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Synthesis of ZnO nanoparticles for photodegradation of clofibrate acid as organic pollutant

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***Abstract*---**Zinc oxide nanoparticles (ZnO NPs) is unique studied semiconductor substance for photocatalytic utilization like light-emitting diodes, solar cells, photo-diode, sensor, and photo-detector. The ZnO nanoparticles ratio of surface to volume as increases with reduces size and afford an increase to improve the reactivity of the surface. Among all the possible approaches for the ZnO nanoparticles preparation, the sol-gel process is individual and simple for the synthesis of metal oxides nanoparticles. ZnO NPs was synthesized by the sol-gel approach and characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), x-ray diffraction (XRD), and UV-visible spectroscopy techniques for structural and morphological investigations. The obtained SEM, AFM and XRD experimental findings showed the spherical shapes of ZnO NPs. The purpose of the current investigation was to prepare ZnO NPs via the sol-gel technique for utilization as a photo-catalyst for the organic pollutant namely clofibrate acid photodegradation below the irradiation of UV light. The rate of photodegradation of clofibrate acid enhanced with the additional loading of ZnO NPs. The entirely degradation of the clofibrate acid had been recognized. The as-prepared ZnO NPs have the ability to completely degrade to a high beginning concentration up to 30 mg/L within 5 h of the irradiation period. The photolysis efficiency of clofibrate acid by ZnO NPs was up to 95% and complete removal was performed.

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Introduction

Semiconducting photocatalytic materials such as ZnO and TiO_2 have been widely used for the complete destruction and mining of hazardous organic compounds in water, soil and air over the past few decades [1]. Due to their unique qualities such as non-toxicity, chemical stability, high catalytic activity, and low cost, catalysts based on zinc oxide and titanium dioxide are frequently used to decompose hazardous organic compounds in both aqueous and gaseous phases [2]. Several related agencies in recent years have expressed interest in using renewable energy and energy-saving initiatives in wastewater treatment in order to mitigate the current environmental challenge. A key aspect is the manufacture and use of the photocatalyst during the project. The photocatalysis used for photodegradation were semiconducting metal oxides such as titanium dioxide, zinc oxide, and copper oxide, which are acceptable for process in the environment [3]. ZnO has received a lot of attention due to its ability to detoxify the environment. ZnO material [4] has a broad bandgap (3.3 eV), [5] strong photosensitivity, and stability [6]. Several investigations have noted that the results of ZnO as a photocatalyst are superior to those of TiO2, which is the most widely used photocatalyst. Despite the fact that these semiconductors have almost the same energy bandgap, [7] it was shown that TiO2 absorbs a higher proportion of solar radiation. Moreover, ZnO has great thermal stability at ambient temperature [9] and is inexpensive. ZnO is a viable semiconductor for photocatalytic decomposition due to its diverse properties and investigations by other scientists [10]. Relatively homogeneous deposition [11], hydrothermal synthesis [12], microwave radiation [13], melt heat [14], sol-gel technology [15] and liquid chemical synthesis [16] are some of the techniques that have been used for zinc oxide synthesis. In the current investigation, a sol-gel technique was utilized for the preparation of zinc oxide nanoparticles, as this process is easy, ready, inexpensive, which offers great purity performance outcomes with low-temperature necessary for the preparation technique. The catalytic performance of a synthetic catalyst was investigated in-depth concerning its photocatalytic performance in the photodegradation of clofibrate acid.

Materials and Methods

Chemicals

All of the basic materials were purchased from Suka Chemicals (M) Sdn Bhd, Shah Alam, Selangor, Malaysia. Materials that used to synthesis ZnO NPs were zinc nitrate, citric acid, ethylene glycol and deionized water. The Clofibric Acid solution is used as a pollutant for its removal under UV illumination.

Instruments

Scanning Electron Microscope (SEM) (FEI Type: Inspect-S50, University Industry Research Laboratory, Universiti Teknologi Malaysia, Johor, Malaysia) and Atomic Force Microscopy (AFM) (Bruker Multimode 8 AFM, Nano-Analytical Platform, Monash University, Bandar Sunway, Malaysia) were utilized in this study and were used to investigate the morphological properties of the ZnO NPs. Absorption properties of the prepared samples were carried out and recorded by Perkin Elmer Lambda 650 UV-Vis Spectroscopy, All of the prepared nanomaterial structures were investigated by X-ray diffraction pattern (XRD) (PanAnalytical, Type: ExperQt Pro, University Industry Research Laboratory, Universiti Teknologi Malaysia, Johor, Malaysia).

