Metal Oxide Nanomaterials as Photo-Catalyst for Dye Degradation

Sayed M Saleh¹,²*

¹Chemistry Department, Science College, Qassim University, Buraidah, KSA
²Chemistry Branch, Department of Science and Mathematics, Faculty of Petroleum and Mining Engineering, Suez University, Egypt

*Corresponding author: Sayed M Saleh, Chemistry Department, Science College, Qassim University, Buraidah, KSA
Email: sayed.saleh@suezuniv.edu.eg, e.saleh@qu.edu.sa

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Abstract

One of the most important metal oxide nanoparticles, zinc oxide (ZnO) nanoparticles, were synthesized by a simple hydrothermal method. The synthesis ZnO nanorods were carried out using an organic solvent (methanol) and in the presence of hexadecyltrimethylammonium bromide (CTAB) as an organic additive. The size of the synthesized ZnO nanorods (around 100 nm in length and 10-15 nm diameter). The main point of this study is to investigate the influence of the ZnO nanocatalysts on the photocatalytic degradation of methylene blue (MB) dye. As-synthesized ZnO nanorods were characterized utilizing Transmission Electron Microscope (TEM), X-ray diffraction (XRD), Brunauer, Emmett, and Teller, (BET) and UV-Visible spectroscopic techniques. The XRD data analyses provide that ZnO nanorods have hexagonal crystalline structure. ZnO nanorods provide high photocatalytic activity on the degradation process of MB, a widespread water contaminant. The photocatalytic process was carried out under UV radiation. The influences of significant parameters as the adsorption efficiency of nanorods to MB molecules in dark, the nanocatalysts load, the initial dye concentration, cause substantial harm in the aquatic environment [1-3]. Also, these compounds cause color changes in the fresh water. Thus, the contamination can be detected easily as an indication for the existence of dye molecules in fresh water. These pollutant molecules prevent sunlight reach the aquatic plant and animal species and quenches the Photo-synthetically active radiation (PSA) in the ecosystem [4-7]. Methylene blue (MB) is one of the most applied dyes in industry. Additionally, this dye has been utilized in many manufactured products such as plastics, textile, paper and in many toxicology studies. Also, it has been provided as an indicator in clinical medicine and as an antidote in the treatment of methemoglobinemia. MB is an insignificant hazard material causes many dangerous effects such as eye irritation, anemia, nausea and vomiting [8]. Thus, treatment of contaminated water with MB dye is of noteworthy importance.

The wastes rising from textile manufacture, especially the dyeing process, have a substantial influence on the ecosystem, which change the physical properties of water and the sunlight access, and consequently, change the activity of photosynthetic processes and the gases solubility in water. Most of the water contamination based dye wastes may be attributed to the dyeing processes in textile manufacture [9,10]. Recently, several treatment routes were utilized in order to treat wastewater containing pigment or dye molecules as incineration, bio-treatment, ozonation, and adsorption processes based on solid adsorbents [11-14]. However, these methods show some disadvantages such as (i) production of toxic volatile constituents in incineration process; (ii) evolution of bad smell in biological treatment; and (iii) influence of significant parameters in the medium as pH, salt ions content, and temperature in ozonation process. For these important reasons, the metal oxide photocatalysis introduces an appropriate substitute for pigments and dye degradation. This developed technique has several advantages over other conventional techniques such as the dye degradation process ends with harmless final products [15,16]. However, biological decolorization is not a commonly effective technique for most of the azo dyes. Recently, metal oxide photocatalysis utilizing semiconductors such as zinc oxide has provided much attention cause its capability for dye degradation from wastewater [17,18]. This process helps to convert the composition of organic dyes entirely into H₂O, CO₂ and other non-

Keywords: Metal oxide; ZnO; Nanorods; Photocatalysts; Methylene blue; Photo-degradation

Introduction

Nowadays, Dyes and pigments are the most significant pollutants cause an extremely dangerous effect on water resources. Moreover, these organic materials, even with minimum concentration, cause substantial harm in the aquatic environment [1-3]. Also, these compounds cause color changes in the fresh water. Thus, the contamination can be detected easily as an indication for the existence of dye molecules in fresh water. These pollutant molecules prevent sunlight reach the aquatic plant and animal species and quenches the Photo-synthetically active radiation (PSA) in the ecosystem [4-7]. Methylene blue (MB) is one of the most applied dyes in industry. Additionally, this dye has been utilized in many manufactured products such as plastics, textile, paper and in many toxicology studies. Also, it has been provided as an indicator in clinical medicine and as an antidote in the treatment of methemoglobinemia. MB is an insignificant hazard material causes many dangerous effects such as eye irritation, anemia, nausea and vomiting [8]. Thus, treatment of contaminated water with MB dye is of noteworthy importance.

