet\text{OH}$ concentration from CaO_2 hydrolysis (Buxton et al. 1988, Lu et al. 2017) and the forms of compounds due to protonation or deprotonation (Jasper and Sedlak 2013), and thus affects the degradation of test PhACs.

As shown in Fig. 3(a), during UV/ CaO_2 , the initial pH = 2.4, significantly promoted the removal of test PhACs with a final pH of 2.7, while the pH from 4.5 to 10.5 has little influence on the K , with a final pH at 11.1-11.2. The big increase of K with initial pH = 2.4 may be related to a final pH = 2.7, since the acidic solution promoted the H_2O_2 release rate and the final yield from CaO_2 (Wang et al. 2016), and facilitated the formation of $\bullet\text{OH}$ under UV irradiation to decay test PhACs (Liu et al. 2015a). The lower K with a final pH at 11.1-11.2 was because the alkaline solution may decrease the H_2O_2 release rate and final yield (Wang et al. 2016), and decrease the $\bullet\text{OH}$ concentration and its oxidation potential (Buxton et al. 1988). Meanwhile, the similar K with initial pH at 4.5-10.5 may be related to a similar final pH = 11.1-11.2.

Test PhACs under protonation and deprotonation may result in different direct and indirect photolysis (Boreen et al. 2004, Jasper and Sedlak 2013). 1) To assess the

forms of test PhACs on their direct photolysis, the effects of different pH conditions on the degradation of test PhACs under sole UV were evaluated. As shown in Fig. 3(b), at a pH from 2.4 to 11.3, the protonated CBZ and PMD ($pK_a > 11.5$, Table S1) was not influenced by pH; however, at a pH > 8.2 , K of the deprotonated PBB ($pK_a = 7.3/8.14$, Table S1) increased, and at a pH > 10 , K of the deprotonated TAP ($pK_a = 7.2/9.76$, Table S1) and FF ($pK_a = 9.03$, Table S1) increased. Considering the final pH was 11.1-11.2 during UV/ CaO_2 , PBB, TAP, and FF at deprotonation performed a higher direct photolysis. Actually, direct photolysis of PhACs containing amines may be affected by pH because of changes in molar absorption coefficients or quantum yields of different forms of the compounds (Jasper and Sedlak 2013), which was further proved in Fig. S6 that the UV absorbance of the mixed test PhACs increased upon pH > 8.2 , especially at 200-280 nm. 2) The indirect photolysis may be affected by pH because the protonated or deprotonated PhACs reacted with the reactive radicals ($^1O_2$ and $\bullet CO_3^-$) at second-order reaction rates that varied over more than 2 orders of magnitude (Jasper and Sedlak 2013). Additionally, Fig. S7 reveals PBB, TAP and FF underwent degradation through base-hydrolysis at pH > 8.2 . Previous investigations showed phenicols such as TAP and FF underwent base-hydrolysis via the breakage at the amide linkage (Glazko et al. 1950) and the chloro-group linkage (Mitchell et al. 2015).

3.2 Degradation mechanism of test PhACs under UV/ CaO_2

3.2.1 Effect of CaO_2 hydrolysates

Experiments using the combination of CaO_2 hydrolysates (Ca(OH)_2 or H_2O_2) with UV were conducted to explore the chemical mechanisms of PhACs degradation by UV/ CaO_2 in aqueous solution. As shown in Fig. 4(a), H_2O_2 played a vital role in the UV-photolysis of CBZ and PMD while Ca(OH)_2 had an insignificant influence. For PBB, TAP and FF, both H_2O_2 and Ca(OH)_2 improved their K values under UV. The significant improvement under UV/ H_2O_2 was due to the $\bullet\text{OH}$ generation during photolysis of H_2O_2 (Cater et al. 2000). As shown in Fig. 4(b), the pH of CaO_2 and Ca(OH)_2 were much higher than others. Results from the K under UV, UV/ CaCl_2 and UV/ NaCl showed that Ca^{2+} had no effect on the degradation of test PhACs. Therefore, the improvement of K under UV/ Ca(OH)_2 was attributed to the alkaline condition which was defined as base-catalytic UV-photolysis in this paper. According to 3.1.3, PBB, TAP and FF containing amines were deprotonated under Ca(OH)_2 , probably improving their hydrolysis and resulting in the increase in direct photolysis during UV irradiation. Therefore, the UV/ CaO_2 treatment of test PhACs can be considered as the combination of UV/ H_2O_2 and UV-base-photolysis.

