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# Ba-ZnO Nanoparticles for Photo-catalytic Degradation of Chloramphenicol

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## Abstract

Pristine ZnO (PZO) and 5% barium doped ZnO nanoparticles (BZONP) were prepared by in expensive chemical precipitation method. The techniques used to characterize prepared nanoparticles are X-ray powder diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDX), Scanning Electron Microscope (SEM), UV-visible absorption spectroscopy and Transmission Electron Microscope (TEM) analysis. The particle size of PZO and BZONP were calculated using Scherrer equation. The photo-catalytic efficiency of 5% BZONP was studied with photo-degradation of chloramphenicol (CLP) under UVC (254 nm) irradiation in aqueous suspension. Pseudo-first order rate constants ( $k_{obs}$ ) were found to increase with the decrease in pH. The effect of initial concentration, photo-catalyst loading, light intensity, the effect of pH on the photo-degradation rate was also examined and elaborately discussed. The results showed that BZONP is a better photo-catalyst compared PZO. The HPLC and LC/MS were used to identify photo-degradation products.

**Keywords:** Photo-catalyst; Nanoparticles; Degradation; Zinc oxide; Chloramphenicol

**PACS:** 81.07.Wx, 81.05.Dz

## INTRODUCTION

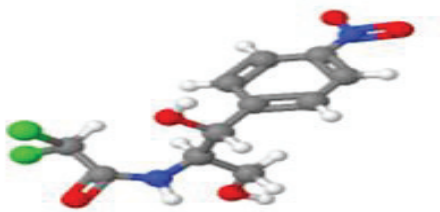
The ground water and surface water contaminated by the industrial outfall, irrigation runoff, chemical spills, commercial operations that contain many non-biodegradable substrates that are harmful to the human kind and also significant threat for flora and fauna of the environment [1]. Many conventional treatments like chlorination [2-3] permanganate treatment [4-6] nano-filtration and reverse osmosis [7] were reported for the treatment of pharmaceuticals in the literature. So far it is difficult to treat these organic contaminants by usual conventional and biological treatment methods [8]. During past twenty years, advanced oxidation process (AOP) is considered to be effective method for removal of toxic organic contaminants, which uses photo-catalytic process involving zinc oxide and titanium dioxide semiconductor nanoparticles, under UV or visible light elucidation has been potentially helpful in the management of waste-water contaminants [9-10].

AOPs have been extensively used for the photo-catalytic degradation of hazardous organic contaminants, which are susceptible to conventional and biological treatment methods. AOPs produces highly potent reactive radical species ( $HO_2$ ,  $HO\cdot$ ), which demineralise many organic contaminants with-out being choosy, by chemical or photochemical method [11-13]. The technique mainly focuses on usage of semiconductor particles activated by UV or visible light for degradation of environmental contaminants yielding to complete or partial mineralization of the organic contaminants [14-15]. Amongst AOPs semiconductor heterogeneous photo-catalysis is an effective method. This can be easily applied for the treatment of drug containing waste-water.

The PZO nanoparticles have been widely used in the field of photo-catalytic degradation [16]. PZO is believed to be a right substitute to  $\text{TiO}_2$  (3.2 eV), due to their wide-band gap (3.3 eV), low cost, greater efficiency and stability semiconducting material with a broad excitation binding energy, vast in nature and environmentally friendly and these characteristics make this material to captivate increasing attention as it is a potentially useful material for a wide range of applications. The efficiency of the photo-catalyst depends on the rate of electron-hole recombination in PZO, the rate of recombination can be minimized by doping the PZO with transition metals such as silver, ruthenium, copper, barium etc.

Decorating PZO with impurity/dopant (transition metal ions) improves the electronic structure of PZO and enhances the optical, electrical, magnetic properties and showing other improvement in the different application like photo-reaction and photo-catalytic activity. These transition metal ions not only served as trapping sites, it also reduces charge re-combination and to facilitate interfacial electron transfer process that in turn enhance the surface reactivity. Doping also induces the widening of wavelength from UV to the visible-range [17].

Now-a-day, antibiotic and public care products are largely discharged into the water bodies with no limitation. This is promising as a major contaminant in the ecosystem and threat to public concern. Among these antibiotics, Chloramphenicol (CLP) is a unique drug (Fig 1). CLP belongs to tetracycline family and commonly known as Chloromycetin. CLP is believed to be proto-typical wide range spectrum antibacterial agent [18]. Hence, it can be used to cure a variety of microscopic organisms causing illness [19]. These antibiotics dose are released into the public waste water streams due to the incomplete metabolism of antibiotics within the human body [20].



