

## **Preparation of Nano Zinc Oxide and its Application in the Photocatalytic Degradation of Ampicillin**

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### **ABSTRACT**

**T**his study was undertaken to prepare Nano zinc oxide (ZnO) by precipitation and microemulsion methods. Scanning electron microscopy (SEM), X-ray diffraction (XRD), FTIR spectrometry, atomic force microscopy (AFM), and Brunauer Emmett Teller (BET) surface area were the techniques employed for the preparation. The particle size of prepared nano ZnO was 69.15nm and 88.49nm for precipitation and microemulsion methods, respectively, which corresponded to the BET surface area 20.028 and 16.369m<sup>2</sup>/g respectively. The activity of prepared nano ZnO as a photocatalyst was estimated by the removal of ampicillin (Amp) under visible light. This study, therefore, examined the effect of pH in the range of 5-11, initial concentration of ampicillin in the range 30-70ppm, and nano ZnO concentration in the range 0.25-0.75g/L in a time period of 5h. The optimum operating conditions were pH 11, zinc oxide 0.5g/L, ampicillin initial concentration 70ppm, and that achieved for precipitation method to obtain degradation efficiency of 86% after 5h.

**Keywords:** Nano zinc oxide, Photocatalytic degradation, Photocatalyst, Microemulsion, Precipitation

### **تحضير نانو اوكسيد الزنك واستخدامه كمحفز ضوئي لتحلل الامبسلين**

مرؤة فائق عبد الجبار

مدرس

كلية الهندسة-جامعة النهرين

### **الخلاصة**

أجريت هذه الدراسة لتحضير نانو أوكسيد الزنك (ZnO) بطرق الترسيب والاستحلاب وكانت التقنيات المستخدمة في التحضير هي المسح المجهر الإلكتروني (SEM)، حيود الأشعة السينية (XRD)، مطياف (FTIR)، الفحص المجهر الإلكتروني (AFM) ومساحة Brunauer Emmett Teller (BET). كان قطر الجسيمات من nano ZnO المحضر

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69.15 نانومتر و 88.49 نانومتر لطرق الترسيب والاستحلاب ، على التوالي والتي تقابل مساحة 20.028 و 16.369 م<sup>2</sup>/غم على التوالي. تم تقدير نشاط نانو ZnO المحضر كمحفز ضوئي عن طريق إزالة الأميسيلين (Amp) تحت الضوء المرئي. لذلك قامت هذه الدراسة بفحص تأثير الأس الهيدروجيني في نطاق 5-11 ، والتركيز الأولي للأميسيلين في المدى 30-70 جزء في المليون وتركيز أوكسيد الزنك النانوي في النطاق 0.25-0.75 غم / لتر في فترة زمنية تصل 5 ساعات. وكانت ظروف التشغيل المثلى pH 11 ، وكمية أوكسيد الزنك 0.5 غم / لتر ، وتركيز الأميسيلين الأولي 70 جزء في المليون والذي تم تحقيقه لطريقة الترسيب للحصول على كفاءة تحلل بنسبة 86% بعد 5 ساعات.

**الكلمات الرئيسية :** نانو أوكسيد الزنك , التحلل الضوئي , العامل المحفز الضوئي , الاستحلاب , الترسيب

## 1. INTRODUCTION

The releasing of contaminants such as pesticides, hormones, and pharmaceutically active components to the environment has been an increasing concern that won much interest from the public and the scientific community as a result of their effect on human health, soil, plants, and aquatic systems (Wang, et al., 2015). Ampicillin, amoxicillin, and cloxacillin are considered as semi-synthetic penicillin attaining their antimicrobial characteristics from the existence of  $\beta$ -lactam ring (Elmolla and Chaudhuri, 2012).

In the field of wastewater treatment, photocatalytic degradation has reported some advantages such as reusability, complete degradation, have low cost, and are ecofriendly (Homem and Santos, 2011). In this technique, the semiconductor materials are photoactivated by sunlight, or artificially, that leads to the formation of strong oxidants such as OH<sup>-</sup> radicals and superoxide radical anions (Li, et al., 2012). Among the semi-conductor materials, zinc oxide is considered as cost-effective and a valuable photocatalyst that can be applied to large scale hospital, industrial and municipal wastewater treatment plants (Lam, et al., 2012). The activity of zinc oxide photocatalytic is considerably enhanced when nano-sized semi-conductor crystallites are used, thereby increasing the surface area available for photocatalytic reactions (Yang, et al., 2010).

Also, the quantum capability of zinc oxide is considerably more than that of titanium oxide which preferable efficiency than titanium oxide (Mai, et al. 2008). It absorbs solar light to great extent than titanium oxide (Chen, 2006). Hence, it is assumed to be adequate material for photodegradation of organic contamination.

The properties of the ZnO nanocrystals rely closely on their particle sizes, morphology, surface area, and activity. Various synthesis methods have evolved, including thermal decomposition of organic precursor (Rataboul, et al., 2002), sol gel technique (Manuel, et al., 2016), mechanochemical processing (Tsuzuki and McCormick, 2001), spray pyrolysis and drying (Okuyama and Lenggoro, 2003), pulsed laser deposition (Pronin, et al., 2014), supercritical water processing (Viswanathan, et al., 2003), hydrothermal processing (Liu and Zeng, 2003), homogeneous precipitation (Kim, et al., 2005), direct precipitation (Kumar, 2012), and microemulsion synthesis (Kang, et al. 2012). However, many of these methods have limitations as they often require complicated synthetic conditions, such as complex technologies and specific physical processes which are expensive and harmful to the environment and may limit application in the future (Zare, et al., 2018). Subsequently, the search for easy, rapid, and morphologically controllable method to synthesize the structure of ZnO nanoparticles has attracted significant research attention. Therefore, the synthesis of nano zinc oxide using precipitation and microemulsion was conducted. The precipitation method has several advantages over other growth processes such as low cost, use of simple equipment, uniform production, large surface area, environmental friendliness, and fewer hazards (Kumar, 2012). For microemulsion, the surfactant layer acts as a steric stabilizer to prevent the aggregation of the formed nanoparticles.