3.2.2 Effect of reactive radical scavengers

Fig. 5(a) shows the effects of radical scavengers on the removal of test PhACs, and Fig. 5(b) shows contributions of direct-photolysis and indirect-photolysis caused by different oxidative species ($\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, O_2^1 , $^3\text{DOM}^*$ and H_2O_2) for the removal of test PhACs. It appears the removal mechanism of each test PhAC was different during UV/ CaO_2 process. 1) UV direct-photolysis showed little contribution to CBZ and

363 PMD removal, and a minor contribution to PBB removal (~14%), while appreciable
364 contribution to TAP (~68%) and FF (~55%) removal. 2) IPA at the given
365 concentration (i.e., ~0.1 mol L⁻¹) can almost completely quench •OH (reaction 6),
366 whereas reactions of O₂^{•-} and ¹O₂ were unaffected (Singh 1982). With IPA addition,
367 CBZ and PMD degradations were almost completely inhibited (Fig. 5(a)), indicating
368 that •OH accounted for much of K of CBZ and PMD (with ~100% and ~99%
369 contribution, respectively (Fig. 5(b))). However, •OH accounted for 20-40% for K of
370 PBB, TAP and FF (Fig. 5(b)). 3) When comparing the UV/CaO₂ treatments with IPA
371 and IPA+DABCO additions, we can find only PBB and FF underwent obvious
372 indirect photolysis by ¹O₂ with ~18% and ~5%, respectively. The little observed
373 removal of CBZ by ¹O₂ is consistent with the investigation of Jasper and Sedlak
374 (2013). 4) Due to SOD, a O₂^{•-} scavenger, can react with •OH and ¹O₂ at 5.3×10¹⁰ M⁻¹
375 s⁻¹ and 2.5 ×10⁹ M⁻¹ s⁻¹, respectively (Singh 1982), IPA was added to remove •OH and
376 N₂-sparging was used to remove O₂ and ¹O₂ in advance. Comparison of K between
377 N₂+IPA and N₂+IPA+SOD showed O₂^{•-} had little contribution to the degradation of
378 all test PhACs (Fig. 5(b)). 5) During the UV/CaO₂ treatment of test PhACs, ³DOM*
379 may be introduced via the UV-excitation of test PhACs or their intermediates. As IPE
380 quenches both ³DOM* and •OH (Huang et al. 2011), IPA was used to exclude •OH
381 first. Meanwhile, N₂-sparged condition can remove O₂ from the CaO₂ decomposition,
382 and inhibit the reaction of ³DOM* with O₂ forming ¹O₂. The decrease of PBB and FF
383 under IPA+IPE compared to IPA and the increase under N₂-sparging, suggests a

contribution of $^3\text{DOM}^*$ to the degradation of PBB (~28%) and FF (~19%). However, $^3\text{DOM}^*$ had an insignificant influence on the removal of CBZ, PMD and TAP. Moreover, the attenuation of K upon sparging with air, a $^3\text{DOM}^*$ quencher, further revealed PBB and FF could be removed by $^3\text{DOM}^*$. However, the K of CBZ and PMD increased slightly under air-sparged condition and decreased slightly under N_2 -sparged condition (Fig. 5(a)). As CBZ and PMD were mainly removed by $\bullet\text{OH}$, this phenomenon may be explained as follows: When sparged with O_2 , extra reactive oxygen species (ROS) generating under UV irradiation may promote the removal of intermediates of test PhACs, thereby reducing their competition for $\bullet\text{OH}$ with CBZ and PMD; the sparged N_2 removed O_2 generated from CaO_2 (reaction 2) that might reduce the generation of ROS, resulting in a decrease in the overall removal of intermediates. 6) Although large amounts of H_2O_2 was produced from CaO_2 hydrolysis (Lu et al. 2017), sole H_2O_2 had an insignificant contribution to the removal of test PhACs compared with other degradation mechanisms. In summary, $\bullet\text{OH}$ played a vital role on CBZ (~100%) and PMD (~99%) degradation; direct photolysis (~14%), $\bullet\text{OH}$ (~36%), $^3\text{DOM}^*$ (~28%) and $^1\text{O}_2$ (~18%) mainly contributed to PBB removal; direct photolysis (~68%) and $\bullet\text{OH}$ (~35%) contributed to TAP removal; direct photolysis (~55%), $\bullet\text{OH}$ (~21%), and $^3\text{DOM}^*$ (~19%) contributed to FF removal.

