PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE DYE BY ZINC OXIDE NANOPARTICLES OBTAINED FROM GREEN METHOD

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TÓM TẮT

NGHIÊN CỨU HOẠT TÍNH QUANG XÚC TÁC PHÂN HỦY METHYLEN XANH CỦA VẬT LIỆU ZnO KÍCH THƯỚC NANO TỔNG HỢP THEO PHƯƠNG PHÁP HÓA HỌC XANH

Trong nghiên cứu này chúng tôi tổng hợp vật liệu ZnO kích thước nano bằng phương pháp hóa học xanh: nhiệt phân trực tiếp $Zn(CH_3COO)_2$ ở các nhiệt độ 450, 550, 650, 750^{0}C, không sử dụng các dung môi độc hại. Vật liệu nano ZnO được đặc trưng bằng các phương pháp phân tích hóa lý XRD,TEM. Kết quả cho thấy hạt ZnO có cấu trúc lục phương wurtzite, kích thước tinh thể lần lượt là 33, 36, 38 and 42 nm, hình thái vật liệu thay đổi từ dạng hình que sang dạng hình cầu khi tăng nhiệt độ nung. Vật liệu nano ZnO được ứng dụng làm chất xúc tác quang phân hủy chất màu xanh methylen dưới ánh sáng đèn UV. Kết quả cho thấy khả năng phân hủy chất màu methylen xanh phụ thuộc theo thời gian chiếu đèn UV, kích thước và hình thái của vật liệu nano ZnO. Hiệu suất phân hủy methylen xanh cao nhất là mẫu ZnO nano tổng hợp ở nhiệt độ 750^{0}C đạt được là hơn 95% sau 40 phút chiếu đèn UV. Quá trình phân hủy quang xúc tác chất màu methylen xanh tuân theo phương trình động học phân hủy bậc một với hằng số tốc độ k lần lượt là 0,0512, 0,0636, 0,1077 và 0,1286 phút^{-1} tương ứng với mẫu nano ZnO tổng hợp ở các nhiệt độ 450, 550, 650, 750^{0}C.

Keywords: *Photocatalytic, Zinc oxide, nanoparticles, green method.*

1. INTRODUCTION

Every year, textile industry generates a huge amount of organic dyes in its wastewater, resulting in serious impacts on the environment. Therefore, it is essential to remove them from wastewater. Numerous different technologies have been applied to remove organic dyes in wastewater such as adsorption, co-precipitation, advanced oxidation process (AOP), ozonation, membrane filtration, and biological methods. In particular, AOP is noticeable because it could quickly remove various types of dyes. Among AOP techniques, the technique of using heterogeneous photocatalytic catalyst is gaining attention as it is able to remove not only organic dyes but also many different organic pollutants [1-3].

ZnO is a semiconductor with broad band gap ennergy (3.3 eV) and n-type conductivity. In addition, it is very common in nature and environmentally friendly. That is the reason

why ZnO is considered as a very promising material for many different applications such as making solar cells, photocatalysts, electrical equipment, and gas sensors [2]. In the recent years, researchers have focused on synthesizing nano-size ZnO materials, a good semiconductor photocatalyst, for dye removal. ZnO nanomaterials can be synthesized using different methods including electrochemical precipitation, sol-gel method, microwave method, hydrothermal method, laser cutting method and precipitation method [4,5]. In this study, ZnO nanoparticles were synthesized by a green method without adding any chemical solvents. The material was characterized and tested for photocatalytic activity.

2. EXPERIMENTAL

2.1. Materials and method

In a typical procedure the amount of 3g zinc acetate dihydrate ($Zn(Ac)_2 \cdot 2H_2O$) was grinded in a agate mortar. The samples were then transferred to closed porcelain crucible and left in an oven (Nabertherm, Germany) for thermal decomposition at different temperatures of 450^0C, 550^0C, 650^0C, and 750^0C winthin 4 hours with the temperature increasing rate of 10^0/min. The samples were alowed to cool down to room temperature and grinded in the agate mortar to obtain the final ZnO nanoparticles. Obtained products were named as ZnO-450, ZnO-550, ZnO-650 and ZnO-750, respectively [5].

2.2. Characterization methods

The structure properties of the ZnO nanoparticles were determined by X-ray diffraction (XRD, Bruker D8 advanced X-ray diffractometer) with Cu Kα radiation (λ = 1.54 Å) and scan rate 0.02 s^{-1}. During the analysis the samples were scanned from 20° to 70°. Morphology of ZnO nanoparticles was analyzed by transmission electron microscope (TEM), JEOL JEM-1010. Absorbance measurements were carried out using UV Vis-spectrophotometer (Agilent 8453).