Synthesis of ZnO NPs

Initially, a zinc nitrate solution was prepared by dissolving a certain amount of zinc nitrate in 25 ml ethylene glycol and deionized water. The same steps were repeated for preparing the citric acid solution at the same time as the previous one. Thus, we got two separated solutions of 0.4 M concentration each. After the dissolution was complete, the citric acid solution was added to the nitrate solution. Then, the mixture was left stirring at 80 C for 4 continuous hours and a homogeneous solution was obtained. The next step was cooling the solution gradually in air down to the room temperature for 24 continuous hours. Finally, a tube furnace was used to place the sample in and annealing it for 2 hours at 700 ^{o}C

Evaluation of Photocatalytic Activity of Clofibric Acid

In this study a photocatalytic reactor was used complemented with UV radiation to perform the photolysis experiments at room temperature and pH 6.3. Clofibric acid pollutant was used as an aqueous solution for the purpose of pollutant removal under UV rays illumination. Which is considered a dangerous pollutant in water and its deterioration to safety levels is considered a challenging task for researchers at the present time due to its resistance to chemical and biological deterioration. 50 mg of ZnO, TiO2, and ZnO-TiO2 catalytic NPs were added and the mixture was stirred for half an hour in the dark to reach the adsorption equilibrium at each type of catalyst. In the next step, the resulting mixture was placed inside the reactor at a distance of 4 cm from the UV lamp, then it has been covered with a dark box to prevent leakage of UV radiation. Samples obtained from the mixture were analyzed with a UV-Vis spectrophotometer.

Results and Discussion

X-ray Diffraction (XRD) of ZnO NPs

X-ray diffraction have been utilized to study the crystallinity type in materials employed in addition to knowing if the variation (if any) occurred through the doped of ZnO. Figure 1, shows the XRD pattern of ZnO NPs, the appeared peaks for zincite type of ZnO. Figure 1 which represents the XRD Pattern analysis of the prepared ZnO nanocomposite sample. Between 20° and 80°, there are eleven diffraction peaks. At 2 = 36.4°, the strongest distinctive peak was discovered. The peak is classified as wurtzite depending on phase identification analysis. The intensity of distinctive peaks altered the crystallographic structure of the particles, according to Burton [17]. Because there are no major peaks in the XRD pattern that can be connected to contaminants, the XRD data confirmed that the synthesis process used in this work is effective in creating pure ZnO photocatalyst.

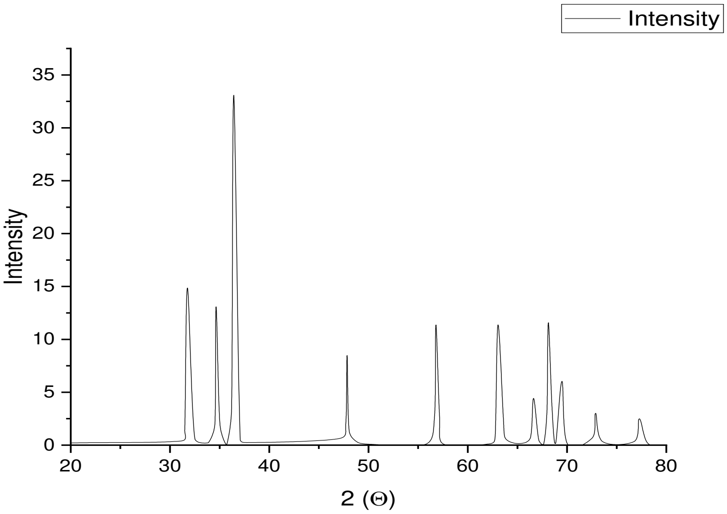

Figure 1. XRD pattern ZnO NPs

Surface Morphology Analysis

The Micrographs of ZnO generated using the sol-gel technique is shown in Figure 2. Figure 2 shows spherical morphology of ZnO, as well as ones in a broad rode form. It was also discovered that particle production in nanostructures is not well-ordered. Some nanoparticles are large and spherical, while others are tiny. The particle size range for ZnO is 10 to 150 nm. The vast variety of particle sizes could be related to crystallite development. The size of the particles will be affected by the formation of crystallite on the surface of ZnO. As a result, the chemical composition used to synthesise ZnO played a significant impact in determining the size of the ZnO formed.