This process can be employed to produce highly monodispersed nanoparticles at room temperature and pressure using a simple glass apparatus (Sarkar, et al., 2011).

There are many studies for using zinc oxide as a photocatalyst. (Shabnam, et al., 2015) synthesized nano zinc oxide used for photocatalytic removal of amoxicillin and sulfamethoxazole from contaminated water. (Rana and Hassan, 2019) used ZnO as the photocatalyst and ultraviolet (UV) light as a source for catalysts activation to degrade three contaminants involving ibuprofen (IBU), progesterone (PGS), and naproxen (NAP). (Vijaykumar and Raviraj, 2019) prepared nano zinc oxide without and with 5% barium for degradation pharmaceutical zidovudine drug.

In this work, zinc oxide nanopowder was prepared as a catalyst using two various methods; microemulsion and precipitation, and then were assessed by XRD, AFM, and FTIR. The innovation of the present work is evaluating the activity of synthetic zinc oxide as a photocatalyst for the degradation of ampicillin under visible light without doping other material or oxidant. Other studies apply UV or hydrogen peroxide for activated the catalyst. The effect of different parameters on the rate of photocatalytic degradation, such as the catalyst amount, exposure time to light, pH of the solution, and initial concentration of ampicillin, was studied.

## 2. EXPERIMENTAL WORK

### 2.1 Materials

Zinc sulfate heptahydrate [ $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ] was purchased from Fluka chemicals with an assay 99.5%. Ethanol and chloroform were supplied by Sigma-Aldrich, sodium lauryl ether sulfate (SLES) as a surfactant was supplied from the General Company for Vegetable Oils, Baghdad. Sodium hydroxide and sulfuric acid were used to adjust the pH of the solution. Ampicillin supplied by the pharmacy was used as a pollutant. Distilled water was utilized in this study.

### 2.2 Preparation of photocatalyst

#### 2.2.1 Microemulsion method for nano ZnO synthesis

Nano-sized zinc oxide was prepared in water employing the oil microemulsion method by the addition of water solution of zinc sulfate heptahydrate (5g of salt in 50ml distilled water) to the oil phase mixture, including 25ml ethanol, 25ml chloroform, and 2.5g sodium lauryl ether sulfate (SLES) as a surfactant. An aqueous solution of sodium hydroxide with 50ml (1M) as the precipitating agent was added dropwise, and the solution was stirred for 3h. The resulting mixture was left aside overnight. The solid was withdrawn by filtration and rinsed with distilled water until the pH reached 7. Finally, the sample was dried overnight at 120°C and then calcined at 400°C for 3h.

#### 2.2.2 Precipitation method for nano ZnO Synthesis

The aqueous solution of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  was prepared by dissolving 5g of heptahydrate zinc sulfate in 50 ml distilled water. Then, 50 ml of sodium hydroxide solution in a concentration of 1M was added dropwise to the prepared solution. The mixture was stirred persistently for three hours and left aside overnight. The resulting precipitate from the reaction was collected by filtration and washed many times with distilled water even pH reached 7. The collected precipitate after washing was dried overnight at 120°C for 24h to compose the precursors of zinc oxide. The sample was then calcined at a temperature of 400°C for 3h in a programmable furnace to obtain nano-sized zinc oxide powder.



### 2.3 Photocatalysis

The aqueous solution of antibiotics was made by dissolving a specified quantity of ampicillin in distilled water. It was prepared with ampicillin in a concentration of 70, 50, and 30 mg/L, respectively. These concentrations were chosen depending on previous works in the same field with a different photocatalyst. A 150 mL aqueous solution of ampicillin was put in a 250 mL beaker with the needed quantity of zinc oxide and was stirred by a magnetic stirrer. Adjusting of pH to the desired value was maintained by 1N H<sub>2</sub>SO<sub>4</sub> or 1N KOH. The mixture was kept in the dark for 60 min for adsorption. Subsequently, the mixture was exposed to light, and timing began. The origin of light was visible that was placed directly above the solution at a distance of 10cm from the sample. The samples were taken every hour using a syringe and filtered through filter paper to separate ZnO from the solution. The reaction stopped 5 hours later. The ampicillin concentration was measured by visible, ultraviolet spectrophotometer (Jenway model 6800) at its maximum wavelength of 260nm and then degradation was calculated via the formula below:

$$X\% = \frac{C_0 - C}{C_0} \times 100$$

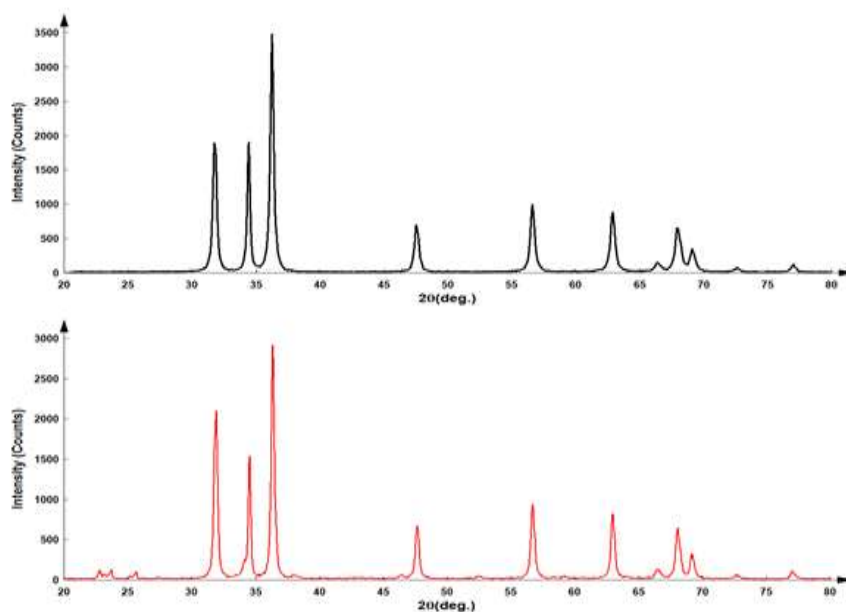
Where C<sub>0</sub> is the initial concentration, and C is the concentration at a specified time.