3.2.3 Identification of the main reactive oxidative species by EPR.

The EPR was used to further ascertain main reactive radicals during UV/CaO₂. As shown in Fig. 6(a), the DMPO-OH signal (four split lines with 1:2:2:1 height ratio, the red solid diamonds) shows the probable existence of •OH during CaO₂ and UV/CaO₂, and •OH generation was significantly improved under UV/CaO₂ treatment compared to CaO₂ (Li et al. 2015). As DMPO-OOH is easily converted into DMPO-OH, DMSO and thiourea, •OH quenchers, were separately used in the trapping experiments (Li et al. 2015, Lipovsky et al. 2012). When DMSO was added, Fig. 6(b) shows the minor DMPO-OH signal and the primary spectral features of DMPO-CH₃ (six split lines with same height ration, the green open triangle), which confirmed the major existence of •OH radicals, because •OH radicals react with DMSO to produce •CH₃ radicals which convert DMPO into DMPO-CH₃. When thiourea was used to quench •OH, the major DMPO-OOH and minor DMPO-OH signals in Fig. 6(c) implies the generation of O₂^{•-} during UV/CaO₂. Meanwhile, a DMPO-CH₃-like signal appeared upon adding test PhACs under UV/CaO₂ in Fig. 6(b), indicating the probable formation of alkyl radicals (•C-R) (Zhang et al. 2015). Thus, •OH, O₂^{•-} and probable •C-R radicals are presented during the UV/CaO₂ treatment of test PhACs.

3.3 The transformation products of test PhACs under UV/CaO₂

3.3.1 IC analysis

Results for the main organic and inorganic ions analyzed by IC are shown in Table S3 and Fig. S8. Formate increased at the first 50 min, and then kept stable

during the degradation of CBZ, TAP and FF, but it continuously increased in the degradation of PMD and PBB. Acetate experienced a slow increase during CBZ, TAP and FF degradation, while a large increase in PMD and PBB degradation was observed. Oxalate was significantly generated after 2 h treatment of CBZ, TAP and FF, and after 3 h treatment of PMD and PBB. Maleate was detected in the treatment of all test PhACs, and fumarate was detected in the degradation of CBZ and PMD (Table S3), indicating that the central heterocyclic ring or aromatic rings were attacked and then opened, because of an *ipso*-attack on C-carrying chlorine, amino or carboxyl (Ozcan et al. 2008). Succinate was also detected in the degradation of CBZ, PMD and PBB. A previous study reported that organic nitrogen may be transformed into N_2 , NH_4^+ and NO_3^- during the oxidative degradation of CBZ (Vogna et al. 2004). As shown in Fig. S8, NH_4^+ was produced significantly, while production of NO_2^- and NO_3^- was insignificant during the treatment of test PhACs.

