

# Photocatalytic degradation and Products of Chloramphenicol by ZnO<sub>2</sub>/ZnO nanocomposite

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## Abstract

This study reports used the photocatalysts of ZnO<sub>2</sub>/ZnO nanocomposite for photocatalytic degrading aqueous Chloramphenicol (CAP) under UV irradiation. The precursor of ZnO<sub>2</sub> nanoparticles had been synthesized by sol-gel method with photochemical reaction process. And, ZnO<sub>2</sub> nanopowder was hydrothermal treated in teflon-lined stainless steel autoclave with different temperatures from 120°C to 180°C. The ZnO<sub>2</sub>/ZnO precipitate was obtained when the temperature at 140°C of ZnO<sub>2</sub> by hydrothermal treatment. When the temperature of hydrothermal treatment was increased to 180°C, ZnO<sub>2</sub> would be transformed to ZnO. The obtained powder (ZnO<sub>2</sub>, ZnO<sub>2</sub>/ZnO, ZnO) was characterized by XRD, FT-IR, DRS, CL, and FE-SEM. In a previous study, we found that ZnO<sub>2</sub>/ZnO nanocomposite had better photocatalytic degradation efficiencies for Crystal Violet Dye of those obtained powder (ZnO<sub>2</sub>, ZnO<sub>2</sub>/ZnO, ZnO). So, we used ZnO<sub>2</sub>/ZnO nanocomposite for photocatalytic degradation of CAP in this study. In order to get better understanding on the products and the mechanistic details of the photocatalytic degradation of CAP in aqueous ZnO<sub>2</sub>/ZnO suspensions under UV light irradiation, the technique of HPLC was used for separating the photodecomposed products and intermediates. The intermediates formed in the CAP degradation processes were separated and identified by HPLC-ESI-MS technique. The possible degradation pathways were proposed and discussed in this research. The study was useful for synthesizing a series product of ZnO<sub>2</sub>, ZnO<sub>2</sub>/ZnO, ZnO and to degrade CAP at future applications of environmental pollution and control.

Keywords: Chloramphenicol, ZnO, ZnO<sub>2</sub>, nanocomposite, HPLC-ESI-MS

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## 1 Introduction

In the past decades, the development of nanocomposite photocatalysts has attracted considerable interests. Moreover, modified ZnO has been intensively studied to increase the photoactivity of ZnO by adding other materials to form nanocomposites such as Ag/ZnO, ZnO/TiO<sub>2</sub>, CuO/ZnO ect[1-3]. ZnO is broadly used as a photocatalyst for degrading a wide range of organic pollutants because of its photochemical stability and low cost. Literature indicated the zinc peroxide being mostly used in the rubber industry and plastic processing. It could also be used as precursors for the preparation of ZnO[4-5]. In this study, we presented a simple method to prepare ZnO<sub>2</sub> particles by photochemical process[5-7] and to form ZnO<sub>2</sub>/ZnO nanocomposite by using hydrothermal method. We used the ZnO<sub>2</sub>/ZnO nanocomposite for the photocatalytic degradation of CAP and separated and identified the intermediate products by HPLC-ESI-MS technique. It could further understand the fundamental photocatalytic degradation mechanisms of antibiotic by HPLC-ESI-MS.

## 2 Experimental

### 2.1 Synthesis of ZnO<sub>2</sub>/ZnO nanocomposite

1g of zinc acetate dehydrate was dissolved in 25ml H<sub>2</sub>O<sub>2</sub>(3.5%). Then, the ZnO<sub>2</sub> precursor sol was obtained when the solution being irradiated under UV light (365nm) for 6 hour. And, the precursor sol was continuously stirred in the dark for two day. Finally, the ZnO<sub>2</sub> precipitate (Catalyst Code. S25) was filtered and washed with de-ionized water and dried at 60°C. The ZnO<sub>2</sub>/ZnO nanocomposite was synthesized by ZnO<sub>2</sub> nanopowder,

which was hydrothermally treated in teflon-lined stainless steel autoclave with different temperatures from 120°C to 180°C (Catalyst Code: S25-120~S25-180). And then, ZnO<sub>2</sub>/ZnO precipitate was obtained. The precipitate was filtered and dried at 60°C.