## 3. RESULTS AND DISCUSSIONS

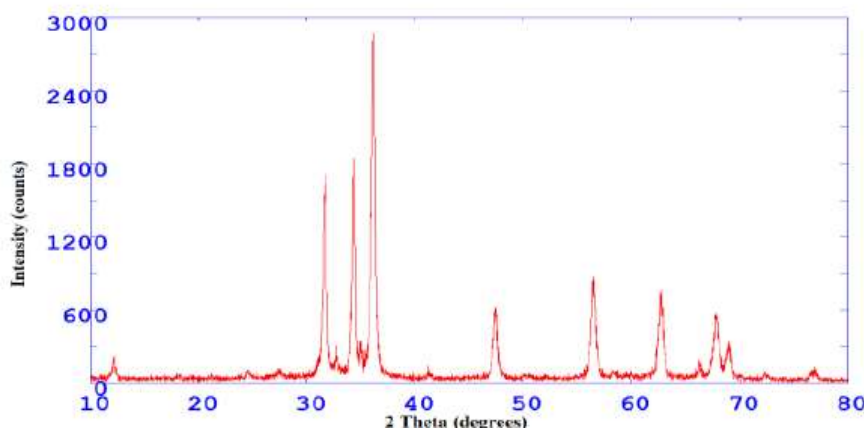
### 3.1 Photocatalyst Characterization

#### 3.1.1 X-ray diffraction analysis

X-ray diffraction (XRD) of the synthesized nano zinc oxide for powder prepared by the two methods was confined to a range of  $2\theta = 20-80^\circ$ , as illustrated in **Fig.1a** and compared with a standard one that appeared in **Fig.1b**. The obtained diffraction peak position was  $31.8^\circ$ ,  $34.45^\circ$ ,  $36.25^\circ$ ,  $47.55^\circ$ ,  $56.6^\circ$ ,  $62.9^\circ$ ,  $68.0^\circ$ , and  $69.1^\circ$  for the precipitation method and  $31.9^\circ$ ,  $34.55^\circ$ ,  $36.35^\circ$ ,  $47.65^\circ$ ,  $56.7^\circ$ ,  $62.95^\circ$ ,  $68.1^\circ$ , and  $69.15^\circ$  for the microemulsion method, which confirmed the hexagonal phase of ZnO.



**Figure1a.** XRD for synthesized nano ZnO (upper) precipitation method (lower) microemulsion method.



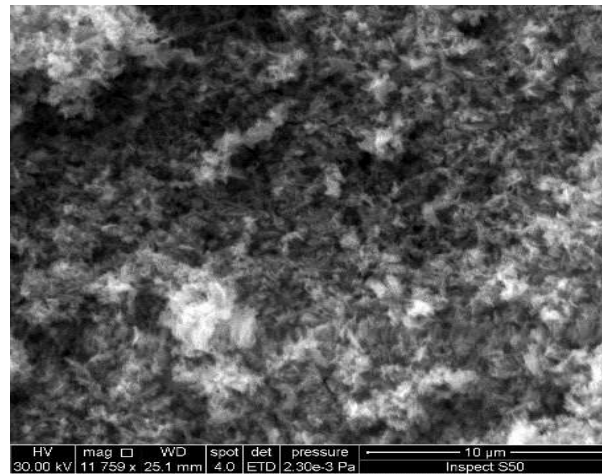
**Figure1b.** XRD for ZnO.

### 3.1.2 SEM image

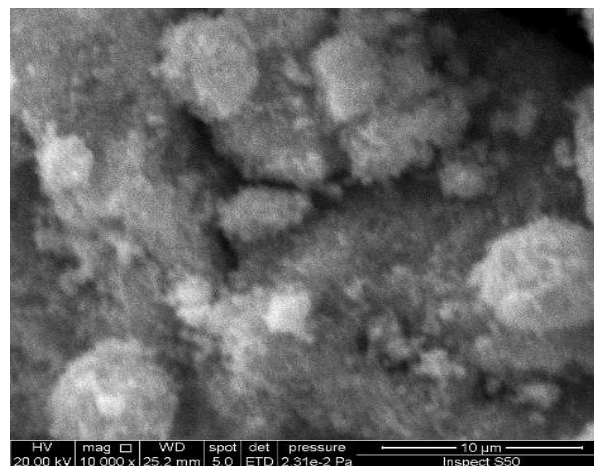
The morphology of the surface for zinc oxide nanopowder prepared by precipitation and microemulsion methods was obtained using SEM, as shown in **Fig. 2**. It shows the image of SEM for nano ZnO at several instances of magnification. It is important to mention that the image for the precipitation method showed the flake shape of the nanoparticles, and for the microemulsion method, it showed some semi-spherical particles. This means the preparation method affects the morphology and shape of particles. This agrees with (**Bodke, et al., 2018**) who found that ZnO prepared by two precipitation method gave different morphology



(a)



(b)