**FIGURE1. Chemical Structure of Chloramphenicol**

## EXPERIMENTAL

### 1 Materials and methods

From Sigma Aldrich (Bangalore) analar grade chloramphenicol (CLP) was obtained and it is used without any further purification. The CLP stock solution was prepared by dissolving an known quantity of CLP in deionised water. The  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , NaOH and  $\text{Ba}(\text{NO}_3)_2$  procured from HIMEDIA. The analytical grade chemicals were used to prepare acetate (pH 4-5), phosphate (pH 6.0-8.5) and borate (pH 9) buffers.

### 2 Photo-catalyst preparation

For synthesizing PZO and BZONP, 0.1M zinc nitrate salt was dissolved in deionized water and 10 mg  $\text{dm}^{-3}$  of sodium dodecyl sulphate (surfactant) was added to control particle size, and serves as a capping agent during preparation of zinc nitrate solution [21]. 0.1M NaOH solution was prepared separately in deionized water. NaOH was added dropwise with steady stirring thoroughly (2000 RPM) to zinc nitrate solution for 3 hrs. The resultant mixture was permitted to settle for 24 hrs then the suspension was decanted carefully, the residual solution was washed and filtered several times with distilled water then with ethanol to treat the impurities which are adhered to the nanoparticles. Then the powder was dehydrated in an oven at 120  $^{\circ}\text{C}$  for 3 hrs then powder was grounded in a mortar then calcined at 500  $^{\circ}\text{C}$  for about 1 hr in a muffle furnace (with a heating rate about 10  $^{\circ}\text{C}$  per minute). During the drying process, the complete transformation of zinc hydroxide to PZO takes place. The same procedure was followed to synthesize 5% BZONP the only difference was the addition of 0.1M barium nitrate solution in zinc nitrate solution. The barium concentration was 5 (% mole ratio). The BZONP it enters into the interstitial position of PZO lattice. Similar works were earlier reported [22].

### 3 The Photo-catalysis Process

To study the photo-catalytic degradation of CLP, a required quantity of CLP and buffer mixture was kept in a pyrex beaker. A dose of  $0.10 \text{ g dm}^{-3}$  of 5% BZONP was added. Before illumination, the suspensions were stirred for 60 min in dark place to reach adsorption and desorption equilibrium between CLP and photo-catalyst. Then, it was transferred into the photoreactor and then kept under 8 W UV lamps (Philips) with a wavelength peak at 254 nm and of  $4 \text{ mW/cm}^2$  intensity with continuous magnetic stirring. After every 10 minutes interval, the solution was taken out and centrifuged at 5000 rpm for 5 min. The decrease in the concentration of CLP was monitored at 278 nm ( $\epsilon = 27471 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) using visible spectrophotometer (a CARY 50 Bio UV-Visible Spectrophotometer) and the degree of mineralization was studied.

## RESULTS AND DISCUSSION

### 1 Comparison of different photo-catalysts

The rate of photo-catalytic activity of CLP with UV, UV/PZO, and UV/ BZONP was reported. It was observed that the degradation effect of CLP treatment with UV/ (5%) BZONP was more efficient than other two treatments namely UV and UV/PZO.

Effect of BZONP was studied by using 5% (mole ratio) of barium, higher content of barium may facilitate efficiently separating charge carrier and hindered the recombination of electron-hole pairs, and this increases the photo-catalytic activity. The photo degradation rate was maximum with 5% BZONP compared with UV and UV/PZO, hence, further studies were carried out with 5% BZONP. An attempt was also made to prepare higher than 5% percentage BZONP but barium started depositing on the surface instead of doping. The % degradation activity of CLP was carried out under same conditions with UV, UV/PZO, and UV/ BZONP and % adsorption in dark was also studied.

### 2 X-ray diffraction studies (XRD)

XRD pattern of BZONP was obtained using a Siemens X-ray Diffractometer (Cu source) AXS D5005. The XRD pattern of BZONP revealed that nanoparticles have hexagonal wurtzite structure Fig. 2. The sharp peak of (101) indicates that the expansion of nano crystal has taken-up along the easy route of crystallization of zinc oxide (Lin et al. 2005). No other visible impurity peaks can be observed in XRD.