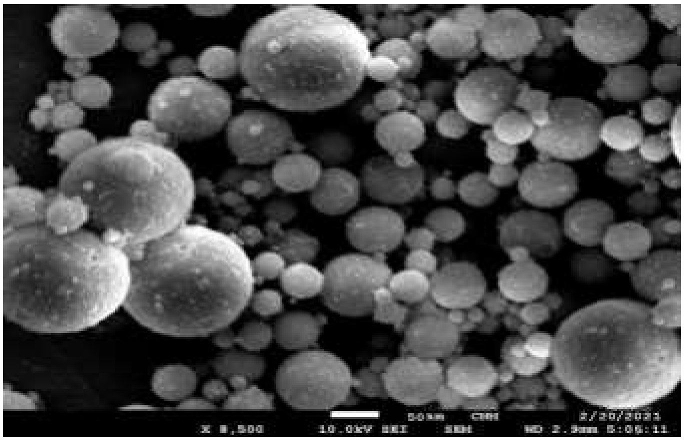

Figure 2, The SEM image of ZnO nanoparticles

AFM spectroscopy was used to analyze the surface morphology of the synthesized ZnO-NPs, and the 3D images and plot of the micro-accumulation distributions of ZnO-NPs are shown in Figs 3(a) and 3(b)(b). The images show that the ZnO particles are distributed in a semi-uniform manner and tend to aggregate into larger particle sizes, with an average size of 100 nm, as shown in the grain distribution diagram.

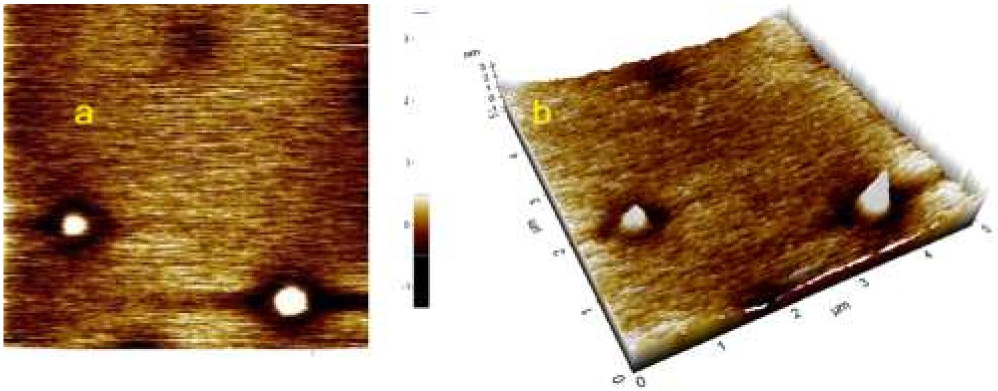

Figure 3, AFM images of ZnO nanoparticles

Photodegradation

UV-Vis spectroscopy instrument was applied to evaluate the clofibrate acid concentration as in Figure 4. Standard concentrations of clofibrate acid at various periods 0.0-120 minutes were utilized to evaluate the λ_{max} (highest wavelength), it is observed that the highest wavelength of clofibrate acid is 447 nm as presented in Figure 4 [18]. The achieved clofibrate acid removal was 85 and 95% after 120 minutes of illumination time (T1), 94 % when using 5 mole % of ZnO after 75 and 120 minutes of UV illumination. The calibration curve was determined by outlining the various periods versus their absorbance at λ_{max}=447 nm for all utilized concentrations as presented in Figures 5 and 6. The absorbance of any specimen of clofibrate acid before and after degradation was reported at 447nm and analyzed with calibration curve to evaluate the concentration of clofibrate acid [19]. After 2 hours of exposure, the clofibrate acid removal achieved 31.52 in presence of ZnO [20], in presence of 5 mol%. In absence of photocatalyst, there is no photocatalytic reaction. Also, there is no significant degradation when the dye mixture was kept in dark for 24 hours. It has been taking a very long time of reaction to degrade the pollutant under visible light illumination in comparing to the required time under UV illumination.