**Figure 2.** SEM image of nano ZnO (a) prepared by precipitation method (b) prepared by the microemulsion method.

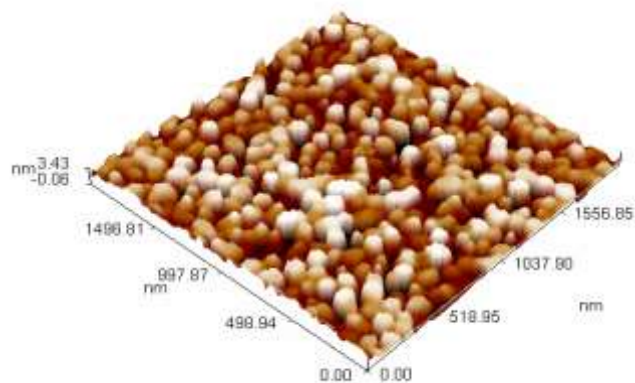
### 3.1.3 Atomic Force Microscopy (AFM)

The average particle diameter for prepared nano zinc oxide prepared by two methods was found to be 88.49nm and 69.15nm for microemulsion and precipitation methods, respectively. The particle size and morphology of the particles depend on the raw materials used and the molar ratio of water/surfactant (Kachbouri et al., 2018). This behavior agrees with (Jeyaseelan et al., 2010), who found The average particle size was found to increase with an increase in water to surfactant molar ratio and (Zhiguo et al., 2018). Figs. 3a and 3b show the AFM for three-dimensional surface profiles. Tables 1 and 2 show the results of AFM for precipitation and microemulsion method

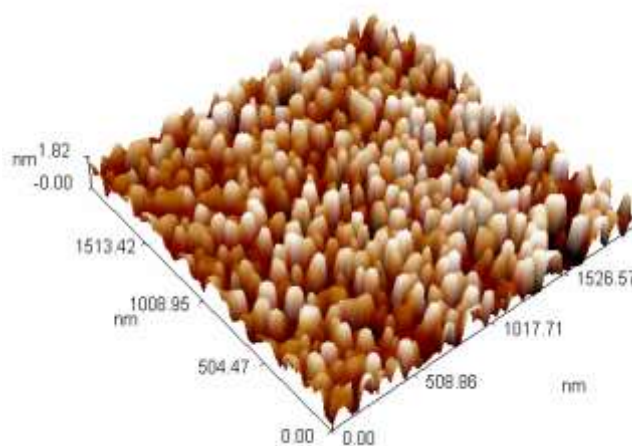




(a)



(b)



**Figure 3.** AFM for nano ZnO prepared (a) microemulsions method (b) precipitation method.

**Table 1.** Granularity Cumulation Distribution for precipitation method.

Diameter (nm)<	Volume(%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
15.00	0.46	0.46	60.00	8.05	37.93	105.00	5.29	94.02
20.00	0.46	0.92	65.00	8.51	46.44	110.00	2.53	96.55
25.00	1.38	2.30	70.00	6.44	52.87	115.00	1.38	97.93
30.00	2.53	4.83	75.00	7.59	60.46	120.00	0.92	98.85
35.00	1.84	6.67	80.00	6.21	66.67	125.00	0.46	99.31
40.00	4.83	11.49	85.00	5.75	72.41	130.00	0.46	99.77
45.00	4.60	16.09	90.00	4.60	77.01	135.00	0.23	100.00
50.00	5.29	21.38	95.00	6.21	83.22			
55.00	8.51	29.89	100.00	5.52	88.74			



**Table 2.** Granularity Cumulation Distribution for microemulsion method.

Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
40.00	0.60	0.60	70.00	2.40	14.97	95.00	7.78	53.29
45.00	1.20	1.80	75.00	5.99	20.96	100.00	14.97	68.26
55.00	2.99	4.79	80.00	7.19	28.14	105.00	16.77	85.03
60.00	4.79	9.58	85.00	9.58	37.72	110.00	10.78	95.81
65.00	2.99	12.57	90.00	7.78	45.51	115.00	4.19	100.00

### 3.1.4 Surface area

The BET surface area for the two nano ZnO samples was 16.369 m<sup>2</sup>/gm for that prepared by the microemulsion method and 20.028 m<sup>2</sup>/gm for the one prepared by precipitation method. These small values for surface area agree with the study conducted by (Wang et al., 2002), who obtained a surface area of 17.6 m<sup>2</sup>/gm by the precipitation method and also (Wei and Chang, 2008), who prepared nano ZnO with a surface area located within the range of 17.5 - 38.9m<sup>2</sup>/gm. The surface area is the crucial factor for the photodegradation of organic substrate. When the surface area of the photocatalyst is increased, the photodegradation of organic substrate increases. This is because the number of the active site increased by increasing the surface area (Azad and Gajanon, 2017).

### 3.1.5 Fourier Transforms Infrared Spectroscopy (FTIR)

FTIR measurement was evaluated in the range of 400 to 4000 cm<sup>-1</sup> wavenumber by employing the KBr method to promote the formulation of crystalline zinc oxide nanoparticles by microemulsion and precipitation methods, as illustrated in Figs. 4a and 4b. For the FTIR absorption spectra of zinc oxide nanoparticles prepared by precipitation method, a wide band of about 3426.2 cm<sup>-1</sup> was noticed, which normally occurs because of stretching and bonding patterns of (O-H) group. Absorption stretching of ZnO was observed at about 891.05 cm<sup>-1</sup> and the band at around 550 cm<sup>-1</sup> of the stretching pattern of zinc oxide (Bodke et al., 2018). For the type prepared by the microemulsion method, wideband appeared at about 3458.13cm<sup>-1</sup>, which occurs because of stretching and bonding patterns of (O-H) group. The band appearing from the absorption atmospheric CO<sub>2</sub> on the metallic cations was observed at about 1012.56 cm<sup>-1</sup>. Zinc oxide absorption stretching was detected at about 900.7 cm<sup>-1</sup>, and the band at 500 cm<sup>-1</sup> of the stretching pattern of zinc oxide (Drazin and Castro, 2016).