The broadening of the wurtzite main intense peak (101) was used to calculate the crystallite size of BZONP, using Scherrer formula (1). The mean crystallite size of BZONP was found to be  $35.2 (\pm 3)$ , using the following equation [23] (Kulkarni et al. 2016)

$$D = \frac{0.94 \lambda}{\beta_{1/2} \cos \theta} \quad (1)$$

Where D is the average crystalline diameter,  $\lambda$  is the wavelength in angstrom,  $\beta$  is the line width at half-maximum and  $\theta$  is the Bragg angle.

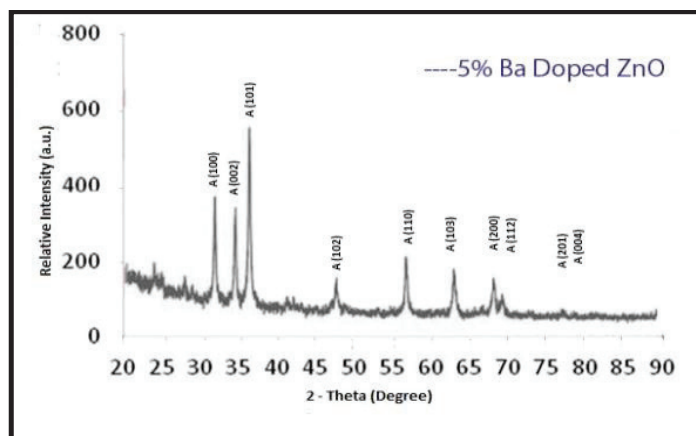


FIGURE 2. XRD pattern of 5% BZONP

### 3 Scanning electron microscope and EDX studies

The surface morphology of BZONP was obtained by a JEOL JSM 6360 SEM. The SEM analysis of PZO and 5% BZONP was done to study the surface morphology (Fig. 3 A and Fig. 3 B). It shows that 5% BZONP are irregular shape and size. This irregular shape the surface area of the nanoparticles is very high [24]. The elemental composition was also performed with Energy Dispersive X-ray Spectroscopy (EDX) and shown in Fig. 4 A and Fig 4 B (5% BZONP). The peaks from the spectrum reveal the presence of Zn, O and Ba at 8.630, 0.525 and 4.464 keV respectively. The atomic percentage of Zn, O and Ba is 71.30, 23.99 and 4.71 respectively. It was clear from the elemental analysis that 4.78% barium is present in 5 (mol %) BZONP, which lead to better photo-catalytic activity.

