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Efficiency of Low-Ag-Content Biosynthesized ZnO/Ag on Photodegradation of Paracetamol

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Photocatalysis technology is gaining interest as an alternative wastewater treatment due to its fast and complete pollutants removal advantages. It utilizes light energy and semiconductor catalysts to degrade organic pollutants such as paracetamol (PCM), a common household medication drug. Pharmaceutical wastewater may cause significant hazards to humans and the environment if no advanced treatment is applied. In this study, zinc oxide/silver (ZnO/Ag) nanocomposite was biosynthesized using banana peel extract (BPE) and low Ag content (1 mM and 3 mM) as biomaterial via sol-gel and precipitation for photocatalytic degradation of PCM. Fourier Transform Infrared Spectrophotometer (FTIR) analysis showed a sharp peak of Zn-O band for all catalysts with the success of BPE incorporation. The band gap energy of ZnO/Ag was 3.281 eV, increasing with Ag content. Field Emission Scanning Electron Microscope (FESEM) images of ZnO/Ag exhibit a smaller size of 29.49 nm and a distinct spherical shape. The uniform shape of biosynthesized ZnO/Ag confirms the roles of BPE as stabilizing and capping agents. The highest photocatalytic degradation of PCM was 76% with a reaction constant of 0.0086 min^{-1} when ZnO/Ag was used as a catalyst, compared to the pristine ZnO was 70%. The as-prepared ZnO/Ag nanocomposite from organic solid waste has a high potential for being reutilized as an advanced catalyst for pharmaceutical wastewater treatment.

1. Introduction

Emerging contaminants such as pharmaceuticals, hormones, pesticides, and personal care products in water and wastewater are significantly hazardous to humans and the environment. Among the emerging contaminants, pharmaceutical waste is frequently and highly detected in drinking, surface, and wastewater due to its high demand, production, and uses. Overdosage of pharmaceutical waste in water may lead to antibiotic resistance and endocrine disruption (Shipingana et al., 2022). In addition, wastewater containing pharmaceutical waste is only partially removed by conventional treatment systems (Nassiri Koopaei and Abdollahi, 2017). Conventional treatment includes adsorption, biodegradation, flocculation, and sedimentation techniques. Paracetamol (PCM) is an over-the-counter (OTC) drug that does not need a prescription from a medical expert. It is commonly available in each household for fever and pain relief. Hence, advanced and complete removal treatment would require removing these pollutants from water. For instance, a superior removal of over 98% of PCM was achieved via photocatalysis (Mohamed Isa et al., 2021) while only 60% removal was performed using the conventional activated carbon adsorption technique (Streit et al., 2021). Advanced oxidation processes (AOPs) are gaining interest in generating reactive oxidant species (ROS) to degrade organic pollutants. Hydrogen peroxide-based, photocatalysis, ozone-based, photolysis, and Fenton-based are AOPs for treating organic pollutants. Photocatalysis promotes complete degradation and mineralization by utilizing light energy and catalyst to remove organic water pollutants such as textile dyes (Ahmad et al., 2022) and pharmaceutical waste (Thang et al., 2021). Photocatalysis reaction initiates with the photocatalyst receiving light energy greater than its band gap energy. Then, the photoexcited electron will jump from the valence band (VB) to the conduction band (CB), producing electron (e^-) – holes (h^+) pairs to produce radical species by reacting with hydroxide ion,

