

# Photodegradation of Paracetamol using Electrosynthesized Silver Supported on Durio Zibethinus Husk

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**Abstract.** An advanced oxidation process (AOPs) using heterogeneous semiconductor photocatalysts such as TiO<sub>2</sub>, ZnO, CuO, and ZrO<sub>2</sub> have become a popular method for the removal of toxic pollutants from wastewater. Recently, the noble metal nanoparticles (NPs), such as silver (Ag), gold (Au) and platinum (Pt) has also been intensively studied and show the intense UV and visible light absorbance capability. However, the usage of pure noble metal might be limited due to its cost, hence the utilization of support material is needed. Herein in this study, a simple electrochemical method was used to prepare a series of Ag (5, 10 and 15 wt%) loaded onto Durio Zibethinus Husk (Ag/DZH) as support material. The synthesized catalyst was examined using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), and Scanning Electron Microscopy (SEM) to measure the crystallinity, chemical composition and morphology, respectively. Additionally, the effect of Ag loading on DZH catalysts was evaluated through photocatalytic reaction to degrade 5 mg/L of pH 9 paracetamol in aqueous solution using 0.03 g/L catalyst. Among the catalysts, 10 wt% Ag/DZH shows the highest degradation rate of 0.01197 mg/L.min due to its size, well distribution as well as metal-support interaction.

## 1. Introduction

Emerging Contaminants (ECs) can be defined as the chemicals which are not controlled properly in an existed specific process and affecting human and ecological life. The Pharmaceutical Contaminants (PhACs) is one of the examples for the ECs that presence in the water. These pharmaceutical compounds can contaminate the aquatic environment via different channels such as pharmaceutical industry, excretory waste, hospital waste, personal care products, effluent and sewage process systems [1]. The presence of these contaminants can leads to a critical environmental threat whereas it will give the bad impact to the human health and also environment [2]. Therefore, the wastewater consisting PhACs should be treated properly with the suitable technology in order to protect the welfare of human health and environment [3].

Many techniques have been developed to remove these kind of contaminants from the effluents such as biological, adsorption, coagulation and flocculation, ion exchange and membrane separation [4-6]. However, these methods are usually non-destructive, inefficient and costly or just able to transfer the pollutants from one phase to another. Among the diverse techniques, Advanced Oxidation



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Processes (AOPs), mainly photocatalysis is the most preferable technique with the involvement of UV irradiation and heterogeneous photocatalyst. This technique receive a great and positive recognition [7]. It is basically applied to treat the organic contaminants in wastewater and achieved complete mineralization.

There are many semiconductors have been used as photocatalyst by the researchers such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{ZrO}_2$  and  $\text{CdS}$ . However, it is a growing interest to explore the used of noble metal, such as silver (Ag), gold (Au) and platinum (Pt) as a photocatalyst [8, 9]. Thus, it is a great opportunity to discover the potential of Ag for the photocatalytic degradation process. However, the photodegradation of pollutants might be inefficient due to the limits of mass transfer to the catalyst surface [10]. Thus, previous researches had observed that the adding of support material such as silica, alumina, zeolite and etc. could improve the photocatalytic efficiency of the catalyst [11]. As to discover the new support materials, Durio Zibethumus Husk (DZH), one of the agriculture waste in Malaysia has taken into consideration. Due to its properties which contain cellulose, DZH has been extensively used as an adsorbent for the removal of organic pollutants [12-15]. Therefore, DZH will give an advantage to be a great support material for the catalyst.

Herein in this study, a simple electrochemical method was employed to prepare a series of Ag (5, 10 and 15 wt%) loaded onto DZH (Ag/DZH). The synthesized catalyst was examined using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), and Scanning Electron Microscopy (SEM) to measure the crystallinity, chemical composition and morphology, respectively. Additionally, Ag/DZH catalysts undergo the photocatalytic reaction to degrade paracetamol in aqueous solution.