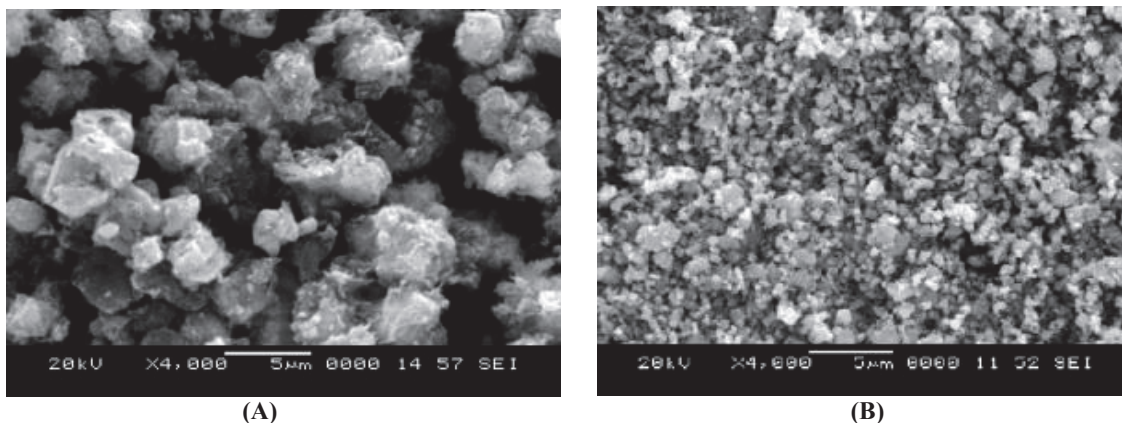


FIGURE 3. SEM micrographs of (A) PZO, and (B) 5% BZONP

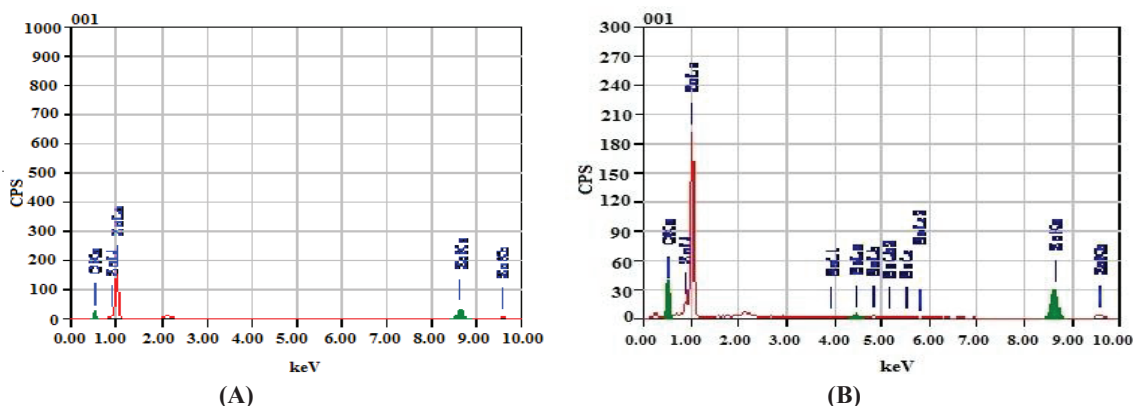
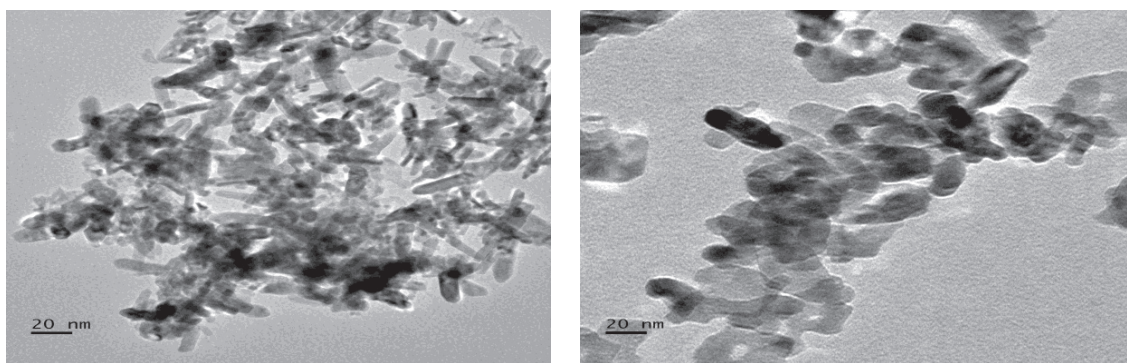


FIGURE 4. EDX analysis of (A) PZO (B) 5% BZONP

### 4 Transmission Electron Microscope studies (TEM)

The morphology and particle size of PZO and BZONP was measured using JEOL JEM-2010 Transmission Electron Microscopy (TEM). TEM images show that BZONP nanoparticles were agglomerated with non-uniformly distributed having barrel shaped crystalline structures as shown in Fig. 5 A and Fig. 5 B. Diffusion of small black spots observed was assumed as Ba atoms on ZnO nanoparticles with approximately 15-20 and 25-30 nm in width and length dimension respectively. It was confirmed that the synthesized nanoparticles crystal dimension is nearer to that of data got from XRD results for PZO nanoparticles.



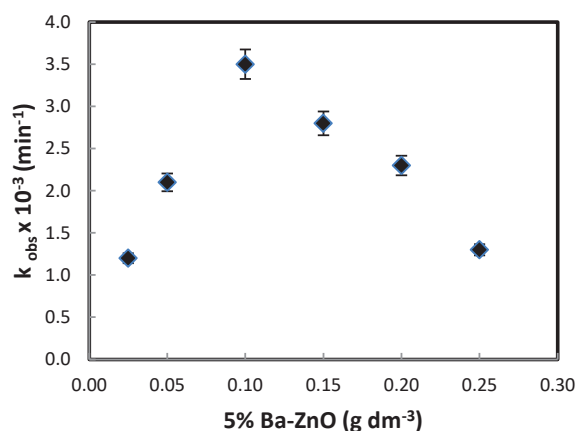
(A)