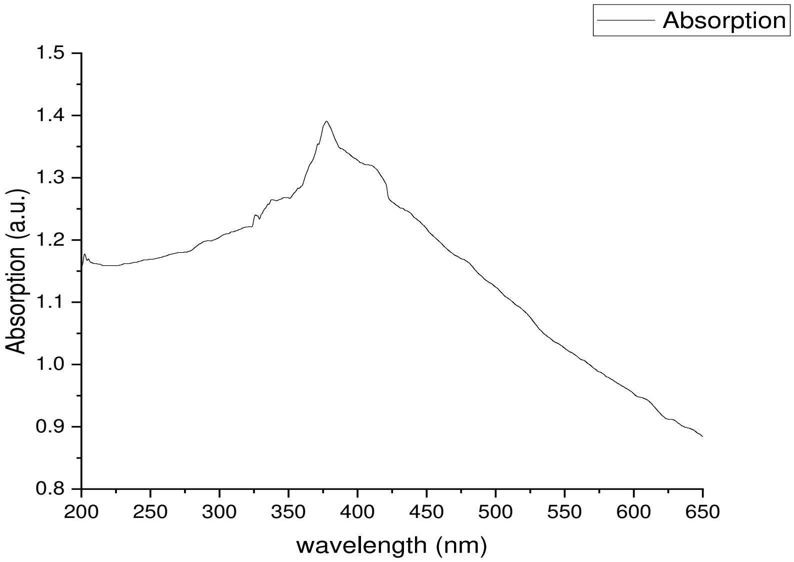

Figure 4, UV-Vis spectrum of ZnO nanoparticles

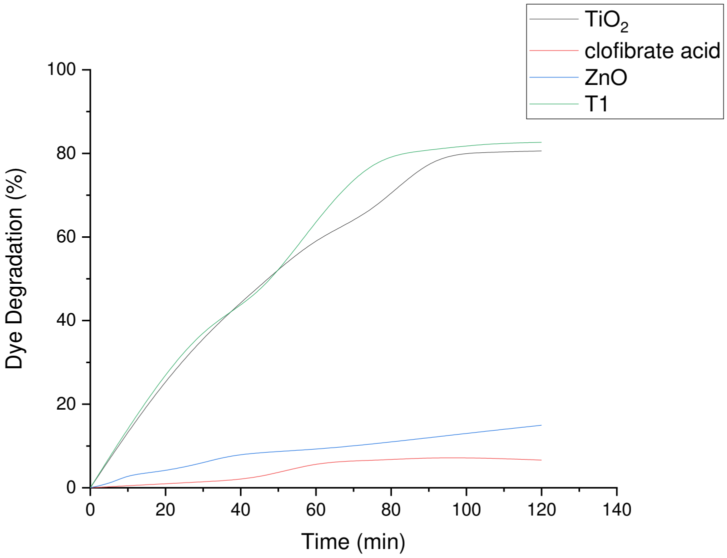

Figure 5. Degrication of clofibrate acid using deferent time of irradiation in presence of ZnO NPs

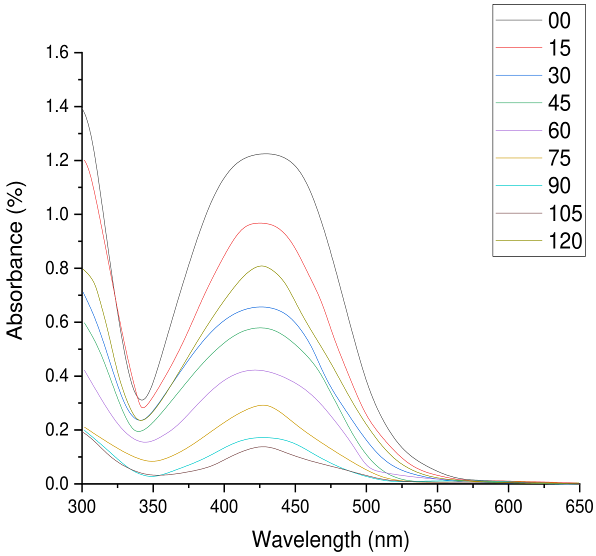

Figure 6. Degridation in sunlight of clofibrate acid in presence of ZnO NPs

Conclusion

The sol-gel approach was used to successfully produce ZnO photocatalyst. The resulting particles have a circular morphology with varying diameters. ZnO has a size range of 10 nm to 150 nm. In the photocatalytic degradation of clofibrate acid, the produced ZnO demonstrated improved photocatalytic properties. Within 0 -140 minutes of reaction, the photodegradation rate of clofibrate acid is related directly to the catalyst loading. Clofibrate acid can be completely degraded using zinc oxide. The quickest degradation was accomplished by increasing the amount of ZnO NPs and adjusting the circumstances. Sol-gel produced ZnO NPs can completely disintegrate a greater concentration of clofibrate acid, with a clearance efficiency of 95% after a minute reaction.

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