2.3. Photocatalytic study

The potential application of ZnO nanoparticles towards the treatment of dye in wastewaters was tested in heterogeneous photocatalysis route. Methylene blue (MB) was used to evaluate the photocatalytic efficiency of the ZnO nanoparticles. Photocatalytic reaction was carried out in a homemade photoreactor equipped with a Osram 250W, high pressure mercury lamp as a source for near-UV radiation. The reactor consists of a Pyrex glass beaker and a magnetic stirring. The lamp was positioned above the beaker. The distance between the lamp and the Pyrex glass beaker was 20 cm. The whole photocatalytic reactor was insulated in a box to prevent the escape of harmful radition. In each experiment, 0.1 g of a prepared ZnO nanoparticles was dispersed in 100 mL of an aquesous solution of MB 10 mg/L. Prior to UV light illumination, the suspension was magnetically stirred in the dark for 30 min for proper homogeneity of the photocatalyst as well as to maintain the absorption-desorption equilibrium. At definite time intervals, 4 mL of the suspension solution was collected and followed by centrifugation at 5000 rpm for 10 min in order to remove the ZnO nanoparticles suspensions from the solution. Each sample was finally analyzed to record UV–vis spectrum through a UV-vis spectrophotometer at the λ_{max} of 664 nm wavelength (Agilent 8453) [6]. The percentage of photocatalytic degradation was calculated using the equation:

$$Percentage\ photodegardation = \frac{A_0 - A}{A_0} \times 100$$

The rate constant of the degradation, k was obtained from the first-order plot according to the equation: $ln\frac{A_0}{A} = kt$

where, A_o = initial absorbance of dye and A = absorbance of dye solution after UV light irradiation [5].

3. RESULTS AND DISCUSSION

3.1. Characterization of ZnO nanoparticles

The XRD patterns of the prepared materilas were shown in Figure 1. The XRD peaks located at angles (2θ) of 31.8°, 34.4°, 36.2°, 47.5°, 56.6°, 62.8°, 66.3°, 68.1°, and 69.3° correspond to the (100), (002), (101), (102),

(110), (103), (200), (112), and (201) planes of ZnO nanoparticles, respectively. The standard diffraction peaks showed the hexagonal wurtzite structure of ZnO nanoparticles. The presence of (100), (002), and (101) planes in XRD patterns indicates the formation of highly pure ZnO nanoparticles. Further more, none of the peaks for impurities was observed. Strong intensity and narrow width of ZnO diffraction peaks suggests that the meterials were well crystalline. Results reveal that the characteristic peaks of the synthesized nanoparticles are completely identical to those from the JCPDS data (Card No. 36-1451) [7].

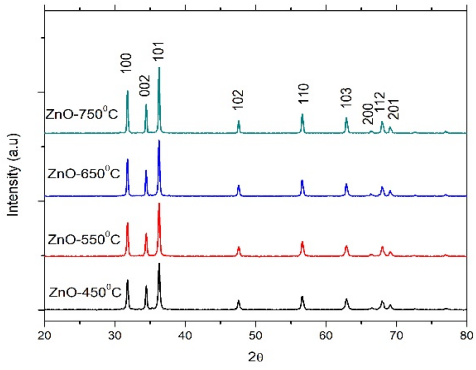

Figure 1. XRD patterns of the nanocrystalline ZnO samples thermally decomposed at 450, 550, 650 and 750^{0}C for 4h

The crystallite size of the nanoparticles was calculated from the peak broadening of diffraction peaks using Debye–Scherer formula $D = \frac{k\lambda}{\beta cos\theta}$, where D is crystallite size, k is constant (0.89), λ= 0.154 nm represents the wavelength of X-ray radiation, β is the full width at half maximum of diffraction peaks (FWHM) in radian, and θ is the Bragg's angle [1]. The size of the crystallites of ZnO nanoparticles was evaluated by measuring the FWHM of the most intense peak (101) because it has a relatively strong intensity and do not overlap with the other diffraction peaks. Approximately, the average crystallite size of ZnO-450 is of 33nm while those of ZnO-550, ZnO-650 and ZnO-750 are of 36, 38 and 42 nm, respectively. The elevated surface energies at higher calcination temperatures may be responsible for the increasing of the crystallite size. Similar phenomenon was also reported in former studies [5]. The surface morphology and size of ZnO nanoparticles were imaged using transmission electron microscopic (TEM) analysis (Figure 2). Both spherical like (diameters of 40-100nm) and rod-like (diameters of 50-200nm and lengths of 200-500nm) ZnO nanoparticles were obtained. Calcination temperatures seem to dramatically affect the morphology of the nanoparticles formed. At the temperature of 450^{o}C, the rod-like particles are predominant. Nevertheless, more spherical like particles are formed as the temperatures raised.