Cl^- and SO_4^{2-} were only detected in the degradation of TAP and FF, which increased quickly at the first 2 h, and then almost remained stable. The detachment of the Cl atom from TAP and FF was 57% and 63% respectively after 4 h reaction. The path of Cl^- generation can be inferred as Path 1 in Fig. 7 because of the oxidation (by $\bullet\text{OH}$) and hydrolysis. However, the detached S atom as SO_4^{2-} accounted for 16% and 15% of the total S from TAP and FF, respectively. A preliminary experiment showed the magenta solution faded upon pouring the gas collected from the UV/ CaO_2 (with 1 mM HCl) treatment while returned to red if heated (not shown here), indicating the

probable existence of $\text{SO}_3^{2-}/\text{SO}_2$. Therefore, the S atom was transformed into SO_4^{2-} and $\text{SO}_3^{2-}/\text{SO}_2$, and the tentative transformation pathway was proposed in Path 2 in Fig. 7. As shown in path 3 of Fig. 7, the detected F^- accounted for 72% of total F atom from FF. It is inferred that the F atom was detached from FF forming F^- .

3.3.2 LC-MS analysis for CBZ, PMD and PBB

3.3.2.1 Carbamazepine

The intermediates from CBZ degradation under UV/ CaO_2 detected by LC-MS are shown in Table S4 and Fig. S9(a) and their changes are shown in Fig. S10(a). Based on intermediates and the aforementioned degradation mechanisms, the tentative degradation pathway of CBZ was proposed in Fig. 8. The $\bullet\text{OH}$ played a vital role in CBZ degradation. Firstly, the C10-C11 double bond in the central heterocyclic ring of CBZ may be hydroxylated into CBZ-10OH (Chiron et al. 2006), and then, it was oxidized into oxcarbamazepine (OXCBSZ) through breaking O-H bond at site *b*, C-H at *c* site and C-C at *d* site of CBZ-10OH (Hu et al. 2009). The second predominant pathway involves the heterocyclic ring contraction process. The reactive 10,11-double bond was attacked by $\bullet\text{OH}$ to yield 10,11-epoxycarbamazepine (CBZ-EP), which has been mentioned in other studies (Li et al. 2013, Miao et al. 2005). CBZ-EP subsequently evolved into diols, which may be identified as 10,11-dihydro-10,11-cis-dihydroxy-CBZ or 10,11-dihydro-10,11-trans-dihydroxy-CBZ (CBZ-DiOH) (De Laurentiis et al. 2012). The central heterocyclic ring of CBZ-EP and CBZ-DiOH underwent structural

alterations, leading to a heterocyclic ring contraction and cyclization reactions to form 4-formyl-9-carbamoyl-acridone (4-AOC) or acridine-9-carboxaldehyde (AIC) (Kosjek et al. 2009) via a pinacol-type rearrangement (Li et al. 2013). 4-AOC may further cleave the carboxyaldehyde and carbamoyl group to yield acridone (AO) (Hu et al. 2009). AIC may transform into acridine (AI) (Kosjek et al. 2009) or undergo a further hydroxylation to hydroxyacridine-9-carboxaldehyde (AIC-OH) (Calisto et al. 2011, Kosjek et al. 2009). AI can transform into AO via UV photolysis, as previously described (Kosjek et al. 2009). The third route is the hydroxylation of aromatic rings to form hydroxy-carbamazepine (CBZ-2(3)OH) and dihydroxycarbamazepine (CBZ-OH-OH) (De Laurentiis et al. 2012, Miao et al. 2005). CBZ-OH-OH was identified as 2,7-dihydroxycarbamazepine 2,8-dihydroxycarbamazepine and 3,8-dihydroxycarbamazepine with the hydroxyl function on the different carbon site of the outside aromatic ring (De Laurentiis et al. 2012). In addition, the CBZ underwent the cleavage of carbamoyl to form iminostilbene (IM), which was also observed in our study (Breton et al. 2005, Kosjek et al. 2009). Fig. S10(a) shows intermediates detected by LC-QQQ-MS increased and then decreased in 4 h, while Fig. S8(a) shows IC products increased or fluctuated during 4 h, indicating intermediates may be converted into SCFAs, and further mineralize into inorganic matters (Vogna et al. 2004).