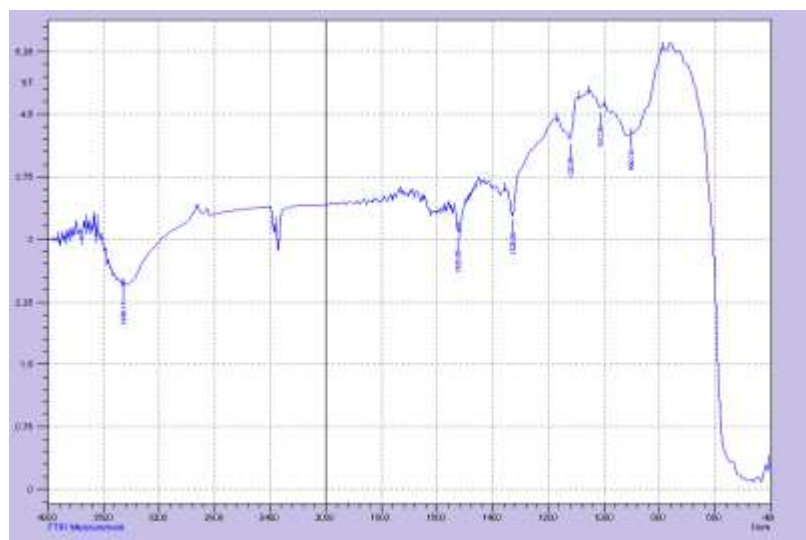




(a)



(b)



**Figure 4.** FTIR spectra of nano ZnO (a) precipitation method (b) microemulsion method.

### 3.2 Parameters affect photocatalytic degradation

#### 3.2.1 Effect of pH

As a result of the amphoteric characteristic of zinc oxide, an important parameter that induces the process of photocatalysis is the pH. The pH of the ampicillin solution influences the charges on the surface of the photocatalyst. The experiments took place at pH ranges of 5, 7, and 11, while ampicillin concentration and catalyst concentration were kept constant at 30ppm and 0.5g/l, respectively, for one hour. Photocatalytic degradation increased when the pH was changed from acidic to basic, as shown in **Fig. 5**. The degradation increased from 12% at pH 5 to 21% at pH 11. This was because both the substrate and catalyst have positive charges at acidic pH level, gathering limited forces between them, thereby decreasing substrate adsorption.

The degradation of antibiotics in alkaline conditions was high as a result of two reasons. First is the hydrolysis of the antibiotics by virtue of in stabilization of the  $\beta$ -lactam ring (is part of the core structure of several antibiotic families, the principal ones being



the penicillins, cephalosporins, carbapenems, and monobactams, which are, therefore, also called  $\beta$ -lactam antibiotics) at high pH as reported by (Elmolla and Chaudhuri, 2012), second is the existence of large amounts of  $\text{OH}^-$  ions on the surface of zinc oxide favoring the formation of  $\cdot\text{OH}$  radicals (Kansal, et al. 2007).

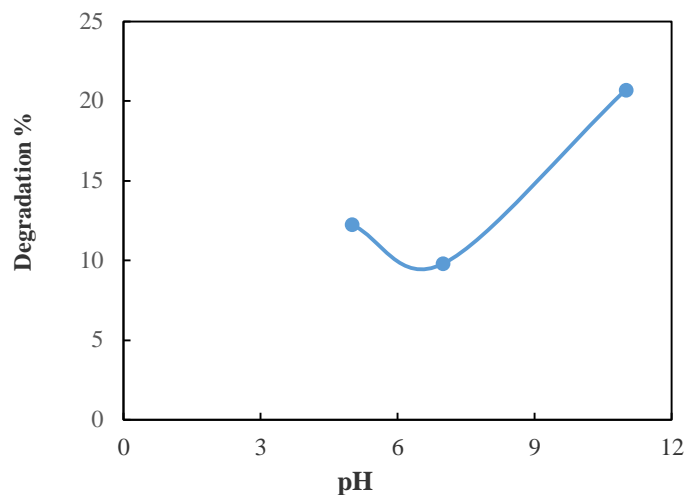


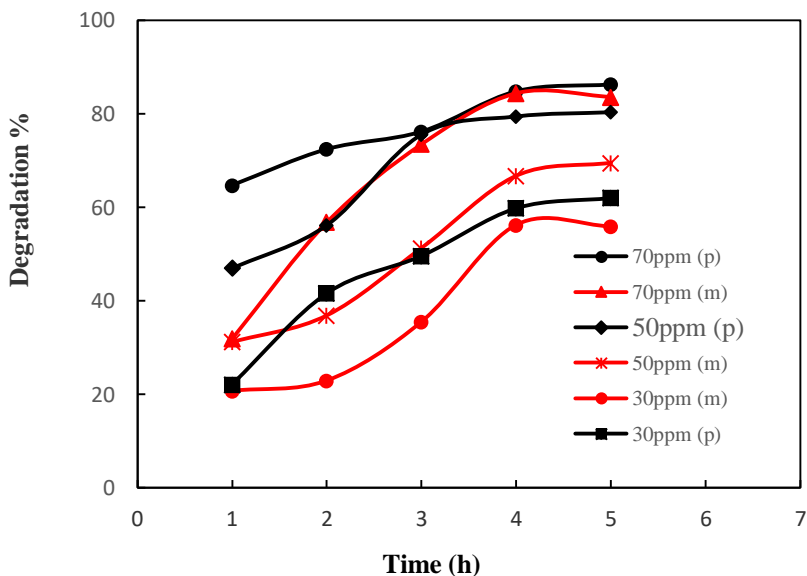
Figure 5. pH Effect on AMP degradation

### 3.2.2 Effect of initial ampicillin concentration

The initial amount of pollutant has an essential effect on the rate of degradation of photocatalytic reactions. The effect of different initial concentrations of ampicillin on photocatalytic degradation was considered using concentrations in the range between 30 and 70 ppm with catalyst concentration (ZnO) 0.5g/L at pH 11 of the solution and the results are illustrated in Fig.6.