## 2.2 Characterization

The obtained products(S25, S25-120~S25-180) were characterized by Powder X-ray diffraction (XRD), performed on a MAC Sience, MXP18 X-ray diffractometer with Cu K $\alpha$  radiation, and operated at 40 kV and 80 mA. FE-SEM-EDS measurements were carried out with a field-emission microscope (JEOL JSM-7401F) at an acceleration voltage of 15 kV, and an HRXPS measurement was carried out with ULVAC-PHI XPS. The Al K $\alpha$  radiation was generated with a voltage of 15 kV. The photocatalytic activity evaluation used absorption measurements, which were carried out by using a Shimadzu UV-2100S spectrophotometer. Separating and identifying the intermediate products by HPLC-PDA-ESI-MS system consisted of a Waters 1525 binary pump, a 2998 photodiode array detector, and a 717 plus autosampler

## 2.3 Photocatalytic reaction

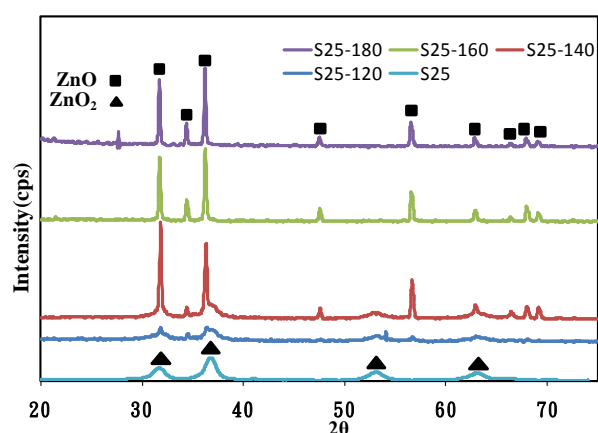
Photocatalytic activities of ZnO<sub>2</sub>/ZnO were studied by the degradation of CV and CAP under visible light irradiation of a 20 watt lamp. An average irradiation intensity of 5.2 W/m<sup>2</sup> was maintained throughout the experiments and measured by internal radiometer. Aqueous suspensions of CV (100 mL, 10 ppm) and CAP (100ml, 50ppm) with as-prepared catalyst powder were placed in a Pyrex flask. The pH value of the suspensions was adjusted by adding NaOH solution to 9. And then, the suspensions were magnetically stirred in the dark for 30 min to reach an adsorption/desorption equilibrium between the analytes(CV, CAP) and the surface of the catalyst under ambient air-equilibrated conditions. After the adsorption/desorption equilibrium, to give the irradiation with time intervals, 5 mL aliquot was collected and centrifuged to remove the catalyst. The supernatant was analyzed by HPLC-ESI-MS after readjusting the chromatographic conditions in order to make the mobile phase compatible with the working conditions of the mass spectrometer.

## 3 Results and Discussion

### 3.1 Characterizations of as-prepared powder

#### 3.1.1 XRD analysis

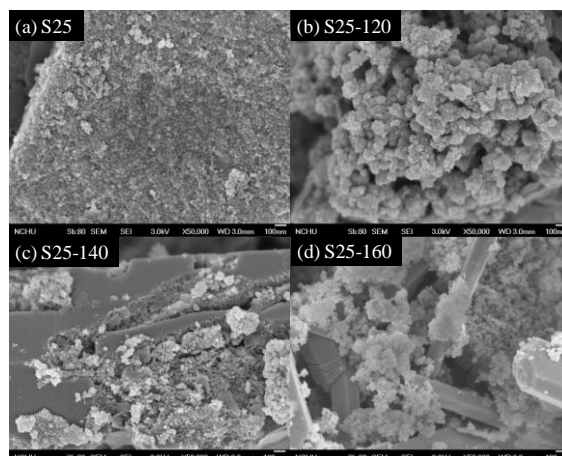
Fig.1 shows the XRD pattern of ZnO<sub>2</sub> (S25) and ZnO<sub>2</sub> at different hydrothermal temperatures. Clearly from the figure, there were changes from ZnO<sub>2</sub> to ZnO with the increase in the hydrothermal temperature from 120°C to 180°C (S25-120~S25-180). And the ZnO<sub>2</sub>/ZnO nanocomposite was obtained when the temperature was 140°C.