3.3.2.2 *Primidone and Phenobarbital*

The transformation products of PMD and PBB were studied together because

PBB is the active metabolite of PMD. Major intermediates of PMD and PBB detected by LC-MS were shown in Table S5 and Fig. S9(b and c), and their changes are shown in Fig. S10(b and c). The tentative degradation pathway of PMD and PBB in water was proposed together in Fig. 9. During the reaction, PBB and hydroxyl-primidone (PMD-OH) were detected with $\bullet\text{OH}$ attacking the pyrimidine ring and aromatic ring of PMD, which was also found in previous investigations (Liu et al. 2015b, Sijak et al. 2015). Meanwhile, the cleavage of N[1]–C[2] bond and N[3]–C[2] bond of the pyrimidine ring in PMD and PBB led to phenylethylmalonamide (PEMA) (MacLeod et al. 2008). As the reaction continued, three new intermediates emerged: 4-hydroxyphenobarbital (PBB-4OH), 5-Ethyl-1,3-diazinane-4,6-dione (EDD), and benzoic acid (BZC). The oxidation of PBB or PMD-4OH produced PBB-4OH and the cleavage of C-C bond between the aromatic ring and pyrimidine ring of PMD-4OH led to EDD, which was also found in electron beam radiolysis of PMD in water (Liu et al. 2015b). The branch chain on the benzene ring of PEMA was easy to be transformed into carboxyl, producing a simple aromatic carboxyl molecule identified as BZC, which was further oxidized into small molecules like fumarate and maleate (Ozcan et al. 2008). PBB-OH, PEMA, and BZC were also detected in the degradation of PBB. The intermediates of PMD and PBB detected by LC-QQQ-MS were close to detection limits after 4 h (Fig. S10(b and c)), while the simple ions detected by IC increased or fluctuated in Fig. S8(b and c), indicating the intermediates may finally transform into SCFAs or inorganic matters (Sijak et al. 2015).

3.3.3 GC-MS analysis for TAP and FF

The intermediates of TAP and FF detected by GC-MS are shown in Table S6 and Fig. S9(d and e), and their changes in Fig. S10(d and e). The tentative transformation pathway of TAP and FF was proposed together in Fig. 10, since FF can be transformed into TAP, and some intermediates of FF and TAP are identical, which are in sequence-number from A to F in Table S6. The photolysis for the two phenicols are similar in three parts: the methylsulfonyl group, the benzene ring and the carbon branch chain containing amide and halogen group (Fig. 10). The reactions involve photo-induced hydrolysis, photo-oxidation, dehalogenation and $\bullet\text{OH}$ addition (Ge et al. 2009). (1) The $\bullet\text{OH}$ can attack the aromatic ring of TAP and FF to form product TAP-1 and FF-1, respectively. (2) The cleavage of the methylsulfonyl group underwent photo hydrolysis producing TAP-3 for TAP and FF-3 for FF. (3) The elimination, addition, substitution and oxidation reaction may happen on the branch chain. The defluorination reaction of FF or FF-intermediates led to the formation of double carbon covalent bonds ($\text{C}=\text{C}$) via the elimination reaction like product F or alcohol-compounds via hydrolysis (e.g. FF transformation into TAP) (Ge et al. 2009). The dechlorination reactions of TAP and FF led to products TAP-2 and FF-2 via photo-induced oxidation, respectively, which has also been found during photolysis of phenicols in water (Ge et al. 2009, Liu et al. 2015a). The cleavage of C-C bonds at b position led to products FF-4 and A, and the cleavage at c position led to B with further hydrolysis; FF-4 and B subsequently underwent the photooxidation reactions,

leading to an aromatic acid (product C) and aldehyde (product D), respectively. Product FF-4 may also undergo the elimination reaction, leading to product E which has two isomerides due to the different substituent position of the C=C groups, and their most likely structures are shown in Fig. 10. Finally, the C=C bonds and aromatic ring evolved into small molecular acids via •OH oxidation (Ozcan et al. 2008), which is similar to the previous investigation (Ge et al. 2009, Liu et al. 2015a). As shown in Fig. S10(d and e), the intermediates of TAP and FF detected by GC-MS disappeared in 4 h, while the simple matters detected by IC increased or fluctuated in Fig. S8(d and e), indicating TAP and FF and their intermediates finally evolved into SCFAs or inorganic matters under UV/CaO₂ treatment.