(B)

**FIGURE 5.** TEM micrographs of (A) PZO and (B) 5% BZONP

### 5 Effect of photo-catalyst loading

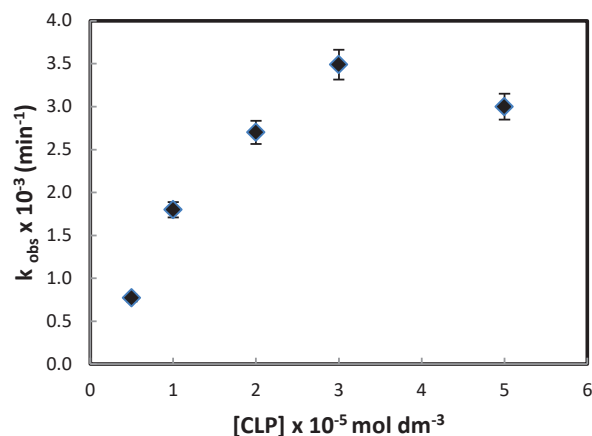
The influence of photo-catalytic degradation of CLP was studied using a different amount of a 5% BZONP photo-catalyst ranging from  $0.025 \text{ g dm}^{-3}$  to  $0.250 \text{ g dm}^{-3}$  whilst [CLP] and pH=5.0 were kept constant. The rate of photo-degradation increases with increase in the quantity of photo-catalyst up to limiting value  $0.10 \text{ g dm}^{-3}$ , beyond  $0.10 \text{ g dm}^{-3}$  the rate of photo-degradation decreases (Fig. 6). This behavior might be due to increase in the amount of photo-catalyst increases the exposed surface area of photo-catalyst which in turn increases the active centers on photo-catalyst. Consequently, which produces a higher number of  $\cdot\text{OH}$  radicals eventually these radicals involve in reaction to increase the rate of photo-catalytic reaction. But after limiting value ( $0.10 \text{ g dm}^{-3}$ ) increase in the amount of photo-catalyst increases the turbidity of the CLP suspension, thus it prevents UV-light to reach the photo-catalyst. Hence, the rate of photo-degradation decreases [25].



**FIGURE 6.** Effect of different amounts of photocatalyst [CLP] =  $3.00 \times 10^{-5} \text{ mol dm}^{-3}$ , at pH=5.0, Light intensity =  $4 \text{ mW/cm}^2$

### 6 Effect of substrate concentration

The rate of photo-catalytic degradation of CLP was studied by taking different [CLP] from  $5.00 \times 10^{-6}$  to  $5.00 \times 10^{-5} \text{ mol dm}^{-3}$  by keeping other reaction conditions constant. It has been experimentally investigated that initially increase in the [CLP], the rate of photo-catalytic degradation increases till [CLP] =  $3.00 \times 10^{-5} \text{ mol dm}^{-3}$ . Further increase in [CLP], decreases the rate of photo-catalytic degradation as shown in Fig. 7. This was due to, as the [CLP] increases, plenty of drug molecules are adsorbed on the active centers of the photo-catalyst surface, hence effective degradation takes place. But after limiting value ( $3.00 \times 10^{-5} \text{ mol dm}^{-3}$ ) the CLP itself acts as a filter for the light. Hence, the photons cannot reach the photo-catalyst surface and thus, the rate of photo-catalytic degradation decreases [26].

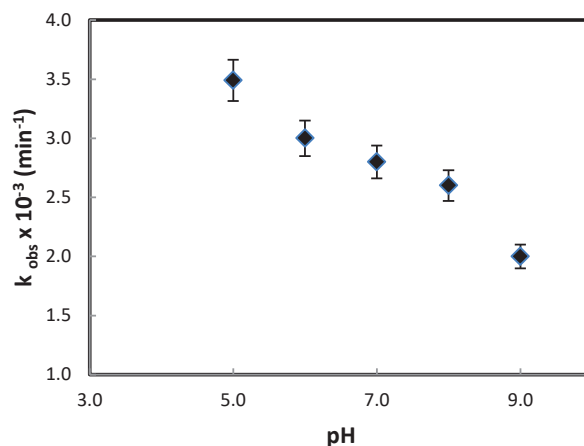


**FIGURE 7.** Effect of variation of [CLP] on photo-catalytic rate constants of photo-catalytic process with 5% BZONP at 25 °C, [5% BZONP] = 0.10 g dm<sup>-3</sup>, at pH=5, light intensity = 4mW/cm<sup>2</sup>