The wastes rising from textile manufacture, especially the dyeing process, have a substantial influence on the ecosystem, which change the physical properties of water and the sunlight access,
Among various photocatalysts, the semiconductor metal oxides, TiO$_2$, and ZnO are widely used in the degradation of organic pollutants because of their environmental feasibility, extreme photocatalytic activity, and simplicity of production [20,21]. The ZnO nanocatalysts have 3.37 eV band gap energy extreme exciton binding energy of approximately 60 meV [22] at room temperature. Thus, these type of semiconductor nanoparticles shows higher photocatalytic degradation proficiency with respect to other materials such as TiO$_2$ [23-25]. Additionally, ZnO nanomaterials are simply prepared, abundant and eco-friendly material. Therefore, these nanocatalysts were developed as a significant treatment tool in many environmental applications [26]. In the dye photocatalytic degradation process based ZnO nanomaterials, the energy of incident photons is higher than that of the energy of the band gap energy of the ZnO metal oxide. This energy has the attendance to generate photo-induced electron-hole pairs [27].

Several methodologies were developed in order to prepare ZnO nanomaterials with different shapes. We have obtained bundled nanowires grown on ZnO hexagonal disks, well-aligned ZnO whisker arrays. Many types of research have discussed the usage of organic additives to synthesis controlled and tuned nano-sized ZnO photocatalysis. Also, this can provide a smart tool for improving the adsorption efficiency of the as-synthesized nanomaterials and for controlling the removal of organic spicas at interfaces. Recently, several methods were developed to obtain hierarchical ZnO nanorod with hollow super-structures for Applying in many photocatalysis and photoluminescence applications based on a hydrothermal method using water-soluble biopolymer sodium carboxymethylcellulose (CMC) [28]. Moreover, Researchers used a hydrothermal route to prepare ZnO with a facile amino acid histidine to yield hierarchical architectures, such as prism-like, flowerlike structures and hollow microspheres. The resulting nanomaterials show precious photocatalytic activities [29]. These studies provided significant routes for controlling the morphology of ZnO nanomaterials.

In this work, we provide a simple route for synthesizing hierarchical ZnO nanostructure via methanol solvent based on the hydrothermal method and their significant application a photocatalyst. Solvent plays important roles in the formation and self-assembly of ZnO architectures. We have studied the photocatalytic degradation process of significant dye solution MB. The photocatalytic reaction is depending on the adsorption process of the UV radiation by the nanocatalysts, typically a semiconductor, which is zinc oxide ZnO. The benefit of this route is that no chemical compounds other than ZnO were presented in the medium solution to be treated after the degradation process of the MB dye pollutant. The Photocatalytic dye degradation process based ZnO nanomaterials is gradually providing an unconventional technology for the treatment of water pollution. The purpose of the current work is to introduce a fast, economical and eco-friendly solution to water treatment. Moreover, this study investigates the photocatalytic degradation of MB dye molecules using ZnO nanorods and their performance based on various parameters.

**Materials and Methods**

**Chemicals and reagents**

Zinc nitrate Zn(NO$_3$)$_2$·6H$_2$O, potassium hydroxide (KOH), methanol (CH$_3$OH), hydrochloric acid (HCl), sodium hydroxide (NaOH), methylene blue (C$_{16}$H$_{11}$N$_3$O$_2$SNa) as shown in Figure 1. and hexadecyltrimethylammonium bromide (CTAB), were purchased from Sigma Aldrich and with the highest purity and used as obtained.

![Figure 1: Chemical structure of methylene blue.](Image)

**Instruments**

A JEOL instrument (TEM, JEOL Inc., Tokyo, Japan) was utilized for collecting TEM images of the ZnO nanorods with adjustment of an acceleration voltage of 200 kV. The powder XRD patterns were executed using a Philips® diffractometer (type PW 1730) with Ni-filtered, Co radiation ($\lambda = 1.79$) at 30 kV and 20 mA. The specific area of the as-synthesized nanorods was determined utilizing, Brunauer, Emmett, and Teller, nitrogen adsorption method. This measurement was carried out using a Micrometrics instrument model ASAP 2010. The UV-visible recording spectrophotometer Shimadzu-Japan was used to detect the absorbance of light wavelengths.