3.4 Electrical energy comparison

Electrical energy per order (E_{EO} , kWh m⁻³ order⁻¹) is used to better understand the electrical energy required to reduce the concentration of a pollutant by one order of magnitude (90%) under UV/CaO₂ systems (Cater et al. 2000). In the case of pollutant concentrations (≤ 100 mg L⁻¹), the efficiency of UV-based AOPs can be measured with the E_{EO} (Cater et al. 2000), which can be calculated from equation 7.

$$E_{EO} = \frac{Pt}{60V(\log(\frac{C_i}{C_f}))} \quad (7)$$

where P is the UV lamp power (0.01 kW); t is the irradiation time (min); V is the volume of the treated water (0.05 L); C_i and C_f are the initial and final test concentrations (mg L⁻¹).

According to equation (7), the calculated E_{EO} of test PhACs for UV and

UV/CaO₂ processes are summarized in Table 2. It is noted that a smaller E_{EO} value indicates a more efficient process. The addition of CaO₂ could greatly reduce E_{EO} , and therefore save energy consumption of UV irradiation. The E_{EO} of CBZ, PMD, and PBB exhibits more drastic decrease than that of TAP and FF upon adding CaO₂, because the UV photolabilities of TAP and FF were better than the other three (seeing in 3.1.1). Additionally, E_{EO} value of PMD not available because its degradation cannot be achieved by UV direct photolysis.

3.5 Application to the treatment of test PhACs in secondary WWE

Of the 5 test PhACs, only CBZ and PMD were detected in the secondary WWE with concentrations of 309.6 ng L⁻¹ and 228.1 ng L⁻¹, respectively. As shown in Fig. 11, the removals of CBZ and PMD were significantly enhanced with the addition of CaO₂ and H₂O₂ under UV irradiation, and the degradation efficiencies of CBZ and PMD increased with increasing UV and CaO₂ dosage. Furthermore, UV/CaO₂ underwent a higher removal efficiency for CBZ and PMD compared to UV and UV/H₂O₂, suggesting the addition of CaO₂ is better than the addition of H₂O₂ for removal of PhACs during the UV irradiation of WWE. The degradation of CBZ and PMD in WWE followed the pseudo-first-order kinetic model very well with $R^2 > 0.96$, and 0.91, respectively (Table S8). According to K in Table S8, a UV dose at 3.8 and 4.6 J cm⁻² with 100 μM CaO₂ resulted in the removal of 90% CBZ and PMD, respectively.

The pH and turbidity may be the limiting factors for the application of UV/CaO₂

as an advanced treatment of secondary WWEs. Thus, the changes in pH, absorbance and turbidity were conducted for CaO_2 addition. As shown in Fig. S11(a), the pH fluctuated between 8.7 and 7.7 during the 7 days when 0.1 mM CaO_2 was added. Specifically, $\text{pH} < 8$ after 2 days indicated the pH of treated WWE may have little influence on the receiving water after UV/ CaO_2 treatment. Moreover, the UV absorbance of WWE with 0.1 mM CaO_2 had little change (Fig. S11(b)). The WWE turbidity upon adding 0.1 mM CaO_2 decreased from 15 NTU to 4.7 NTU within 1 h, and the final turbidity was similar to the turbidity of WWE without adding CaO_2 (Fig. S11(c)). In all, the dosage of CaO_2 at 0.1 g L^{-1} combined with UV can be used for the advanced treatment of PhACs in WWE. However, more detailed investigation should be conducted for the treatment of WWE by UV/ CaO_2 for its reuse in the future.