## 7 Effect of pH

The pH normally influences the adsorption capacity of the adsorbent in an aqueous medium by altering the surface properties of adsorbent. The effect of pH on the rate of photo degradation of CLP was studied by varying the pH from 5.0 - 9.0 while keeping other reaction conditions constant. The rate of photo-catalytic degradation of CLP  $P_{k_a}=5.5$  [27] (Marvin 2012), was higher in the pH range 5.0 - 6.0 and lower in the pH range 7.0 - 9.0 as shown in Fig.8. This increase in the rate of photo-catalytic degradation may be due to the fact that in acidic medium the photo-catalytic surface is positively charged (PZC=6) and it adsorbs more partial negatively charged CLP ions hence, an effective collision between CLP and BZONP photo-catalyst takes place so the rate of degradation was maximum at pH 5.0-6.0.

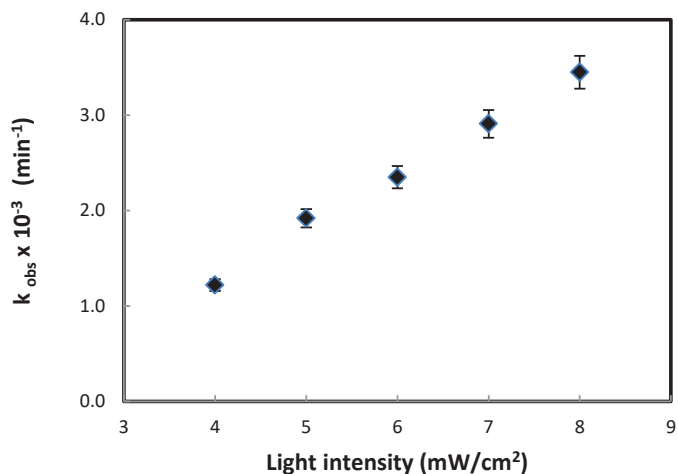
On the contrary, in the alkaline medium, the OH<sup>-</sup> ions accumulate on the surface of photo-catalyst making it negatively charged and CLP is also negatively charged in alkaline medium. Hence, the electrostatic repulsion between CLP ion and photo-catalyst takes place leading to decrease the rate of photo-degradation at pH 7.0 to 9.0. This observation is in line with the earlier report [28].



**FIGURE 8.** Effect of pH on the rate constant of photo catalytic degradation of CLP with 5% BZONP at 25 °C, [BZONP] = 0.10 g l<sup>-1</sup>, [CLP] = 3.00 x 10<sup>-5</sup> mol dm<sup>-3</sup>, light intensity = 4mW/cm<sup>2</sup>

## 8 Effect of UV lamp distance

To study the rate of photo-catalytic degradation of CLP at different UV light intensity the distance of UV lamp was varied from the surface of the mixture. It was observed that an increase in UV intensity of light increases the rate of photo-catalytic degradation of CLP, as depicted in Fig. 9. that, as the light intensity increases, the amount of BZONP excitation also increases, hence, more electron - hole pairs are generated consequently the hole degrade the CLP moiety adsorbed on the photo-catalyst surface and oxidize to carbon dioxide and water. This results in the effective demineralization of CLP.