**Synthesis of ZnO nanorods**

Synthesis of the ZnO nanorods was executed according to the following procedure, 20 mL of 1 M KOH was mixed with 100 mL of CH$_3$OH and the mixture was stirred for 10 min using magnetic stirrer, and then, 20 mL of 0.4 M Zn(NO$_3$)$_2$·6H$_2$O solution was mixed with the above solution. The mixture was stirred for 10 min, and then, 20 mL of the mixed solution was transferred to a Teflon-lined stainless-steel autoclave (25 mL capacity). The autoclave was firmly blocked. The autoclave transferred to furnace and the temperature was adjusted at 120 °C for 5 hrs. CTAB as an organic precursor was added to the resulting solution in order to monitor the morphology of the ZnO particles. After the reaction was finished, the autoclave was cooled down in air, and the white ZnO nanorods powder was centrifuged and washed several times with water and ethanol respectively.

**Photocatalytic degradation process**

The stock solution of MB dye aqueous solution 100 mL of given concentration was added to a definite amount of ZnO nanorods catalysts in a reaction tube manufactured from quartz. The mixture solution was kept in dark for 30 min in order to reach adsorption
equilibrium. The tube was exposed to a UV radiation lamp. The mixture of photocatalysts and dye was stirred and concurrently purged with a current of air. A solution portions were withdrawn at consistent intervals of 5min. Before investigation of dye degradation process, the collected portions were centrifuged at 4000 rpm for 10min to remove all nanocatalysts from solution. The UV-spectra of the clear supernatants were measured at 669nm [30].

**Results and Discussion**

**Characterization of nanomaterials**

![Figure 2: TEM image of the ZnO nanospheres synthesized using methanol as solvent.](image)

The morphology of zinc oxide nanorods structure is acquired by using methanol as solvent. Figure 2 provides the distinctive TEM images of the synthesized ZnO nanorods. The particles are lentic with a length of 100nm and an approximate diameter of ZnO nanorods is about 10-15nm. the typical SAED pattern with intense rounded circles related to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes confirm that the resulting ZnO nanorods are extremely hexagonal crystalline. Moreover, the small particle size and the large surface area to volume ratio of the ZnO nanorods, these could promote the aggregation of ZnO nanorods. Thereby, they are applied in the photocatalytic degradation of Methylene Blue (MB). The BET analysis was applied to measure the specific surface area of the synthesized nanorods. Data of the BET analysis provided a specific surface area of 62.8m²/g and total pore volume 0.18cm³/g [31].

**X-ray powder diffraction patterns of ZnO nanorods**

The ZnO nanorods were characterized using in term of crystal structure using X-ray diffraction (XRD). The patterns were detected within a 2θ range of 20-80° with a scanning step of 0.01° (Figure 3). the XRD data analyses show high coincidence with the JCPDS file of ZnO, which can be referred to as a hexagonal phase. The absence of any impurities peak indicates the high purity of the nanoparticles. Furthermore, the sharpness of the diffraction peaks indicates that the synthesized nanorods have an extraordinary crystal structure. The sharp peaks related to the planes (100), (002) and (101), showing a clear randomness orientation of ZnO nanorods [32].

![Figure 3: XRD patterns of the ZnO nanorods.](image)

**Absorption spectra measurements**

Methylene blue exhibit characteristic absorption peaks. These peaks centered at 292 and 664nm respectively. In the presence of the nanocatalysts (ZnO nanorods), a considerable dramatic decrement in 664nm band is detected under UV radiation. This attributes to the photocatalytic degradation of MB based on the ZnO nanorods as an efficient photocatalyst (as shown in Figure 4a). Also, the ratiometric absorbance of the MB versus time was plotted in Figure 4b and indicated that the degradation process of MB dye professionally carried out in presence of ZnO nanorods within only 1 hour. For more investigations, the absorption spectra of MB with time was collected at 664nm using ZnO nanorods in darkness. The dye shows high stability in absence of UV radiation, and the degradation process doesn't take place efficiently (see Figure 4c). the data analysis exhibited that the surface adsorption of the MB to the surface of the ZnO nanorods is stabilized after 5min under regular stirring of the mixture in darkness and no more degradation occurs. So, in all degradations experiments to confirm achievement of adsorption equilibrium, the mixture was stirred in darkness for 10min.
Influence of ZnO nanorods load on the degradation process

