Enhanced Degradation Rates of Paracetamol in Aqueous Solution using Silver Doped Durio Zibethinus Husk Catalyst

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Abstract. In the recent years, traces of paracetamol in water body had increases due to the increasing usage and production of it. Since the discharge of wastewater containing paracetamol into water body can cause harm to environment and human health, it is crucial to find a suitable treatment method to overcome this problem. Advanced Oxidation Process (AOPs) with the assist of heterogeneous catalyst received growing interest as one of prospective treatment method. Some of noble catalysts such as platinum (Pt), gold (Au) and Silver (Ag) could serve as alternative to popular semiconductor catalyst. This study report a series of Ag (5, 10, 15 wt.%) loaded to Durio Zibethinus Husk (Ag/DZH) with detailed physicochemical properties using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), X-ray photoelectron spectroscopy (XPS) and Scanning Electron Microscopy (SEM). Then, the respective catalysts were tested for photodegradation of paracetamol (PCT) in aqueous solution. It was showed that the catalysts have a potential to degrade 5 mg/L of paracetamol solution (pH 9) with the highest degradation rate of 0.01197 mg/L.min using 0.03 g/L of 10 wt.% Ag/DZH catalyst. This result could serve as alternative for DZH utilization and reduce environmental pollution.

1. Introduction

The discharge of Emerging Contaminants (ECs) into water stream may become serious problem to environment and human. As one of ECs, more than 80 pharmaceutical compounds and metabolites were detected in ground and surface water over US and Europe in last decades [1]. Improper medication of these contaminants from hospital, personal care and pharmaceutical industry cause several side effect to human [2, 3]. Hence, these pharmaceutical wastes should be handled carefully to conserve environmental sustainability and human welfare.

Many methods were reported to remove these contaminants such as adsorption, coagulation, membrane, and biological. Biological technique was constrained for antibiotics which are bacteria resistance. Meanwhile, adsorption, coagulation and membrane could only transfer pollutant to other places without destruction [4, 5]. Nowadays, the increasing interest was centralized to Advanced Oxidation Process (AOPs), especially on photo-catalysis, which involve heterogeneous catalyst in assistance of external light, such UV irradiation [6, 7]. This method could degrade the contaminants and achieve complete mineralization.

The common photo-catalysts were focus on semiconductor type such as TiO_2, ZnO, CdS, ZrO_2 and SnO_2. However, the latest research shown that noble metal such as platinum (Pt), gold (Au) and silver (Ag) poses as the promising photocatalyst [8, 9]. Despite their high activity, the detailed exploration on

silver as photo-catalyst was still scanty. Previously, some support material such as zeolite, silica, carbon and alumina were successfully enhanced their photocatalytic activity [10-13]. In response to this, an abundant agriculture waste, *Durio Zibethinus Husk* (DZH) that consist of cellulose will gave an advantage as a support material. According to previous report, DZH comprise of 13.1% of hemi-cellulose, 60.5% of α-cellulose and 73.5% of hello-cellulose. This characteristic is attractive to assist adsorption which also lead to high degradation of organic pollutants [14] [10]. Therefore, the investigation to modify DZH as catalyst support will also be beneficial for reducing environmental waste.

In this work, simple electrochemical method was utilize to synthesis Ag (5, 10 and 15 wt%) loaded on DZH (Ag/DZH) catalyst. Then, its physicochemical properties were evaluated with X-ray diffraction (XRD) to identify its crystallinity and purity, Scanning Electron Microscopy (SEM) to observe its morphology. Meanwhile, the responsible functional group that affected PCT degradation was investigate with Fourier Transform Infrared Spectroscopy (FTIR). Then, X-ray photoelectron spectroscopy (XPS) was carry out to identify its chemical oxidation. Furthermore, the synthesized catalyst undergo the photocatalytic reaction to degrade Paracetamol (PCT) in aqueous solution.

2. Materials and Methods

2.1. Reagent and Materials
Platinum and silver plates were purchased from Nilaco Metal, Japan. Tetraethylammonium perchlorate (TEAP) was prepared using our previous procedure[15]. Hydrochloric acid (HCl) and Sodium Hydroxide (NaOH) were obtained from Evergreen Engineering and Resources, Malaysia. The paracetamol was obtained from Pusat Kesihatan Kuala Lumpur. The DZH was collected at Setapak Jaya, Kuala Lumpur, Malaysia.

2.2. Preparation of Support Material
The collected DZH sample was washed with deionized water to remove debris and impurities. Prior to cut into small pieces, the sample was dried under the sunlight for 3 days. Finally, the sample was dried at 110 °C overnight and grounded to 0.67 mesh.