**Figure 1:** X-ray diffraction patterns of the samples prepared by the content of 25ml H<sub>2</sub>O<sub>2</sub>(3.5%) and hydrothermal method at different temperatures (120-180 °C ) for 2 hour.

#### 3.1.2 SEM-EDS analysis

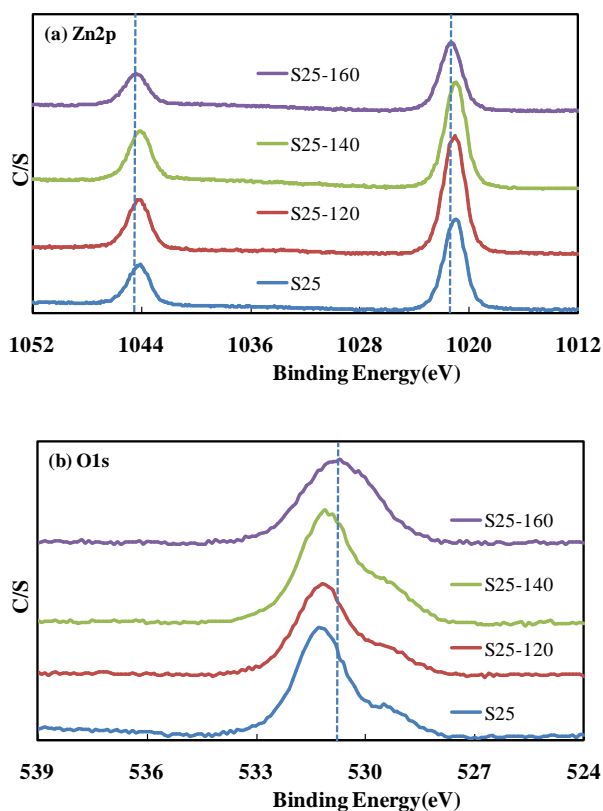
In Fig.2, the SEM micrographs of three types of samples with distinct morphologies are presented. Fig.2a shows the formation of ZnO<sub>2</sub> nanoparticles. By hydrothermal treatment, the formation of the rod with defect structure, and rods with some particles could be observed in parts c, and d of Fig.2, respectively.



**Figure 2:** FE-SEM image of ZnO<sub>2</sub> and ZnO<sub>2</sub>/ZnO. The material prepared by 25ml H<sub>2</sub>O<sub>2</sub>(3.5%) at room temperature (a) and the autoclave hydrothermal method at 120 °C (b), 140 °C (c), and 160 °C (d) for 2 hour.

### 3.1.3 XPS analysis

The characteristic binding energy value of 531.5 eV for O 1s revealed a trivalent oxidation state for oxygen. The binding energy shift of 530.5 eV for O 1s was clearly observed, suggesting the O(+2) formal oxidation state being attributed to ZnO starting to emerge by hydrothermal treatment ZnO<sub>2</sub> around 120°C[4,8]. ZnO<sub>2</sub> was completely converted into ZnO around 160°C.