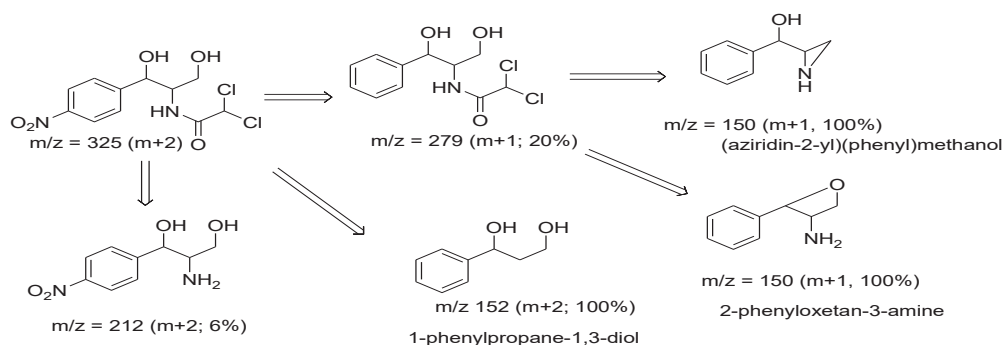


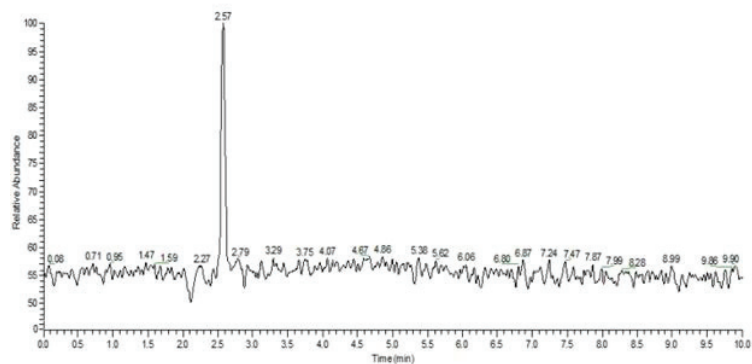
**FIGURE 9.** CLP degradation under different UV intensities CLP with 5% BZONP at 25 °C, [5% BZONP] = 0.10 g dm<sup>-3</sup>, [CLP] = 3.00 × 10<sup>-5</sup> mol dm<sup>-3</sup>, at pH = 5.0

## 9 Proposed Reaction Mechanism

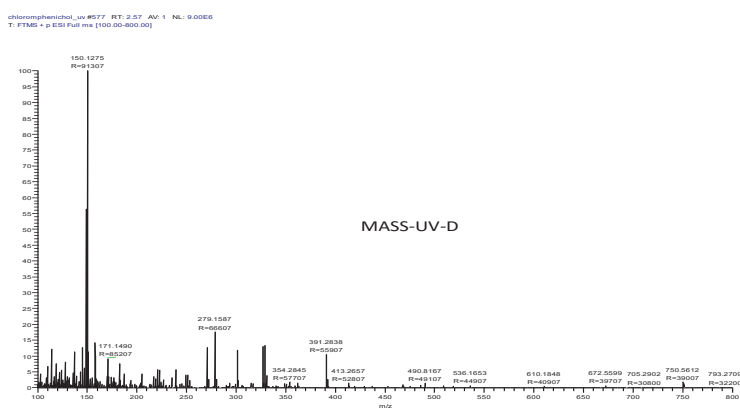
The reaction mixture containing CLP and buffer was kept in a beaker. A dosage of 0.1g dm<sup>-3</sup> 5% BZONP were added. Then, Post-illumination the suspensions were agitated at the black for 1 hr to accomplish adsorption-desorption equilibrium b/n the CLP and photo-catalyst. Then, it was kept into the photo-reactor having 8 W UV lamps (Philips) with a wavelength peak at 254 nm and of 4 mW/cm<sup>2</sup> intensity with continuous magnetic stirring. Then the reaction blend was set aside for one day and the products of CLP were analyzed by Agilent quadrupole 6130 series HPLC system. For HPLC examination 0.1% formic acid, acetonitrile is used as a solvent with a run rate 1.2 cm<sup>3</sup> min<sup>-1</sup>. This was continued using Column-Atlantis C18 (50 × 4.6 mm-5μm) dual model as shown in Fig. 10. Chloramphenicol MS fragmentation indicates no degradation of the molecule under this experimental conditions. In conclusion, only one major product was obtained at (m/z =150). The observed product reveals that only one plausible pathway for the degradation of chloramphenicol oxidation.

The proposed mechanism shows in Scheme 1.





(a)



(b)

**FIGURE 10.** LC/MS spectra of Chloramphenicol oxidation products a) Total ion chromatogram (TIC)  
b) Mass spectrum of reaction product m/z 150

## CONCLUSIONS

PZO and BZONP were synthesized by chemical precipitation method. The average particle size of 5% BZONP is 24.5 to 35.0 nm, exhibited excellent achievable photo-catalytic mineralization of CLP in the acidic condition (pH 5). The XRD patterns show prepared nanoparticles were wurtzite structure. The EDX and TEM analysis showed that the existence of Ba in ZnO. Under optimum conditions, over 92% photo-catalytic degradation of CLP was achieved in 100 min using 5% BZONP photo-catalyst.

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