2.3. Synthesis of Ag Loaded on DZH
The pristine Ag was prepared by modifying our previous protocol [11]. An open system of electrolysis cell consists of silver plate anode (2×2 cm^2) facing a platinum plate cathode (2×2 cm^2). The current density was adjusted at 120 mA/cm^2 and 0 °C at ambient pressure. 10 mL of distilled water and 0.1 M TEAP were utilized as supporting electrolyte. After the electrolysis, the sample was dried at 110 °C for 12 h. The same preparation method was carried out for Ag/DZH sample with addition of DZH before the electrolysis. The required weight of Ag supported on DZH was calculated based on the Faraday's law,

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

where t is total time (s), F is Faraday's constant of 96,486 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).

2.4. Characterization of Catalyst
The crystallinity structures of the catalysts were conducted using Bruker Advance D8 X-ray powder diffractometer (XRD). The functional group in DZH assisted for pollutants degradation was elucidated with Fourier Transform Infrared (FTIR) Shimadzu IRT Tracer-100 at wavelength scan of 400-4000 cm^{-1}. The morphologies of the catalysts were observed using Scanning Electron Microscopy (SEM). Finally, the chemical environment exist in the catalysts were identified with X-ray photoelectron spectroscopy (XPS) conducted on a Kratos Ultra spectrometer equipped with an Mg Kα radiation source (10 mA, 15 kV).

2.5. Photocatalytic Testing
The photocatalytic activities of the samples were evaluated towards Paracetamol degradation in aqueous solution. The experiments were carried out in a batch reactor connected to 36 W of fluorescence lamp as visible light sources. 0.003 g of the catalyst was added to 100 mL of Paracetamol solution with desired concentration. This mixture was stirred for 1 h in dark to obtain equilibrium of adsorption desorption between catalyst and solution. Therefore, the sample was irradiated with lamp for another 2 h. During the reaction, aliquots of 2 ml were take periodically at interval of 10 min and centrifuged before analyzing with UV Vis spectrometry Agilent at 325 nm.

3. Result and Discussion

3.1. Characterization of the Catalyst
The XRD pattern of the pristine Ag and various loading percentage of Ag onto DZH were shown in Figure 1. The peak characteristics of Ag was appeared at 44.40° (200), 64.45° (220), 77.40° (311) and 81.69° (222). The structure of these nanoparticles was face centered cubic as confirmed with JCPDS file no. 01-087-0717 as metallic Ag [16]. The principal peak of these spectra increased when increasing the content of Ag from 5 to 15 wt.%. Then, the crystallite size of these catalysts were estimated using Scherer equation by observing the main peak and position of two theta (2θ), using,

$$D = \frac{0.9\lambda}{\beta cos\theta} \tag{2}$$

where λ is XRD wavelength, β as full width at half maximum (FWMH), and θ is bragg's angle.

From this calculation, the crystallite sizes are 46.91, 18.25, 18.26 and 41.04 nm for pristine Ag, 5 wt.% Ag/DZH, 10 wt.% Ag/DZH, 15 wt.% Ag/DZH, respectively. This result verified that DZH could effective supported smaller size of Ag at 5 wt.% and 10 wt.% as a result of good dispersion of Ag over DZH surfaces.
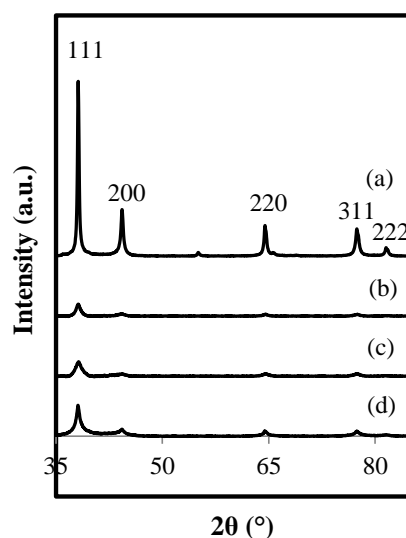

Figure 1. XRD patterns of (a) Ag, (b) 5 wt.% Ag/DZH, (c) 10 wt.% Ag/DZH and (d) 15 wt.% Ag/DZH