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water, and oxygen (Al-Gharibi et al., 2021). Subsequently, the radical species degraded the targeted organic pollutants to form water (H_2O), carbon dioxide (CO_2), and by-products. Nevertheless, photocatalyst synthesis and performance still have significant limitations in photocatalysis reactions. Zinc oxide (ZnO) is an n-type semiconductor suitable for the catalyst in the photocatalytic reaction. Still, the fast rate in electron – holes pairs in ZnO are not favorable due to the low degradation rate of targeted organic pollutants (Ramasamy et al., 2021). ZnO modification with silver (ZnO/Ag) doping is a promising nanocomposite that may improve the drawbacks. Even so, the concentration of Ag in the nanocomposite plays a vital role in the photocatalytic reaction, with major studies using high concentrations for photodegradation activities. As a chemical and physical synthesis alternative, the biosynthesis technique employs biomaterials in the synthesis method, promoting environmental-friendly conditions and sustainability compared to the conventional techniques (El-Desouky et al., 2022). Waste materials such as banana peel extract (BPE), rich in phenolic contents, are suitable for biosynthesis techniques (Abdullah et al., 2021). Studies on biosynthesized ZnO/Ag from waste materials for photocatalytic treatment of pharmaceutical wastewater are still lacking. In this present study, the biosynthesized ZnO/Ag using BPE with low Ag content of 1 mM and 3 mM was synthesized and characterized for photocatalytic degradation of PCM.

2. Materials and methods

2.1 Materials

Fresh bananas were collected from a local farm in Malaysia. Silver nitrate ($AgNO_3$) was purchased from Fisher Scientific. Sodium hydroxide (NaOH) and zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) were purchased from Sigma Aldrich. OTC paracetamol (Panadol, paracetamol 500 mg) was purchased from a pharmacy.

2.2 Biosynthesis of ZnO/Ag

The banana peel (BP) was washed with tap water and then deionized water to remove any dirt and impurities before being dried for one day. The dried BP was mixed with deionized water at a 1:10 ratio (m/v) under continuous stirring for 1 h. Then, $Zn(NO_3)_2{\cdot}6H_2O$ was dissolved with banana peel extract (BPE) at 80 °C before being calcined at 600 °C for 1 h. The product was collected and named BPE/ZnO. A similar procedure was repeated by replacing BPE with deionized water and named ZnO. Several amounts of BPE/ZnO were then dispersed and sonicated in 1 mM and 3 mM of $AgNO_3$ and denoted as Z1A and Z3A. Then, 20 mL of BPE and 10 mL of NaOH were mixed with the solution at 60 °C until precipitates appeared. The final product of ZnO and ZnO/Ag was centrifuged and washed with deionized water before being dried overnight.

2.3 Characterization

The diffuse reflectance spectra (DRS) and absorbance were analysed using Shimadzu UV-2600 spectrophotometer. The Fourier Transform Infrared Spectrophotometer (FTIR) spectra were studied using JASCO (FT/IR-6800) from 399 – 4000 cm^{-1}. The prepared biosynthesized ZnO/Ag morphological analysis was studied using Field Emission Scanning Electron Microscope (FESEM) SU-8020 operating at 10 kV.

2.4 Photodegradation of paracetamol

The photodegradation of paracetamol (PCM) was assisted using UVC light irradiation with synthesized ZnO, BPE/ZnO, Z1A, and Z3A as the catalyst. The reaction suspension was designed by mixing and sonicating 0.1 g of each catalyst with 100 mL of 20 ppm PCM solution (pH 6) in a photoreactor at room temperature. The mixture was continuously stirred for 30 min in the dark to achieve adsorption-desorption equilibrium. Then, 36 Watt light was turned on for 3 h, and every 10 min, the samples were collected and centrifuged. Then, the absorbance was recorded with reference to the maximum absorbance of PCM at 243 nm using a spectrophotometer. The photodegradation percentage of PCM and rate constant by the Langmuir-Hinshelwood model were calculated using Eq(1) and Eq(2).

$$\textbf{Percentage Degradation}\ (\%) = \frac{\mathbf{C_0 - C}}{\mathbf{C_0}} \times \mathbf{100}\% \tag{1}$$

$$\mathbf{ln}\left(\frac{\mathbf{C_0}}{\mathbf{C}}\right) = \mathbf{k_{apps} t} \tag{2}$$

where C_0, C, k_{apps}, and t are the initial concentration, final concentration, first-order kinetic rate constant, and reaction time.