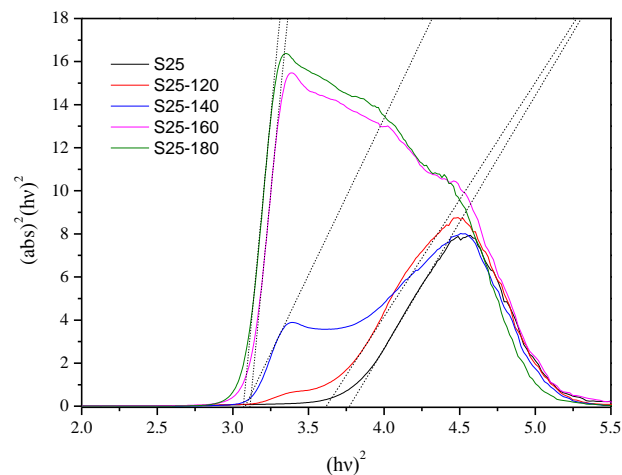


**Figure 3:** High resolution XPS spectra of Zn 2p (a) and O 1s(b). The material prepared by 25ml H<sub>2</sub>O<sub>2</sub>(3.5%) at room temperature and the hydrothermal method at different temperatures (120-160 °C ) for 2 hour.

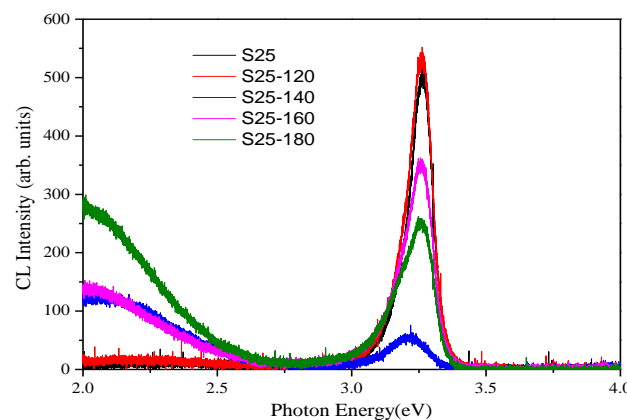
### 3.1.4 CL and UV-Vis DRS analysis

Fig.4 shows UV-VIS optical absorption spectra (Tauc plot). The horizontal intercept of the line fitted to data points measuring those catalysts band gap energy as from 3.08 eV to 3.75eV. The two band gap levels of catalyst S25-140

were due to the nanocomposite structure of ZnO<sub>2</sub>/ZnO. In Fig.5, it was the cathodoluminescence (CL) spectra for the sample of Fig.1. The catalyst S25-140 showed a lower intensity of CL emission than the other catalysts. This indicated the S25-140 with low activity of recombination for electron-hole pairs[9-10].



**Figure 4:** UV-VIS optical absorption spectra (Tauc plot) of the material prepared by 25ml H<sub>2</sub>O<sub>2</sub>(3.5%) at room temperature and the hydrothermal method at different temperatures (120-180 °C ) for 2 hour.

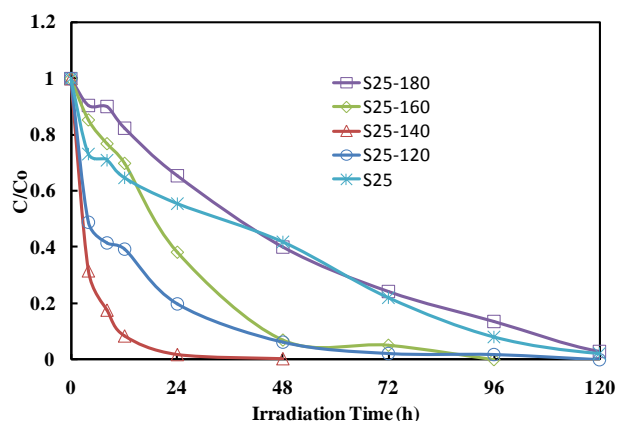


**Figure 5:** The Cathodoluminescence (CL) of the material prepared by 25ml H<sub>2</sub>O<sub>2</sub>(3.5%) at room temperature and the hydrothermal method at different temperatures (120-180 °C ) for 2 hour.