The major morphology of Ag as depicted in Figure 2 (a) ws pre-dominantly spherical as well as rectangular [17]. Meanwhile, some of shiny particles of Ag was observed over DZH surface as presented in Figure 2 (b) for 10 wt.% Ag/DZH. This phenomenon is indication that Ag-NPs can be deposited on DZH with certain loading content.
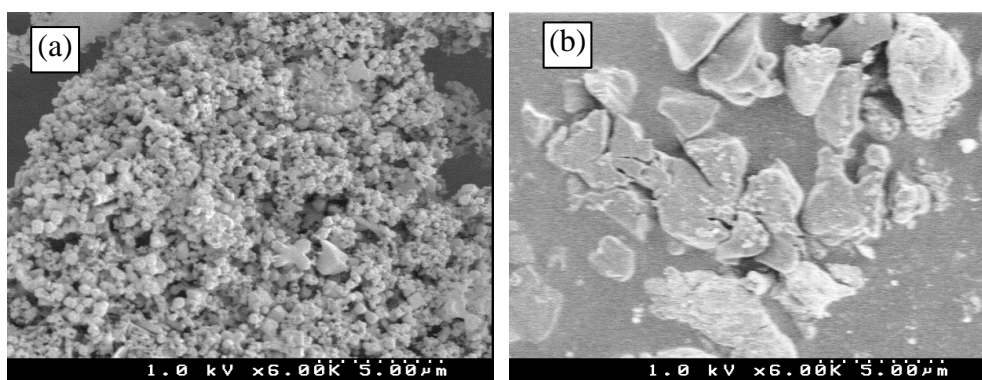
Figure 2. SEM images for (a) Ag (b) 10 wt.% Ag/DZH

Then, FTIR analysis for DZH, Ag and synthesized Ag/DZH catalysts are showed in Figure 3. In DZH spectra as presented in Figure 3 (a), there are three prominent peaks at 1016, 1650 and 3302 cm^{-1}. The intense peak at 1016 cm^{-1} was assigned of C-O bonding of polysaccharide, where 1650 and 3302 cm^{-1} was attributed to hydroxyl group. For Ag catalyst, a broad peak at 631 cm^{-1} can be assigned to Ag peak (Figure 3 (b)). This peak could also be observed when Ag loaded on DZH surface ((Figure 3 (c-e)), with a slightly shift to a lower wavenumber, suggesting the possible interaction of Ag with the DZH support. In addition, the characteristic of C-O bond are shifting of from 1016 cm^{-1} to 1111 cm^{-1}. The C-O in polysaccharide form might helped in the adsorption of paracetamol before the degradation process occurred. In addition, an appearance of new peak at 792 cm^{-1} may be a sign of new bond formation between Ag-NPs and DZH. A broad peak also observed at 3394 cm^{-1} for all the catalyst, attribute to the adsorbed H_2O molecules [18]. This peak tend to decrease 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 cm^{-1} which also assigned to hydroxyl group.
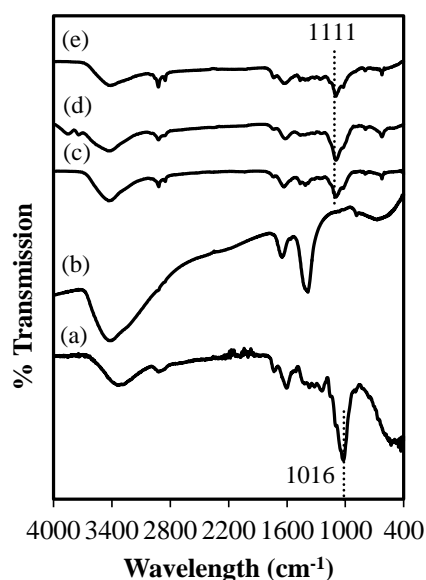

Figure 3. FTIR spectra for (a) DZH, (b) Ag, (c) 5 wt.% Ag/DZH, (d) 10 wt.% Ag/DZH and (e) 15 wt.% Ag/DZH

XPS spectra of Ag and 10 wt.% Ag/DZH were shown in Figure 4 to recognize their chemical oxidation. As expected, the spectra of Ag only exhibit two peak of $3d_{3/2}$ at 374.35 eV and $3d_{5/2}$ at 368.15 eV. However, this peak were shifted to 373.45 eV and 367.75 eV for $3d_{3/2}$ and $3d_{5/2}$, respectively in 10 wt.%

Ag/DZH catalyst. The shifting wavelength and reducing intensity indicate interaction between Ag and DZH, which aligned with the report by Belluso et al. (2019) [19].
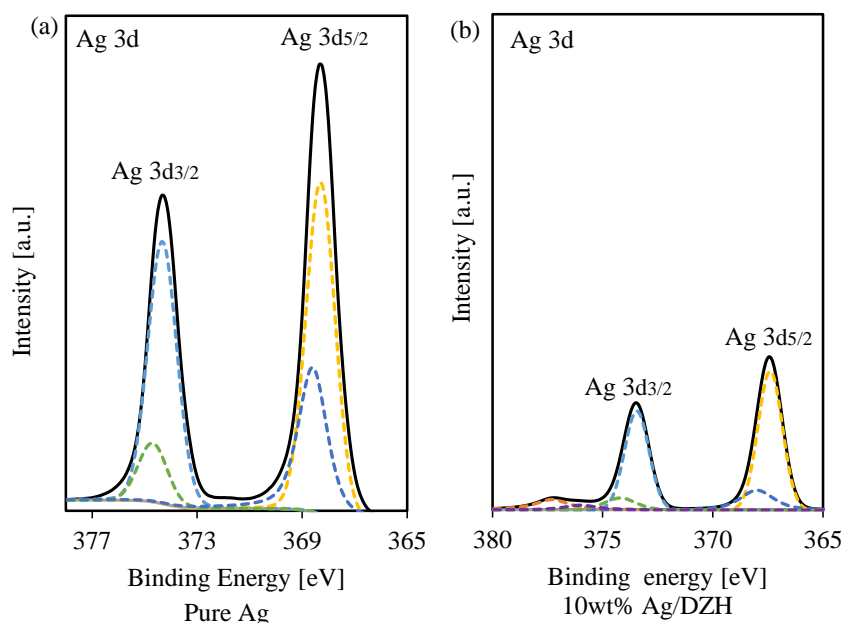