## 2. Materials and Methods

### 2.1. Reagent and Materials

Sodium Hydroxide (NaOH) and Hydrochloric Acid (HCl), were purchased from Evergreen Engineering and Resources, Malaysia. The platinum and silver plates were obtained from Nilaco Metal, Japan. Tetraethylammonium Perchlorate (TEAP) was prepared in accordance with the procedure reported in the literature [16]. An amount of 190 ml of Tetraethylammonium Bromide (TEAB) solution was added into 600 ml of water and 60 ml of aqueous perchlorate acid ( $\text{HClO}_4$ ). The mixture was stirred until clear solution was obtained. Then, the mixture was settle down for the crystallization process before being filtrated to produce perchlorate salt. The salt was washed with cold water and dried to give a pure white needles shape TEAP in 90% yield. The DZH was collected at Setapak Jaya, Kuala Lumpur, Malaysia. The paracetamol tablet was obtained from Pusat Kesihatan Universiti Teknologi Malaysia, Kuala Lumpur.

### 2.2. Preparation of Support Material

The DZH sample was washed with deionized water to eliminate and removed the debris and impurities. The sample was dried under the sunlight for 3 days before cut into a small parts. Then the dried sample was oven-dried overnight at  $110^\circ\text{C}$  before grounded into 0.67 mesh-sized

### 2.3. Synthesis of Ag loaded on DZH

The pure Ag was prepared according to previous reported protocol with some modification [17]. In the procedure, an open system electrolysis cell was fitted with a magnetic stirrer and a platinum plate cathode ( $2 \times 2 \text{ cm}^2$ ) facing a silver plate anode ( $2 \times 2 \text{ cm}^2$ ). A 10 mL of distilled water and 0.1 M TEAP were added in the cell. The electrolysis was conducted at a constant current of  $120 \text{ mA/cm}^2$  and  $0^\circ\text{C}$  under air atmosphere. After electrolysis, the obtained mixture was filter and dried at  $110^\circ\text{C}$  for 12 h to give pure Ag particles. The Ag/DZH catalyst was prepared via the same procedure, except that the DZH was added to the mixture before electrolysis. The required weight of the Ag supported on the DZH was calculated based on duration time of the electrolysis following Faraday's law [17],

$$t = \left( \frac{F}{I} \right) (z \times n) \quad (1)$$

where  $t$  is total time (s),  $F$  is Faraday's constant of  $96,486 \text{ C mol}^{-1}$ ;  $I$  is applied current during electrolysis;  $z$  is number of electron transferred or valence number of metal ions, and  $n$  is number of mole ( $n = m/M$ ). For confirmation, the weight of Ag plate was measure before and after the electrolysis.

#### 2.4. Characterization of catalyst

The crystalline structures of the catalysts were carried out using a Bruker Advance D8 X-ray powder diffractometer (XRD). Fourier transform infrared (FTIR) Shimadzu IRT Tracer-100 was employed to identify functional group with KBr method at wavelength scan of  $400\text{-}4000 \text{ cm}^{-1}$ . The morphology was observe using Scanning Electron Microscopy (SEM).

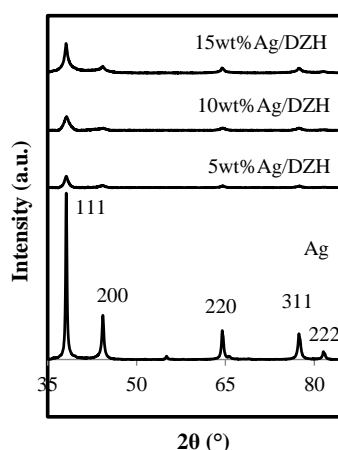
#### 2.5. Photocatalytic Testing

The photoactivity of the catalysts was tested for the degradation of Paracetamol. The photocatalytic experiments were performed in a batch reactor which connected to  $4 \times 9$  Watt fluorescence lamp as a visible light source. These lights source were fitted at 10 cm above the solution for the maximum irradiation exposure. For photoactivity process, 0.003 g of catalyst was added to the Paracetamol solution with desired concentration (100 mL) and stirred for 1 h in the dark condition to achieve adsorption-desorption equilibrium before continued for another 2 h under light irradiation. During the reaction, aliquots of 2 mL were taken out at intervals of 10 min and centrifuged before being analyzed by UV-Vis spectrophotometry (Agilent) at 325 nm.