The influence of the concentration of photocatalyst was investigated. Firstly, the photo-degradation process of the dye was studied in presence of ZnO nanorods in dark as shown in Figure 5a. The percent of the dye adsorption in presence of different concentrations of ZnO nanorods within a time range of [0 to 70 min] was detected. Thus, this will investigate the adsorption effect of the dye molecules (adsorbate) to the surface of the ZnO nanorods (adsorbent). Secondly, the same experiment was carried out under such conditions but under UV radiation (Figure 5b). Memorable, the degradation percent of the MB dye molecules were calculated by subtracting the degradation (adsorption) percent in dark at the same exposure time. In both cases, the degradation percent is directly proportional to the ZnO nanorods load within the range of (25-150 mg) and then decreases with increment the photocatalysts load. This may be attributed to increasing the active sites of the photocatalyst nanorods with increasing the concentration where the carriers easily reach the surface to participate in photoactivity. Also, the small the crystallite size enhances the probability of charge recombination outside the barrier region [33]. But, with the further increment of photocatalyst concentration (100-150 mg), the aggregation of the nanomaterials takes place. Thus, the photons can’t find their way to the surface of the nanorods and most of the active surface suites are blocked.

![Figure 4](image-url)  
(a) Absorbance spectra of methylene blue in the presence of ZnO photocatalyst nanorods using 100 mg/L ZnO nanospheres, MB 20 mg/L;  
(b) Ratiometric absorption spectra versus time at a wavelength of 664 nm under UV radiation;  
(c) Degradation of MB in presence of ZnO nanorods and in darkness.

![Figure 5](image-url)  
(a) Plots of removal percent as a function of MB degradation versus Time (min). (a) degradation process in presence of ZnO nanorods and absence of UV radiation; (b) in presence of ZnO and under UV radiation.
Effect of methylene blue concentration

In order to investigate the initial concentration of methylene blue dye on the photodegradation process, the degradation process was carried out in presence of a definite amount of ZnO nanocatalysts with varying the initial concentration of MB within range of (20 to 120mg/L) during a time of (70min). The results are given in Figure 6a. The data analysis proved that the degradation of MB was significantly affected by enhancing the initial concentration of MB dye. This can be referred to the decreasing of the active sites densities on the surface of the nanorods. Thereby, the amount of produced hydroxyl radicals decreases and this could decrease the performance of the photocatalytic process. On the other hand, increase the number of MB dye molecules also reduce the photon path length that entering the MB stock solution. Figure 6b exhibits the relation between the removal efficiency of the degradation process against the initial concentrations of methylene blue after 60min exposure time. While increase the initial concentration of MB, the dye particles can absorb a significant extent of light radiation larger than the nanocatalysts [34] and this can also affect the proficiency of the degradation process [35,36]. Thus, the proper initial concentration of MB dye concentration was selected to be 20 mg/L for all experiments.

![Image](a) ![Image](b)

Figure 6: (a) Initial concentration influence on dye degradation process, the concentration of ZnO nanospheres of 100mg/L and time 70min, (b) effect of initial concentrations of MB on the removal efficiency at time 60min.

Influence of stirring

![Image](a)

Figure 7: Influence of stirring effect on the efficiency of MB degradation during time 70min, the initial dye concentration of 10mg/mL and 100mg/L ZnO nanorods concentration.

In order to investigate the effect of stirring on the rate of degradation of the MB dye based ZnO nanorods photocatalysts, some experiments were investigated under optimum conditions such as 100mg/L ZnO nanorods, 20mg/L Mb and of time 70min. The data introduced in Figure 7. The data show that the rate of degradation of MB in presence of nanocatalysts increases in presence of stirring the reaction mixture. Firstly, the increase in stirring solution increases the total dissolved oxygen exists between the solution layers. Hence, the additional dissolved oxygen has an important influence on the production of hydroxyl radicals. Memorable, stirring the solution to quench the equilibrium time by enhancing the rate of diffusion of the MB molecules to the nanocatalysts surface [37].