3. Results and discussions

3.1 FTIR analysis

The identification of functional groups in the synthesized catalyst was analyzed using FTIR. Figure 1 shows the FTIR spectra of BPE/ZnO, Z1A, and Z3A within 400 – 3,600 cm^{-1}. A peak at 440 cm^{-1} was noticed, which is associated with the stretching band of Zn-O. In addition, an absorption band at 3,400 cm^{-1} was observed, probably ascribing to the O-H stretching vibration from the polyphenolic compound in BPE (Abdullah et al., 2020). The C-H bending mode at 1,391 cm^{-1} represents alkane and aldehyde. The absorption band of aliphatic amines C-N was observed at 1,040 cm^{-1}. Overall, according to the FTIR spectra, the catalyst was successfully synthesized via biosynthesis using BPE.

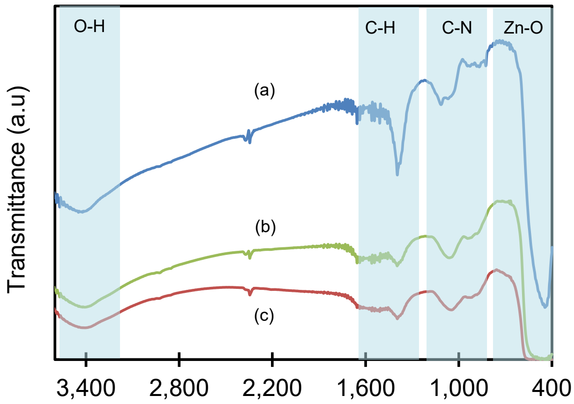

Figure 1: FTIR spectra of the synthesized (a) BPE/ZnO (b) Z1A and (c) Z3A

3.2 Band gap energy analysis

A UV-Visible spectrophotometer was used to analyze the band gap energy for each synthesized catalyst. The band gap energy provides essential information on photocatalytic properties, which correlate to producing electron-hole pairs. Band gap energy can be calculated using Eq (3) where α, h, v, E_g, and A are absorption coefficient, Plank's constant, light frequency, band gap energy, and constant. It was observed that adding Ag into BPE/ZnO slightly increases the band gap energy maybe due to the surface defect in Ag that may produce a new electronic level (Chuaicham et al., 2023). Z3A has the highest band gap energy of 3.281 eV, while Z1A and BPE/ZnO are 3.252 eV and 3.241 eV, as shown in Figure 2. Larger band gap energy is more favorable for better photocatalytic properties (Mohamed Isa et al., 2021).

$$(\alpha hv)^2 = A\,(hv - E_g) \quad (3)$$

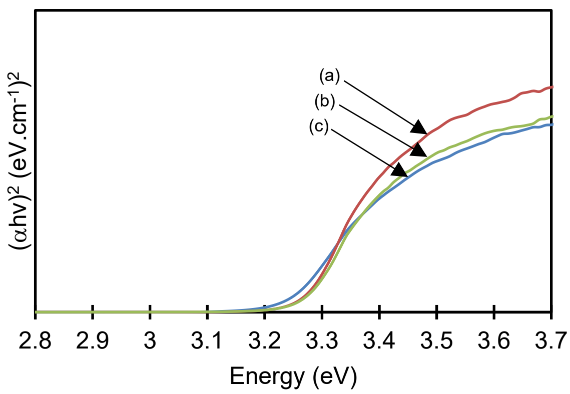

Figure 2: Tauc's plot for band gap energy for synthesized (a) Z1A, (b) Z3A and (c) BPE/ZnO

3.3 Morphological changes

FESEM instrument was used to study the morphology and sizes of the synthesized catalysts as shown in Figure 3. The average size of BPE/ZnO, Z1A, and Z3A are 48.18 nm, 35.70 nm, and 29.49 nm. Z1A and Z3A exhibited a small, uniform spherical and hexagonal shape, while BPE/ZnO showed uniform but larger spherical with agglomeration between particles. Even so, the size of BPE/ZnO was smaller compared to the reported study using plant extract, which was 52.24 nm (Jayachandran et al., 2021). Meanwhile, an increase in Ag content resulted in a smaller size than BPE/ZnO due to Ag^{1+} ions distorting ZnO growth (Iqbal et al., 2021). The roles of BPE as capping and stabilizing the growth of all synthesized photocatalysts corresponded to the uniform sizes of particles (Abdullah et al., 2021).