### 3. Results and Discussion

#### 3.1. Characterization of the Catalyst

Figure 1 shows the XRD pattern of the pure Ag and various Ag loading onto DZH. A series of characteristic peaks was observed for metallic Ag at  $39.28^\circ$  (111),  $44.40^\circ$  (200),  $64.45^\circ$  (220),  $77.40^\circ$  (311) and  $81.69^\circ$  (222) consistent with the typical peaks of metallic silver (JCPDS file no. 01-087-0717) [18]. It could be seen that these corresponding peaks also appeared when the Ag loaded onto DZH. The peak intensity increases as the loading increased from 5 wt% to 15 wt%.

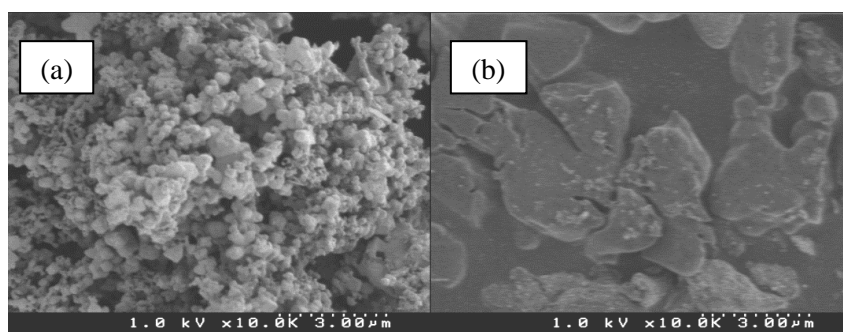


**Figure 1.** XRD pattern of Ag and Ag/DZH catalysts

The particle size of all the Ag/DZH catalysts were calculate using the Debye Scherer equation. The particle sizes of pure Ag, 5 wt%Ag/DZH, 10 wt%Ag/DZH and 15 wt%Ag/DZH were found to be 46.91 nm, 18.25 nm, 18.26 nm and 41.04 nm, respectively. The smaller particles size was obtained

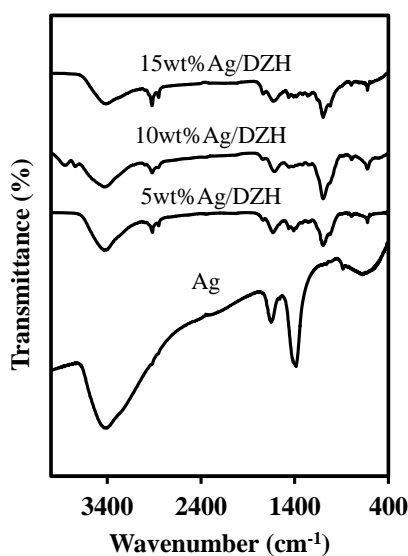
when 5 and 10 wt% loaded onto DZH due to the good dispersion of Ag on the support materials. Additionally, electrosynthesis method with the presence of current density give an advantages to synthesized the nano-size metal oxide, which aligned with the report by Jalil et al. [19].

Then the surface morphologies of the synthesized Ag and 10 wt% Ag/DZH was observed using SEM image. As referred to figure 2(a), the Ag has a spherical shape with an existence of some rectangular shape through. When Ag was loaded onto DZH, it was observed that the shiny Ag nanoparticles were dispersed on the DZH surface (figure 2(b)). This showed that the Ag could be loaded into DZH surface efficiently using electrosynthesis method at a certain weight loading. As proved by previous research, electrosynthesis method was able to disperse the metal oxide onto the support material [20-22].