4 Conclusion

UV/ CaO_2 as a new and efficient AOP for the removal of PhACs was evaluated in this paper. The five test PhACs (CBZ, PMD, PBB, TAP, and FF) were effectively removed and mineralized, with the pseudo-first reaction kinetics. The greatest removal of these PhACs was observed with a CaO_2 dosage at 0.1 g L^{-1} . Lower initial concentrations of test PhACs yielded better reduction of the compounds, indicating that the extent of degradation depends on the initial concentration. UV/ CaO_2 produces various reactive species that are beneficial for the attenuation of diverse compounds with various chemical structures. Direct photolysis and indirect photolysis caused by

•OH, $^3\text{DOM}^*$ and $^1\text{O}_2$ were involved in the removal mechanisms of test PhACs: •OH contributed the most to CBZ and PMD removal; PBB was removed via direct photolysis (~14%), •OH (~36%), $^3\text{DOM}^*$ (~28%) and $^1\text{O}_2$ (~18%); TAP was removed via direct photolysis (~68%) and •OH (~35%); FF was removed via direct photolysis (~55%), •OH (~21%), and $^3\text{DOM}^*$ (~19%). Based on the detected transformation products and the degradation mechanisms, the tentative degradation pathways of CBZ, PMD, PBB, TAP, and FF were proposed, respectively. According to the E_{EO} calculation, the addition of CaO_2 can significantly decrease the energy consumption of UV irradiation compared to solely using UV. When UV/ CaO_2 was applied to WWT treatment, the refractory indicator CBZ and PMD were better removed than using UV/ H_2O_2 . In summary, UV/ CaO_2 is a novel efficient and environmentally friendly AOP to remove wastewater-derived PhACs.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51578392). We thank Mauricius Marques dos Santos, PhD student of University of Arizona, USA, for the help with analysis of CBZ intermediates dissolved in purewater. We also thank the reviewers for valuable insights and suggestions.

Appendix A. Supplementary data

Supplementary data of this article can be found in the online version.

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789

Table 1. Characteristics of the selected wastewater effluent.

Parameters	Mean value ^a
TOC (total organic carbon) (mg L ⁻¹)	7.0±0.3
DOC (dissolved organic carbon) (mg L ⁻¹)	6.7±0.3
UVA (UV absorbance at 254 nm) (L mg ⁻¹ m ⁻¹)	1.87±0.05
pH	7.28±0.08
Alkalinity (mg L ⁻¹ as CaCO ₃)	154.8±5.8
NH ₄ ⁺ (mg-N L ⁻¹)	1.6±0.6
NO ₂ ⁻ (mg-N L ⁻¹)	0.40±0.08
NO ₃ ⁻ (mg-N L ⁻¹)	3.94±2.75

^aData are shown as arithmetic mean of four replicates ± standard deviation.

Table 2. E_{EO} ($\text{kWh m}^{-3} \text{ order}^{-1}$) calculation for UV-based systems ($[\text{CBZ}] = 2.0 \text{ mg L}^{-1}$, $[\text{PMD}] = 2.0 \text{ mg L}^{-1}$, $[\text{PBB}] = 5.0 \text{ mg L}^{-1}$, $[\text{TAP}] = 5.0 \text{ mg L}^{-1}$ and $[\text{FF}] = 5.0 \text{ mg L}^{-1}$; no pH adjustment; $20\text{ }^{\circ}\text{C}$).

Oxidation processes	CBZ	PMD	PBB	TAP	FF
UV	550.9	- ^a	275.8	113.3	105.4
UV/ CaO_2	41.4	108.9	37.9	78.1	60.5

^a E_{EO} value of PMD not available because its degradation cannot be achieved by direct photolysis.

Figure1

Fig. 1. Effect of CaO_2 dosage on (a) the degradation rate constants (K) of the test PhACs and (b) the change of TOC during UV/ CaO_2 process ($[\text{CBZ}]_0 = 2.0 \text{ mg L}^{-1}$, $[\text{PMD}]_0 = 2.0 \text{ mg L}^{-1}$, $[\text{PBB}]_0 = 5.0 \text{ mg L}^{-1}$, $[\text{TAP}]_0 = 5.0 \text{ mg L}^{-1}$, $[\text{FF}]_0 = 5.0 \text{ mg L}^{-1}$; no pH adjustment; 20°C).