It can be shown from the figure that when the concentration increased from 30ppm to 70ppm, the degradation was also found to increase from 60% to 85% after 4hr for the catalyst prepared by precipitation method and increased from 56% to 84% for the catalyst prepared by the microemulsion method. This behavior may be due to the hydrolysis of antibiotics. The hydrolysis reaction takes place through the attack of the nucleophilic  $\text{H}_2\text{O}$  to the  $\beta$ -lactam ring, followed by the opening of the ampicillin ring (Andreozzi et al., 2005). Similar results were obtained from the research conducted by (Nikravan, 2015), who found out that degradation increased with increasing concentration at a low level (less than 100ppm), while for a high-level 100ppm (more than 100ppm), the degradation decreased as the concentration increased.

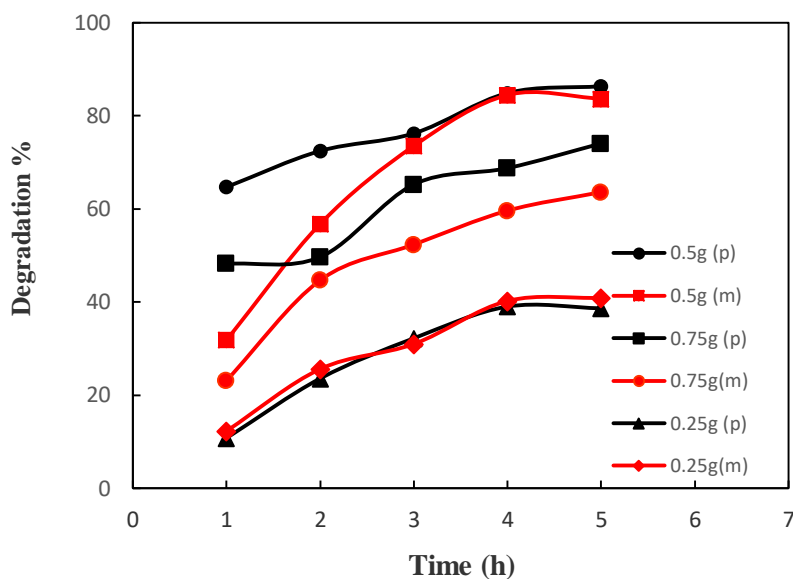
It can also be seen that when the time increased, the degradation of antibiotics increased. For example, at a concentration of 70ppm, it increased from 64% after 1h to reach 85% after 4h for the precipitation catalyst. The rate of degradation for the first 1h was rapid and then became slow. This is due to the fact that more  $\text{OH}$  radicals are generated at the beginning, but with increasing exposure time to light, a greater electron-hole reblending process occurs, which lowers the generation of  $\text{OH}$  radicals. Therefore, the ability of absorbed photons to generate the desired product becomes low as compared to the start of the process (Mills, et al., 2006).



**Figure 6.** Effect of the initial concentration of ampicillin on photocatalytic degradation at the operational condition: catalyst concentration 0.5g/L and solution pH 11 (p denotes to precipitation and m to microemulsion).

### 3.2.3 Effect of nano zinc oxide concentration

The effect of photocatalyst concentration on photocatalysis was studied by taking various concentrations of zinc oxide from 0.25g/L to 0.75g/L. The experimental conditions were ampicillin (AMP) concentration 70ppm, pH 11, and exposure time 5h, and the results are illustrated in **Fig.7**. The removal efficiency after 4h was 39, 85, and 69% for the precipitation method, and 40, 84, and 60% for the microemulsion method at ZnO concentrations 0.25, 0.5, and 0.75g/L, respectively. In general, changes in process conditions or preparation methods result in catalysts with different catalytic activity. As expected, the rate of photocatalysis was found to increase as the concentration increased, but is then reduced with the rise in the catalyst concentration. For 0.75g/L of ZnO, ampicillin degradation decreased, which may be because of unfavorable light dispersion and a decrease of light permeation into the solution with extreme photocatalyst (**Daneshvar, et al., 2004**).

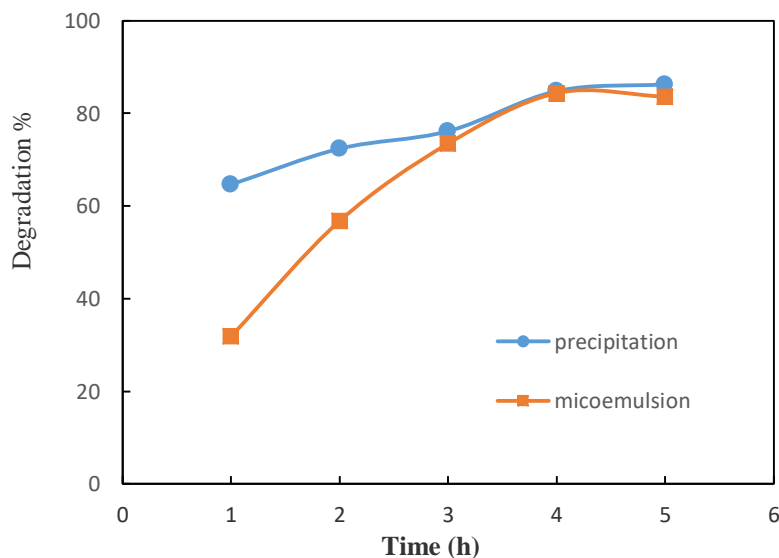


**Figure 7.** Effect of ZnO concentration on AMP degradation at the operational condition: ampicillin concentration 70ppm and solution pH 11 (p denotes to precipitation and m to microemulsion).