Influence of calcination on the optical activity of ZnO nanorods

![Image](a)

Figure 8: Effect of calcination temperatures on the degradation of MB dye. 100mg/L photocatalysts, MB 10mg/L, time 40min.

Different temperatures within the range of 300 to 500 were applied to investigate the influence of calcination temperature on the photoactivity of the ZnO nanorods. The data was introduced in Figure 8. The results analysis show that increasing the calcination
temperatures enhances the photoactivity of the nanorods on MB degradation process. The maximum activity was shown at 450 °C. Moreover, after this calcination point, the photoactivity of the calcined ZnO nanorods starts to quench. This could be attributed to the presence of organic additives residual carbon on the surface of the nanorods which decreases the photoactivity process [38]. At 450 °C, the complete burning takes place, and the percent of ZnO in the sample reached a maximum value.

**Kinetic study of the photocatalytic degradation of MB based on ZnO nanorods**

The kinetics of photocatalytic degradation of MB under UV irradiation was investigated. It is found that the degradation kinetics pursues the pseudo-first-order reaction and follows the following equation [39]:

$$\ln \left( \frac{C_0}{C_t} \right) = k t$$

Where

- $k$: rate constant of the dye degradation,
- $C_0$: initial concentration of the MB dye solution,
- $C_t$: concentration of MB at equilibrium time $t$.

Using MB initial concentration of 20mg/L and varying photocatalyst loads, plots of $\ln \left( \frac{C_0}{C_t} \right)$ versus $t$ (min) offered in Figure 9. The data analysis provides linear relations with $R^2$ (correlation coefficients) with an average value of 0.978 for the ZnO nanorods photocatalysts. This proves the confirmatory of the pseudo-first-order reaction kinetic model form ethylene blue photocatalytic degradation. The pseudo-first-order reaction postulated that one reactant should exist in large excess, thus the participation of this reactant remains unchanged during the kinetic detection process. Therefore, the deviation exists in Figure 9 refers to one of the reactants doesn’t exist inadequately large excess.

### Table 1: Photocatalytic degradation rate constant ($k$) for methylene blue under UV radiation.

| Catalyst load (mg/L) | 25  | 50  | 75  | 100 | 125 | 150 |
|---------------------|-----|-----|-----|-----|-----|-----|
| $K_{rate\,const.} \times 10^{-3}$ min$^{-1}$ | 14.4 | 27.9 | 34.7 | 58.6 | 20.2 | 16.2 |

The photocatalytic process shows highest activity with 100mg/L ZnO nanorods load, thereby $\ln \left( \frac{C_0}{C_t} \right)$ versus time (min) was plotted with varying the initial concentrations of methylene blue dye in order to study the effect of the second reactants (MB) on the degradation process Figure 10. The data analysis provides linear relations with a correlation coefficient ($R^2$) of 0.98. It was noticed that photocatalytic degradation rate of dye quenches with the increasing the dye concentration within a range of (20 to 120mg/L). The rate constant values of the degradation process were calculated and presented in Table 1 as well as figured out in Figure 10.

### Figure 9: The relation of $\ln \left( \frac{C_0}{C_t} \right)$ as a function of time utilizing MB of 20mg/L and monitoring catalyst load concentration within range (25 to 150mg/L).

### Figure 10: The relation of $\ln \left( \frac{C_0}{C_t} \right)$ as a function of time utilizing nanocatalyst concentration of 20mg/L and monitoring MB initial concentration within range (25 to 150mg/L).

**Conclusion**

Herein, ZnO nanorods photocatalyst were synthesized by hydrothermal methods and were characterized in terms of morphology and size by utilizing XRD, TEM, and BET. Photocatalyst synthesized by hydrothermal method had hexagonal crystalline structure. The photocatalytic activity of ZnO nanorods was investigated utilizing degradation of MB dye. The efficiency of the MB degradation process enhances with an increase in the amount of ZnO photocatalyst up to 100mg/L and then decreases with an over-loading concentration of photocatalyst than 100mg/L. However, with a constant photocatalyst concentration, the efficiency of the degradation process...
process decreases with increase MB dye concentration. By utilizing an initial concentration MB of 20mg/L, maximum degradations of MB under UV radiation at 1h was 98.28 % under stirring in the air atmosphere. The degradation process follows pseudo-first-order reaction kinetics, this resembled a rate constant of 58.6 × 10⁻² mol/L.min⁻¹. This study provides an economy eco-friendly solution to water treatment problem.

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