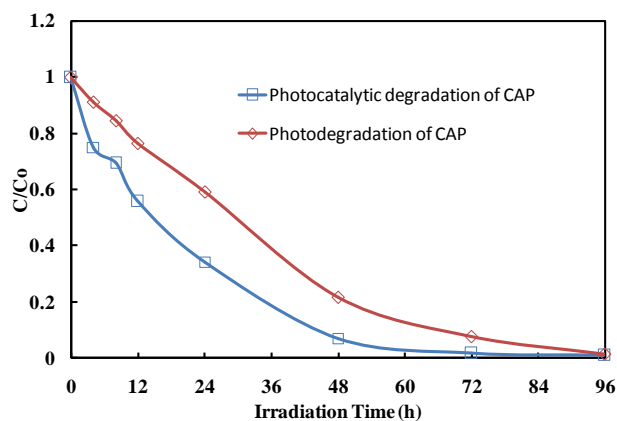
### 3.2 Photocatalytic Activity Evaluation of CV and CAP

The ZnO<sub>2</sub>/ZnO nanocomposite had better photocatalytic degradation efficiencies of Crystal Violet Dye in aqueous ZnO<sub>2</sub>/ZnO suspensions under UV light irradiation, Fig.6. The important thing was that after 24 h irradiation, ZnO<sub>2</sub>/ZnO showed the superior photocatalytic

performance, with CV removal efficiency up to 98%. In order to get better effect of photocatalytic and understanding for the products, mechanistic details of the photocatalytic degradation of CAP. So, we used  $\text{ZnO}_2/\text{ZnO}$  nanocomposite for the photocatalytic degradation of CAP in this study. The results showed that  $\text{ZnO}_2/\text{ZnO}$  could effectively raise the degradation effect than the photodegradation did, Fig 7.



**Figure 6:** Synthesis conditions effect of temperature on the CV degradation rate under UV light irradiation: catalyst, 0.5g $\text{L}^{-1}$ ; CV, 0.01g $\text{L}^{-1}$ .

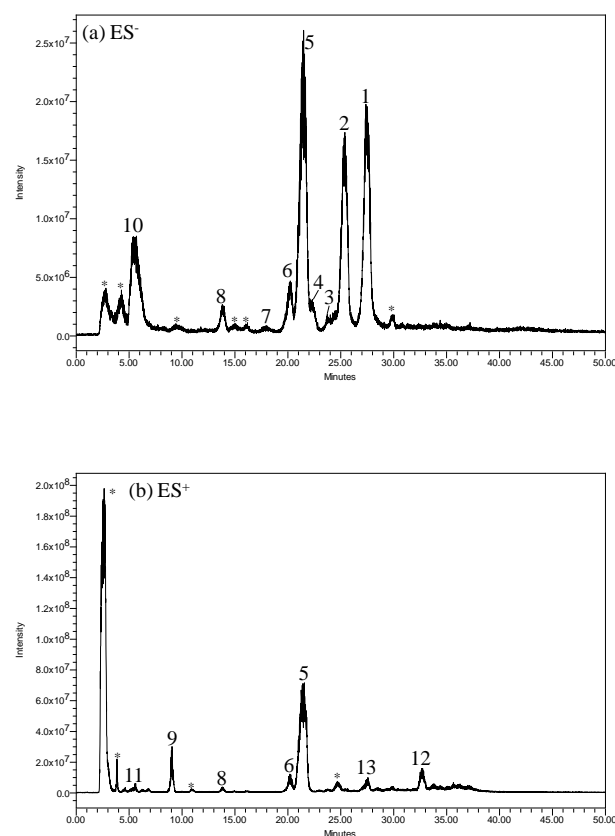


**Figure 7:** The effect of photocatalytic degradation and photodegradation on the CAP degradation rate under UV light irradiation: catalyst  $\text{ZnO}_2/\text{ZnO}$ , 0.5g $\text{L}^{-1}$ ; CAP, 0.05g $\text{L}^{-1}$  at pH9.