### 3.2.4 Comparison of photocatalytic activity of two types of ZnO

A comparative study of photocatalytic activity of nano zinc oxide prepared by microemulsion and precipitation was conducted. The results obtained are demonstrated in **Fig. 8** at parameters of ampicillin concentration being 70ppm, nano zinc oxide concentration being 0.5g/L, and pH of the solution being 11. Nano ZnO prepared by the precipitation method showed better efficiency as compared to that prepared by the microemulsion method. The removal was observed at 65% and 30% for precipitation and microemulsion methods, respectively, after 1h. The results obtained can be attributed to the particle size and morphology of the zinc oxide since they play a key role in the photocatalytic performance.

The sample prepared by the precipitation method exhibits the highest photocatalytic efficiency on the degradation of Ampicillin (AMP) under visible-light irradiation. The enhanced photocatalytic activity could be ascribed to the smaller particle size, higher surface area, and relatively stronger light absorption, which results in the adsorption of more AMP molecules, a shorter diffusion process of more photogenerated excitons, and a stronger oxidation ability of the photogenerated holes. This behavior agrees with (Difa et al., 2014), who prepared catalysts by different methods and compared them, and (Khizar et al., 2001), who prepared ZnO and used for degradation phenol.



**Figure 8.** Photocatalytic activity of two nano ZnO catalysts for photocatalytic removal of ampicillin.

#### 4. CONCLUSIONS

- 1- Nano ZnO synthesized by the precipitation method was found to be more active as a photocatalyst as compared to that synthesized by the microemulsion method employed in this study. This was due to the particle size for precipitation being smaller than that of the microemulsion. Therefore the surface area that received the pollutant was larger.
- 2- pH has a considerable influence on ampicillin degradation; therefore, the best value found was 11.
- 3- As the initial concentration of ampicillin increased, the percent degradation of ampicillin increased
- 3- Ampicillin degradation increased as the concentration of nano ZnO increased from 0.25g/L to 0.5g/L and then decreased when concentration increased to 0.75g/L, which was because of diminishing light permeation due to increasing turbidity.
- 4- The photocatalytic process is affected by some operational factors such as solution pH, initial concentration of ampicillin, and catalyst concentration. The optimum operating conditions were pH 11, initial concentration of 70ppm, and concentration of nano ZnO prepared by precipitation method as 0.5g/L, which gave 86% degradation.

#### NOMENCLATURES

- $C_0$  Initial Concentration  
 $C$  concentration after any time  
 $m$  Catalyst prepared by microemulsion  
 $P$  Catalyst prepared by precipitation  
 $X\%$  percentage of degradation



## REFERENCES

- Abdel Shafy H.I. and Mansour M.S.M., 2013b. Removal of selected pharmaceuticals from urine via Fenton reaction for agriculture reuse. *J. Sustain. Sanitation Practice*, 17, pp., 20-29.
- Andreozzi R., Canterino M., Marotta R., and Paxeus N., 2005. Antibiotic removal from wastewaters: the ozonation of amoxicillin. *J. Hazard. Mater.*, 122, pp., 243-250.
- Azad, K., and Gajanan, P., 2017. A review on the factors affecting the photocatalytic degradation of hazardous materials. *Material Sci & Eng Int J*, 1(3), pp. 106-114.
- Bodke M.R., Purushotham Y., and Dole B. N., 2018. Comparative study on zinc oxide nanocrystals synthesized by two precipitation methods. *Ceramica*, 64, pp. 91-96.
- Chen C.C., 2006. *J. Mol. Catal. A: Chem.*, 264, pp., 82–92.
- Daneshvar N., Salari D., and Khataee A.R., 2004. Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO<sub>2</sub>. *J. Photochem. Photobiol. A: Chem.*, 162, pp., 317–322.
- Difa X., Shaowen C., Jinfeng Z., Bei C., and Jiaguo Y., 2014. Effects of the preparation method on the structure and the visible-light photocatalytic activity of Ag<sub>2</sub>CrO<sub>4</sub>. *Beilstein J Nanotechnol.*, 5, pp. 658-666.
- Drazin J.W., and Castro R.H.R., 2016. *J. Am. Ceram. Soc.* 99, 1105.
- Elmolla E.S. and Chaudhuri M., 2012. Degradation of amoxicillin, ampicillin, and cloxacillin antibiotics in aqueous solution by Chem. Technol. *Biotechnology*, 87, pp., 643–650.
- Homem V., and Santos L., 2011. Degradation and removal methods of antibiotics from aqueous matrices—A review. *J. Environ. Manage.*, 92, pp., 2304–2347.
- Jeyaseelan C., Dong S.B., Muthiah B. and Jongryoul K. 2018, effect of water to surfactant ratio (R) on the particle size of MgAl<sub>2</sub>O<sub>4</sub> nanoparticles prepared via reverse micelle process, *Journal of Alloys and Compounds*, 491(1).
- Kachbouri S., Najib M., Elimame E., and Younes M. 2010, Tuning particle morphology of mesoporous silica nanoparticles for adsorption of dyes from aqueous solution, *Journal of Saudi Chemistry Society*, 22(4), pp. 405-415