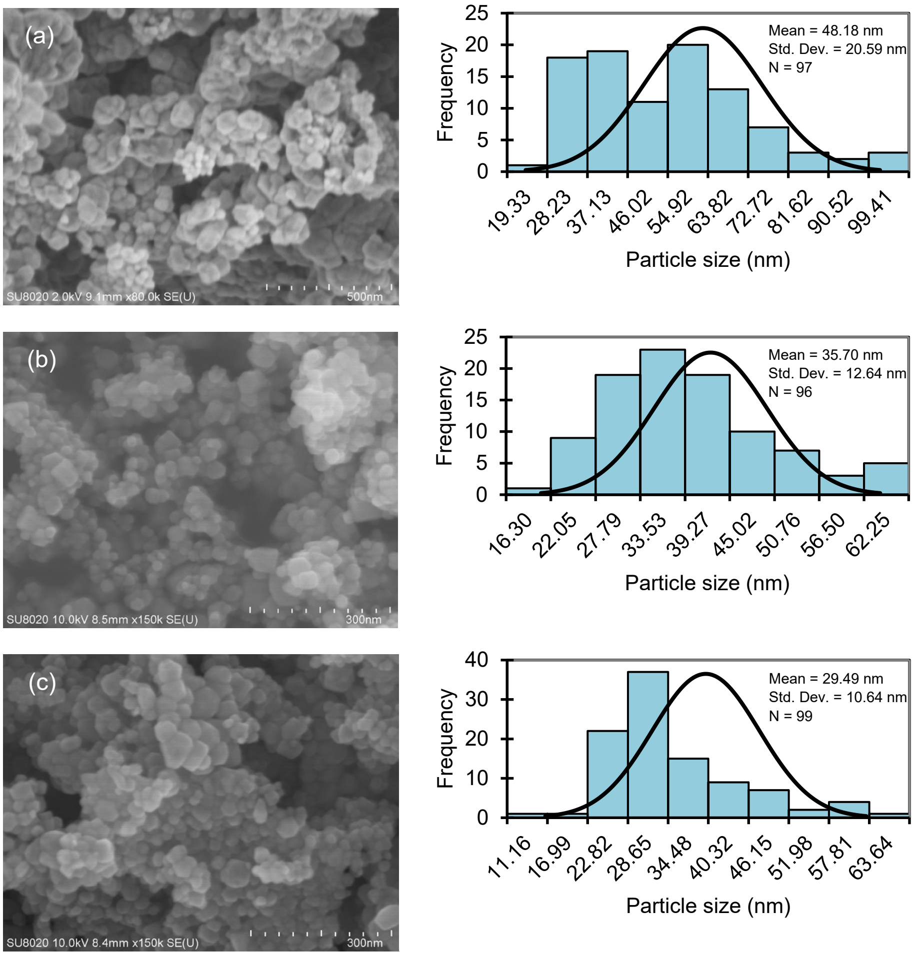

Figure 3: FESEM image and size distribution of (a) BPE/ZnO (b) Z1A and (c) Z3A

3.4 Photocatalytic degradation of paracetamol

The photocatalytic properties of the synthesized catalyst were evaluated using 0.1 g of catalyst dosage with 20 ppm PCM (pH 6) to mimic the pharmaceutical wastewater. Figure 4 shows the percentage and rate of degradation for each catalyst. It can be concluded that BPE/ZnO shows significant performance compared to ZnO, which proves that the biosynthesis technique may have better catalyst properties (Abdullah et al., 2021). The addition of Ag into BPE/ZnO boosts the performance since Ag may inhibit electron-holes pair recombination through surface plasmon resonance (Ramasamy et al., 2021). Z3A shows the best performance among all catalysts, with a PCM degradation rate of 76 % and constant of 0.0086 min^{-1} during this test, probably due to its smaller particle size. Moreover, the Ag particles in Z3A create a Schottky junction with fast transfer of charge carriers which is favorable in photocatalytic reactions (Ahmad et al., 2022). The proposed photocatalytic mechanism of Z3A started with receiving light energy and producing electron (e^-) – holes (h^+) pairs as in Figure 5. Then, e^- reacted with O_2 to produce superoxide anion ($^{\bullet}O^{2-}$) which then both $^{\bullet}O^{2-}$ and h^+ react with H_2O to produce hydroxyl radical ($^{\bullet}OH$). The $^{\bullet}OH$ reacted with PCM to degrade into a harmless by-product of CO_2 and H_2O. Organic pollutants can be degraded using the biosynthesized ZnO/Ag from various biomaterials sources, as shown in Table 1. Most previous studies were conducted with dyes as the pollution model and plant extract as biomaterials. Even so, the photodegradation of pharmaceutical waste is still lacking, and biosynthesized methods via waste material such as BPE are sustainable and eco-friendly.