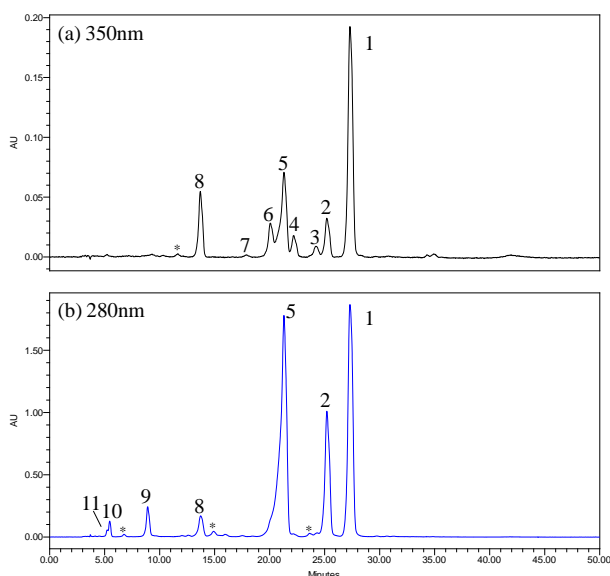
### 3.3 Identification the intermediate products of CAP

The photodegradation process of CAP was examined by HPLC coupled with a photodiode array detector and ESI mass spectrometry. According to HPLC chromatograms, we could identify the CAP and its related intermediates in Fig 8 and Fig 9. As shown in Fig.8a, the  $\text{ES}^-$  mass

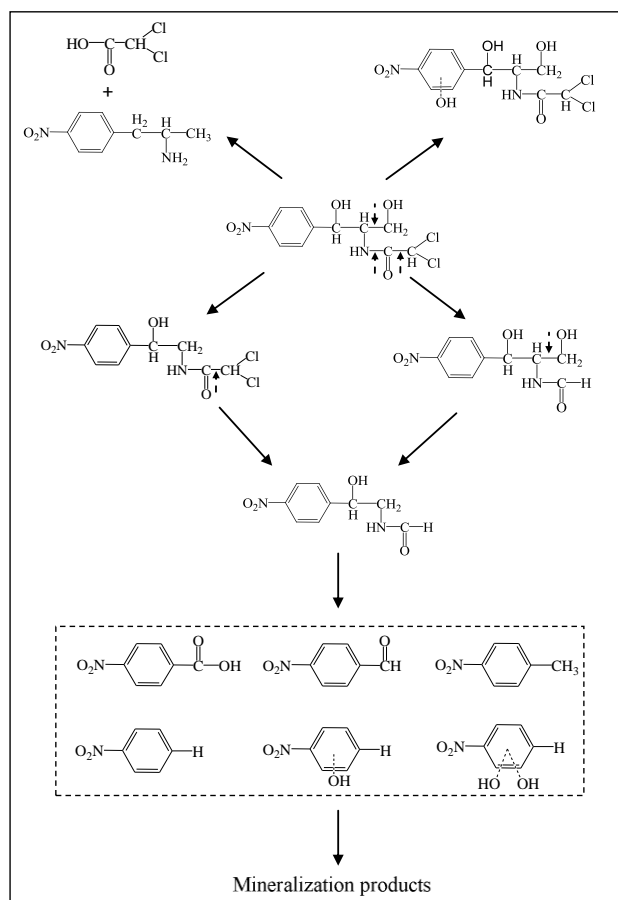
spectral analyses confirmed the components 1( $m/z = 150$ ), 2( $m/z = 166$ ), 3( $m/z = 291$ ), 4( $m/z = 138$ ), 5( $m/z = 321$ ), 6( $m/z = 337$ ), 7( $m/z = 154$ ), 8( $m/z = 122$ ), 10 ( $m/z = 127$ ), and the  $\text{ES}^+$  mass spectral analyses confirmed the components 5( $m/z = 323$ ), 6( $m/z = 339$ ), 8( $m/z = 124$ ), 9( $m/z = 138$ ), 11( $m/z = 181$ ), 12( $m/z = 211$ ), 13( $m/z = 241$ ). =124) in Fig .8b. Fig.9 shows the  $\lambda_{\text{max}}$  of UV–visible spectra for peaks 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 being 286.5, 262.8, 316.3, 318.7, 274.6, 271.1, 355.8, 297.2, 286.5, 267.5, 287.7, and it corresponded to the TIC spectral by retention time. Based on the above experimental results, there were 12 intermediate products being identified [11-12]. The intermediate product analyses and structures are depicted in Table 2 and Table 3. Based on the HPLC-PDA-ESI-MS analyses of intermediates in the photocatalytic degradation process, the photodegradation pathways for CAP are proposed in Fig. 10.