- Kang H.K., Leem, J., Yoona, S.Y., and Sung H.J., 2012. *Nanoscale*. 6, pp., 2840-2846.
- Kansal S.K., Singh M., and Sud D., 2007. Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts. *J. Hazard. Mater.*, 141, pp., 581–590.
- Khizar H., Gondal M.A., Khaled M.M., Ahmed S., and Shemsi A.M., 2001. Nano ZnO synthesis by modified sol-gel method and its application in heterogeneous photocatalytic removal of phenol from water. *Applied Catalysis A: General*, 393, pp., 122-129.
- Kim J. H., Choi W. C., Kim H. Y., 2005. Preparation of mono-dispersed mixed metal oxide micro hollow spheres by homogeneous precipitation in a micro precipitator. *Powder Technol.*, 153, pp., 166-175
- Kumar S. S., 2012. Chemical Synthesis of Zinc Oxide Nanoparticles by Precipitation Method. *International Journal of Engineering and Technical Research*, pp., 1-4.
- Kuo T.J., Lin C.N., Kuo C.L., and Hung M.H., 2007. *Chem. Mater.*, 19, pp., 5143–5147.
- Lam S.M., Sin J.C., Abdullah A.Z., and Mohamed A.R., 2012. Degradation of wastewaters containing organic dyes photocatalyzed by zinc oxide: A review. *Desalin. Water Treat*, 41, pp., 131–169.
- Li W., Guo C., Su B., and Xu, J., 2012. Photodegradation of four fluoroquinolones compounds by titanium dioxide under simulated solar light irradiation. *J. Chem. Technol. Biotechnol.*, 87, pp., 643–650.
- Liu, B., and Zeng H. C., 2003. Hydrothermal synthesis of ZnO nanorods in the diameter regime of 50 nm. *J. Am. Chem.Soc.*, 125, pp., 4430-4431.
- Mai F.D., Lu C.S., Wu C.W., Huang C.H., Chen J.Y., and Chen C.C., 2008. *Sep. Purif. Technol.*, 62, pp., 423–436.
- Manuel A.H., Vides L.M., and Montero O.A., 2016. Sol-gel synthesis of zinc oxide nanoparticle at three different temperatures and its characterization via XRD, IR, and EPR. *Dyna rev. Fac. NAC. Minas*, 83.
- Mills A. Wang J., and Ollis D.F., 2006. *J. Catal.*, 243. pp., 1-6.



- Nikravan, A., 2015. Amoxicillin and ampicillin removal from wastewater by Fenton and photo-Fenton processes. *M.Sc. Thesis. Hacettepe University*.
- Okuyama K., and Lenggoro I. W., 2003. Preparation of nanoparticle via spray route (plenary paper). *Chem. Eng. Sci.*, 58, pp., 537-547.
- Pronin I. A., Kaneva N. V., Bozhinova A. S., Averin I. A., Papazova K. I., Dimitrov D. T., and Moshnikov V.A., 2014. Photocatalytic oxidation of pharmaceuticals on thin nanostructured zinc oxide films. *Kinetics and Catalysis*, 55, pp., 166-170.
- Rana, S., and Hassan, G., 2019. Photocatalytic degradation of pharmaceutical micropollutants using ZnO. *Environmental Science and Pollution Research*, pp., 1-9.
- Rataboul F., Nayral, C., and Casanova M. J., 2002. Synthesis and characterization of monodisperse zinc and zinc oxide nanoparticles from the organometallic precursor [Zn (C<sub>6</sub>H<sub>11</sub>)]. *J. Chem.*, 643/644, pp., 307-312.
- Sarkar D., Tikku S., Thapar V., Srinivasa R. S., and Khilar K.C., 2011. Formation of zinc oxide nanoparticles of different shapes in water-in-oil microemulsion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 381, pp., 123-129.
- Shabnam, P. Ali, M., Farzad, K., and Navid, A., 2015. Photocatalytic removal of two antibiotic compounds from aqueous solutions using ZnO nanoparticles. *Desalination and Water Treatment*, pp., 1-12.
- Tsuzuki T., and McCormick P.G., 2001. ZnO nanoparticles synthesised by mechanochemical processing. *Scripta Mater.*, 44, pp., 1731-1734.
- Vijaykumar, S. B., and Raviraj, M. K., 2019. Photocatalytic degradation of pharmaceutical drug zidovudine by undoped and 5 % barium doped zinc oxide nanoparticles during water treatment: synthesis and characterization. *International journal of applied pharmaceuticals*, 11, pp., 227-36.
- Viswanathan R., Lilly G. D., and Gale W.F., 2003. Formation of Zinc oxide-titanium dioxide composite nanoparticles in supercritical water. *Ind. Eng. Chem. Res.* 42, pp., 5535-5540.
- Wang Y.D., Ma CL, Sun XD, and Li HD, 2002. *Inorg. Chem. Commun.*, 5, p. 751.
- Wang, S., Dong, X., Dai, B., Pan, M., He, S., and Wang, J., 2015. Determination of V, Cr, Cu, As, and Pb ions in water and biological samples by combining ICP-MS with online preconcentration using impregnated resin. *JAOAC Int*, 98, pp., 218–224.



- Yang L.Y., Dong S.Y., Sun J.H., Feng J.L., Wu Q.H., and Sun SP, 2010. Microwave-assisted preparation, characterization, and photocatalytic properties of a dumbbell-shaped ZnO photocatalyst. *J. Hazard. Mater*, 179, pp., 438–443.
- Yu, L., 2013. The research on the photocatalytic performance of one kind of nano zinc oxide. *Advanced Materials Research*, 652-654, pp., 262-266.
- Zare M., Namratha K., Thakur M.S., and Byrappa K., 2019. Biocompatibility Assessment and Photocatalytic Activity of Bio-hydrothermal Synthesis of ZnO Nanoparticles by *Thymus vulgaris* Leaf Extract. *Materials Research Bulletin*, 109, pp., 49-59.
- Zhiguo W., Hongwei L., Fanghua T., Jinxia M., and Xiaofan Z., 2018. A Facile Approach for the Preparation of Nano-size Zinc Oxide in Water/Glycerol with Extremely Concentrated Zinc Sources. *Nanoscale Research Letters*, 13(202).