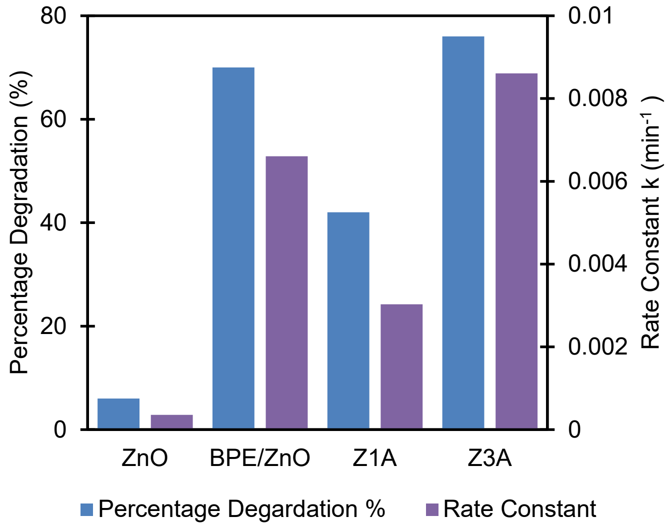

Figure 4: PCM degradation percentage and rate by using the synthesized catalysts

Table 1: Comparison among the biosynthesized ZnO/Ag on photocatalytic degradation of organic pollutants

Biomaterials	Ag concentration (M)	Pollutants	Catalyst dosage (g/L)	Pollutant concentration (ppm)	Time (min)	Degradation percentage (%)	Rate (min^{-1})	Ref.
Urtica dioica	1×10^{-2}	Methylene blue	0.07	3.2	50	82.5	-	Sohrabnezhad and Seifi (2016)
Acacia arabica	1×10^{-3}	Methylene blue	0.1	15	80	90	-	Khan et al. (2021)
Carya illinoinensis	5×10^{-3}	Rhodamine B	0.4	15	60	47	0.0105	Ahmad et al. (2022)
Banana peels	3×10^{-3}	Paracetamol	1	20	180	76	0.0086	This study

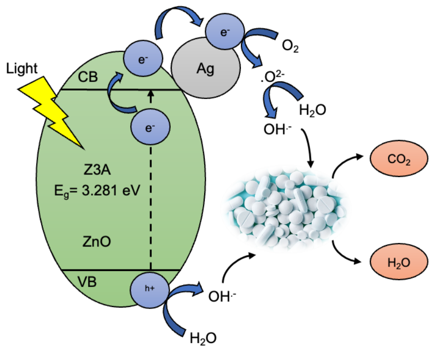

Figure 5: Proposed photocatalytic degradation of PCM mechanism using Z3A

4. Conclusions

Biocatalyst ZnO/Ag was successfully synthesized via sol-gel and precipitation techniques. The effect of low Ag content in the nanocomposite was evaluated and the comparison between biosynthesized and chemically synthesized ZnO was conducted through characterization and photocatalytic degradation of PCM. FTIR analysis confirmed all catalysts with a distinct band of Zn-O, while the band gap energy increases with increased Ag content. FESEM image shows uniform and spherical shape with Z3A having the smallest average particle size and highest degradation of 76 % PCM removal. Overall, the biosynthesized ZnO/Ag possesses an excellent potential for photocatalytic wastewater treatment.

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