**Figure 8:** HPLC chromatogram of the intermediates with  $\text{ZnO}_2/\text{ZnO}$  0.5 g $\text{L}^{-1}$ , pH 9. The total ion chromatogram of (a)  $\text{ES}^-$  and (b)  $\text{ES}^+$ , at 16 h of irradiation.



**Figure 9:** HPLC chromatogram of the intermediates with 16hr of photocatalytic degradation process at pH 9, recorded at (a) 350 nm, (b) 280 nm.



**Figure 10:** The photocatalytic degradation pathway of CAP.

**Table 1:** Physical and chemical properties of prepared ZnO and ZnO<sub>2</sub>/ZnO.

Catalyst Code	EDS element atomic ratio (%)		XPS element atomic ratio (%)		Eg(eV)
	Zn	O	Zn	O	
S25	36.03	63.97	33.03	66.97	3.75
S25-120	43.25	56.75	37.92	62.08	3.58
S25-140	39.63	60.37	35.14	64.86	3.12/3.33
S25-160	39.12	60.88	32.14	67.86	3.07
S25-180	35.97	64.03	--	--	3.08

**Table. 2:** The degraded intermediates of CAP by photocatalytic degradation process.

Peak no.	MW	$\lambda_{max}$ , nm	$t_R(ES^-)$	$[M-H]^-$	$t_R(ES^+)$	$[M+H]^+$
1	151	286.5	27.3	150	--	--
2	167	262.8	25.3	166	--	--
3	292	316.3	23.7	291	--	--
4	139	318.7	22.3	138	--	--
5(CAP)	322	274.6	21.4	321	21.5	323
6	338	271.1	20.2	337	20.1	339
7	155	355.8	17.9	154	--	--
8	123	297.2	13.8	122	13.8	124
9	137	286.5	--	--	09.0	138
10	128	267.5	05.6	127	--	--
11	180	287.7	--	--	05.6	181
12	210	--	--	--	27.5	211
13	240	--	--	--	32.6	241

**Table. 3:** Structure of photodecomposed products in the CAP photodegradation process by ZnO/ZnO<sub>2</sub>.

Peak no.	Compound Structure	Peak no.	Compound Structure
1		8	
2		9	
3		10	
4		11	
5(CAP)		12	
6		13	
7			

## 4 Conclusion

There are changes from ZnO<sub>2</sub> to ZnO with the increase in the hydrothermal temperature from 120°C to 180°C. And the ZnO<sub>2</sub>/ZnO nanocomposite is obtained when the

temperature is 140°C. The study shows that the ZnO<sub>2</sub>/ZnO nanocomposite has better photocatalytic degradation efficiencies due to the low activity of recombination for photoelectron-hole pairs. According to HPLC chromatograms and HPLC-PDA-ESI-MS system, we successfully separate and identify 12 intermediate products in the photocatalytic degradation process of CAP. The reaction mechanisms for ZnO<sub>2</sub>/ZnO under UV light proposed in this study should offer some insight for the future development of environmental pollution control for the degradation of antibiotic.

### Acknowledgments

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