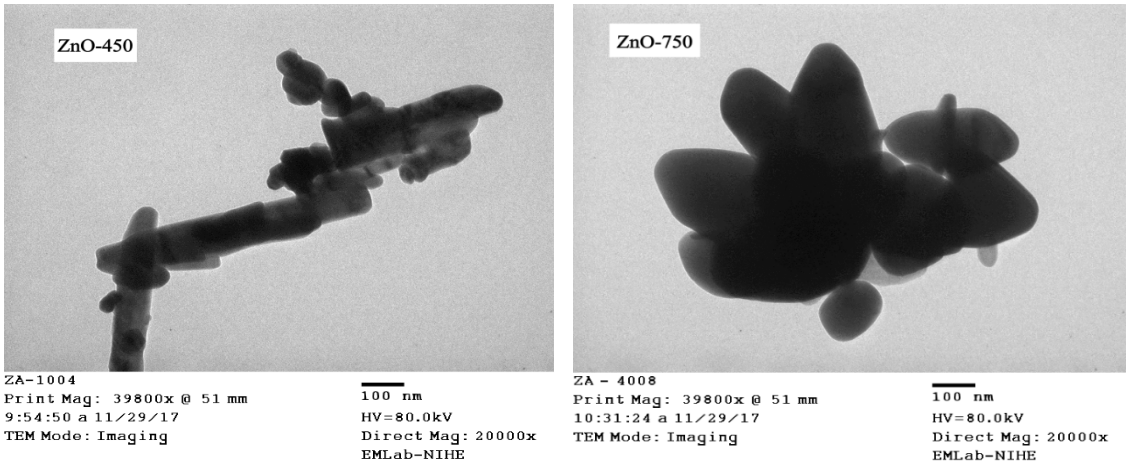

Figure 2. TEM images of the ZnO nanoparticles thermally decomposed at 450 and 750^{0}C

3.2. Photocatalytic properties

In order to demonstrate the potential application for the removal of organic dyes from wastewater, the photocatalytic activities of the obtained ZnO nanoparticles were investigated in the photocatalytic degradations of methylene blue dye. Figure 3 shows the absorption spectra of the degration of the methylene blue under UV light by ZnO nanoparticles. Decrease in absorbance intensity at 664 nm clearly confirms that ZnO nanoparticles are acting as photocatalyst for the degradation of dye.

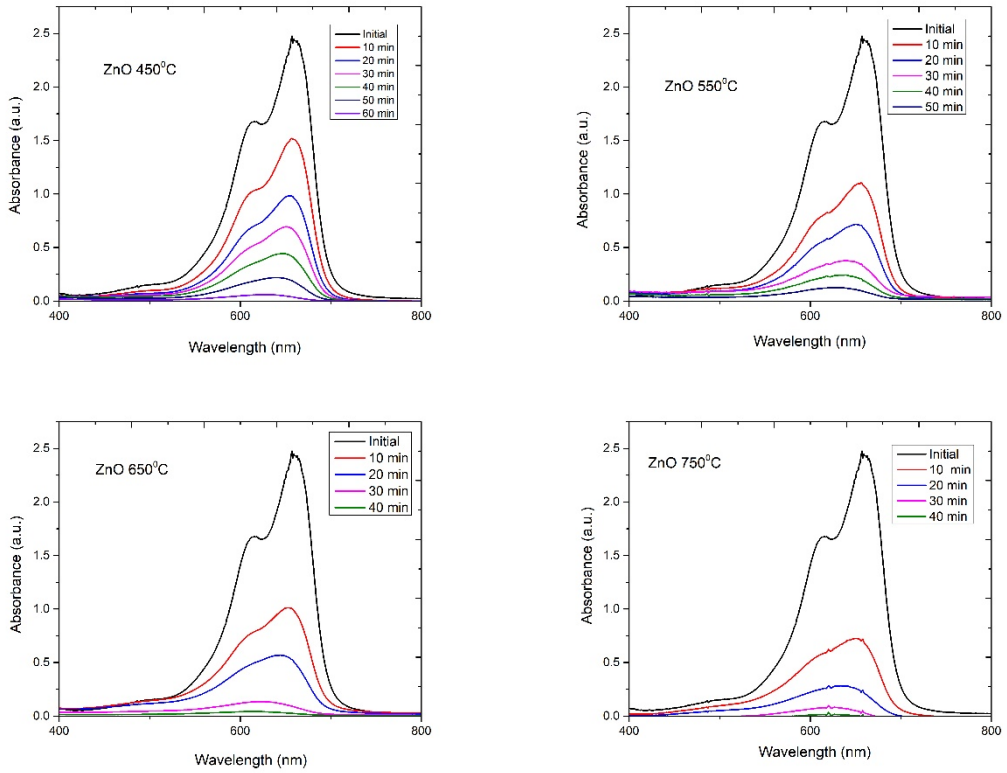

Figure 3. UV–Vis absorbance spectra of methylene blue solution exposure to UV light in the presence of the ZnO nanoparticles thermally decomposed at 450, 550, 650 and 750^{0}C