Figure2

Fig. 2. K of the test PhACs at different initial concentrations during UV/ CaO_2 process, which is fitted as functions of the corresponding initial concentrations of each compound (C_0). ($[\text{CaO}_2] = 0.1 \text{ g L}^{-1}$, no pH adjustment; 20°C)

Figure3

Fig. 3. Effect of initial pH on (a) K of test PhACs and the final pH under UV/CaO₂, and (b) K of test PhACs under UV treatment. ($[CaO_2] = 0.1 \text{ g L}^{-1}$, $[CBZ] = 2.0 \text{ mg L}^{-1}$, $[PMD] = 2.0 \text{ mg L}^{-1}$, $[PBB] = 5.0 \text{ mg L}^{-1}$, $[TAP] = 5.0 \text{ mg L}^{-1}$ and $[FF] = 5.0 \text{ mg L}^{-1}$; 20 °C)

Figure4

Fig. 4. (a) K of test PhACs degradation under the combination of CaO₂ hydrolysates with UV, and (b) the corresponding final pH. ([CaO₂] = 0.100 g L⁻¹, [Ca(OH)₂] = 0.102 g L⁻¹, [CaCl₂] = 0.153 g L⁻¹, [NaCl] = 0.161 g L⁻¹, [H₂O₂] = 0.0354 g L⁻¹, [CBZ] = 1.0 mg L⁻¹, [PMD] = 1.0 mg L⁻¹, [PBB] = 5.0 mg L⁻¹, [TAP] = 5.0 mg L⁻¹ and [FF] = 5.0 mg L⁻¹; no pH adjustment; 20 °C)

Figure5

Fig. 5. (a) Effect of reactive radical scavengers on K of test PhACs under UV/CaO₂; (b) Contributions of direct-photolysis, and indirect-photolysis ($\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, O_2^1 , $^3\text{DOM}^*$ and H_2O_2) on the UV/CaO₂ treatment of test PhACs, respectively. (IPA (~100 mM) was used to quench $\bullet\text{OH}$; SOD (~100 kU L⁻¹) was used to quench $\text{O}_2^{\bullet-}$; DABCO (~100 mM) was used to quench O_2^1 . IPE (~10 mM) was used to quench $^3\text{DOM}^*$; N₂ was used to remove the O₂ and O_2^1 , air was used to remove $^3\text{DOM}^*$; [CaO₂] = 0.1 g L⁻¹, [CBZ] = 2.0 mg L⁻¹, [PMD] = 2.0 mg L⁻¹, [PBB] = 5.0 mg L⁻¹, [TAP] = 5.0 mg L⁻¹ and [FF] = 5.0 mg L⁻¹; no pH adjustment; 20 °C).

Figure6

Fig. 6. EPR spectrum of radicals released under UV/CaO₂ with DMPO spin trap in PW. (Thiourea (~1%, w/v), DMSO (~10%, w/v), [CaO₂] = 0.1 g L⁻¹, test PhACs: [CBZ] =2.0 mg L⁻¹, [PMD] =2.0 mg L⁻¹, [PBB] =5.0 mg L⁻¹, [TAP] =5.0 mg L⁻¹ and [FF] =5.0 mg L⁻¹; mean intensity value from three repeated tests)

Figure8

Fig. 8. The possible degradation pathway of CBZ in PW under UV/CaO₂: the brace means intermediates which have the same hydroxyl number on the different carbon site; short dash line indicates the bond broken; uppercase letters under chemical structure indicates intermediates abbreviation, lowercase letters means the reaction position.

Figure9

Fig. 9. The possible degradation pathway of PMD and PBB in PW under UV/CaO₂: short dash line indicates the broken bond; uppercase letters under chemical structure indicates intermediates abbreviation.

Figure10

Fig. 10. The possible degradation pathway of TAP and FF in PW under UV/CaO₂: R means the OH or F group; the square brackets mean the intermediate not detected but probably existed; short dash line indicates the broken bond; uppercase letters under chemical structure indicates intermediates abbreviation; F⁻ was detected in FF degradation.

Figure11

Fig 11. The degradation of CBZ and PMD in WWE under UV, UV/ CaO_2 and UV/ H_2O_2 . (no pH adjustment; 20 °C)

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