**Figure 2.** SEM images of (a) Ag and (b)10wt%Ag/DZH catalysts

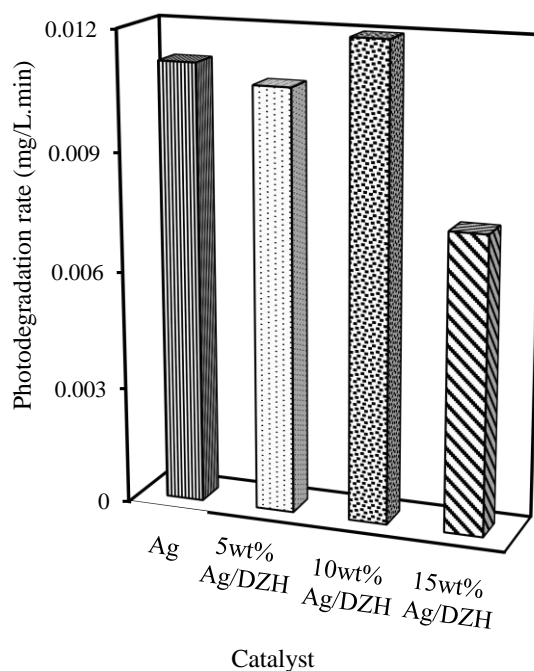
FTIR measurements were carried in order to find out the presence of the functional groups in the pure Ag as well as Ag/DZH catalysts. For Ag catalyst, a broad peak at  $631\text{ cm}^{-1}$  can be assigned to Ag peak. These peak could also be observed when Ag loaded on DZH surface. A broad peak also observed at  $3394\text{ cm}^{-1}$  for all the catalyst, attribute to the adsorbed  $\text{H}_2\text{O}$  molecules [23][20]. This peak decreased with the increasing amount of Ag loading suggesting that the greater the amount of Ag loaded onto the DZH, the fewer hydroxyl groups were adsorbed on the catalyst's surface. The similar trend also observed at peak  $1652\text{ cm}^{-1}$  which also assigned to hydroxyl group. In Ag loaded DZH catalysts, the peak at  $631\text{ cm}^{-1}$  represent the existence of Ag in pure Ag catalyst. This peak was also present in Ag loaded on DZH catalyst with a slightly shift to a lower wavenumber, suggesting the possible interaction of Ag with the DZH support.



**Figure 3.** FTIR spectra of Ag and Ag/DZH catalysts

### 3.2. Photodegradation of Paracetamol

The photodegradation performance of Ag and various Ag loading on DZH catalyst was evaluated for the degradation of Paracetamol.



**Figure 4.** Photodegradation performance of Ag and Ag/DZH catalysts

As demonstrated in figure 4, 10 wt% Ag/DZH shows the highest degradation rate (0.01197 mg/L.min) with 0.03 g/L catalyst in 5 mg/L of pH 9 paracetamol solution at 30°C. The different photocatalytic efficiencies were achieved for each catalyst which most likely due to the influence of the Ag dispersion and composition in the DZH surface. Similar observation was reported by Shen et al. during deposition of ZnO on the silica nanoparticles where well dispersion of ZnO resulted in high photodegradation of methylene blue [24]. Additionally, it was proved by the XRD result that the 10 wt% Ag/DZH catalyst poses a small size which led to high active surface area of Ag contact with the paracetamol solution. The possible interaction between Ag and DZH as observed in FTIR study also reveal the better performance of 10 wt% Ag/DZH compared to pure Ag. Although a high degradation rate was also observed for pure Ag, these results also illustrate the important role of DZH as a support material in reducing the amount of Ag used, which is beneficial from an economic point of view.

### 4. Conclusion

In this study, Ag and a series of Ag/DZH catalyst were prepared using a simple electrochemical method. The physiochemical properties of the synthesized catalyst were studied by XRD, FTIR and SEM. The result shows that the smaller particles size of Ag was obtained when it was loaded onto the DZH support with the formation of possible interaction between the Ag and DZH support. This interaction led to the enhancement of photocatalytic performances of 10 wt% Ag/DZH compared to pure Ag and other Ag/DZH catalysts.

### Acknowledgments

The authors would like to express appreciation for the financial support by the Fundamental Research Grant Scheme from Ministry of Higher Education (Grant No. 5F031).

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