The ZnO nano particles synthesized at higher temperatures tend to yield higher removal efficiencies. Figure 4 shows that the best degradation efficiency can be achieved with the ZnO-650 and ZnO-750 (aprroximately 100% winthin 40 min). This can be explained as a results of the morphology and size modifications when changing calcinattion temperature. While insignificant changes in size were observed, morphology could act as a potential factor strongly influencing the final degradation efficiency. Saravanan et al. reported that spherical-shaped ZnO samples show higher removal efficiency compared with the spindle-and rod-shaped ZnO samples [9]. The kinetic study for the degradation of methylene blue was studied using Langmuir–Hinshelwood Kinetic model: $ln\frac{A_o}{A} = kt$; where, A_o = initial absorbance of dye and A = absorbance of dye solution after UV light irradiation, k is Pseudo first order rate constant [6].

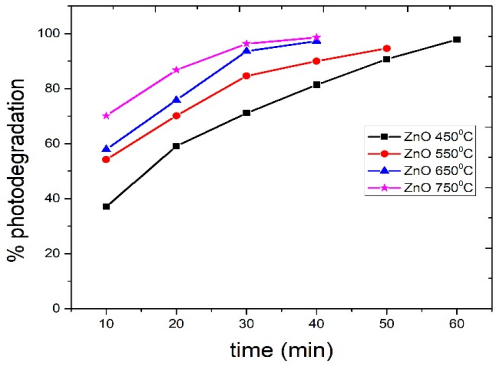

Figure 4. Percentage degradation of methylene blue dye vs irradiation time in the presence of the ZnO nanoparticles thermally decomposed at 450, 550, 650 and 750^{0}C

A plot of $ln\frac{A_0}{A}$ versus t is shown in Figure 5. Photocatalytic activity occurs as a result of the interaction of photocatalyst and UV irradiation that yields highly reactive hydroxyl radicals, which are believed to be the main species responsible for the oxidation.

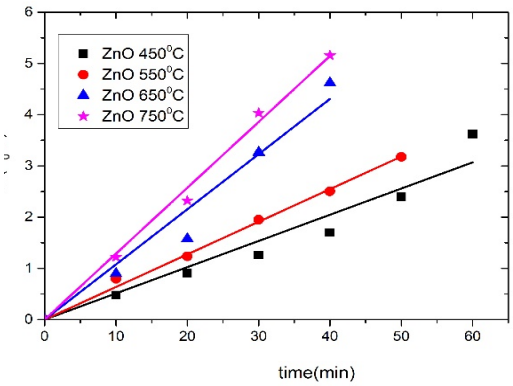

Figure 5. Kinetic plot of ln(A_0/A) vs irradiation time of the ZnO nanoparticles thermally decomposed at 450, 550, 650 and 750^{0}C

Langmuir–Hinshelwood rate expression has been successfully used for heterogeneous photocatalytic degradation to determine the relationship between the initial degradation rate and the initial concentration of the organic substrate [1,9]. The linear plots and relatively high R^2 values (Table 1) proved that the degradation of methylene blue dye obeys the first order reaction kinetics.

Table 1: Rate constant for photo degradation of methylene blue dye

Samples	Rare (min^{-1})	Adj.R^2
ZnO 450^{0}C	0.0512	0.9740
ZnO 550^{0}C	0.0636	0.9984
ZnO 650^{0}C	0.1077	0.9835
ZnO 750^{0}C	0.1286	0.9990

4. CONCLUSION

ZnO nanomaterials were sucessfully generated by a green method, thermal-decomposition of zinc acetate precursor at different temperatures of 450, 550, 650, 750^{0}C. Results reveals wurtzite hexagonal structure of the materials with the crystal sizes of 33, 36, 38 and 42 nm, respectively. The material morphology changes from the rod-like shapes to the spherical-like shapes when increasing decomposition temperature.

ZnO nanomaterials were applied as photocatalyst to decompose methylene blue under UV light. The ability to decompose methylene blue depends on the UV illumination time, the size and morphology of ZnO nanomaterials. The highest methylene blue decomposition is obtained with the ZnO-750. More than 95% of the dye was removed after 40 minutes. Photocatalytic decomposition process of green methylene follows the first order reaction. The reaction rate constants corespoding to the removal process of ZnO-450, ZnO-550, ZnO-650 and ZnO-750 are 0.0512, 0.0636, 0.1077 and 0.1286 min^{-1}, respectively.

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