Figure 4. XPS spectra for (a) Ag and (b) 10 wt.% Ag/DZH

3.2. Photodegradation of Paracetamol

3.2.1 Effect of pH. The degradation rates of PCT can be affected by the pH of solution. pH of the solution can determine the surface charge properties of the catalyst, the size of aggregates formed, the charge of PCT and catalyst surface as well as the concentration of hydroxyl radicals. The experiment was run with 0.03 g/L of 5 wt.% Ag/DZH, 5 mg/L of PCT solution at 30°C. With this condition, the photodegradation of PCT on Ag/DZH was studied in the pH range from 5 to 11. Figure 5 showed that the photodegradation of paracetamol is not favoured in an acidic solution (pH < 5). The paracetamol solution has a non-ionic form that caused the water solubility to be minimized and adsorption onto the catalyst was not effective. However, by increasing the solution pH to 9, it enhanced the photodegradation and increased the rate of reaction up to 0.0107 mg/L.min. This phenomenon happened because high pH caused more hydroxide groups available on Ag/DZH surface and form more OH, which it increased the effectiveness and efficiency of PCT degradation [20]. However, when the pH was increasing to pH 11, it produced a poor adsorption of paracetamol, thus decrease the degradation rates.

3.2.2 Effect of Catalyst Dosage. The effect of catalyst dosage was studied between 0.03 g/L to 0.09 g/L using 5 wt.% Ag/DZH at pH 9, 5 mg/L paracetamol solution in 30°C condition. The results were illustrated in Figure 6. As can be seen, the addition of more catalyst resulted to decrease in the degradation rate from 0.01070 mg/L.min to 0.0008 mg/L.min. When the catalyst dosage was increased, the number of active sites that could be absorbed more photons also increased. However, the increment of catalyst dosage seemed to lead to the excess dosage and caused the suspension turbidity in the solution. As a result, the light penetration reduced and the efficiency of the photocatalytic process decreased [21].
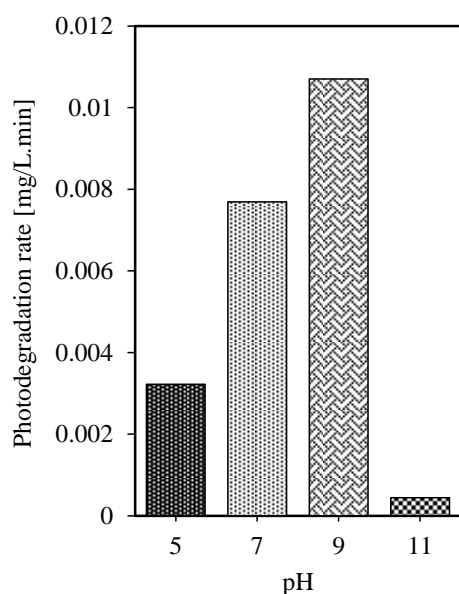
Figure 5. Effect of pH on degradation of paracetamol [Initial Concentration: 5 mg/L; Catalyst: 5 wt.%Ag/DZH; Catalyst Dosage: 0.03 g/L; Temperature: 30 °C]
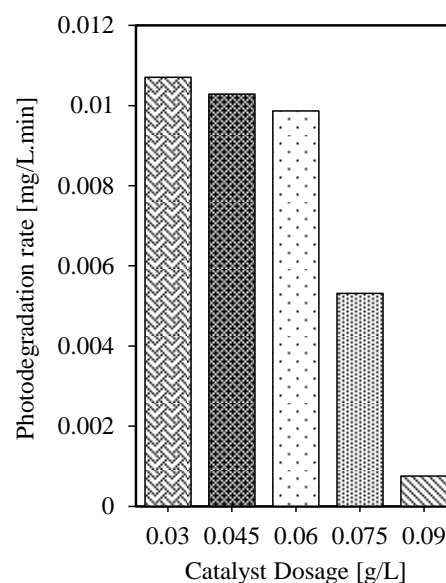

Figure 6. Effect of catalyst dosage on degradation of paracetamol [Initial Concentration: 5 mg/L; Catalyst: 5 wt.%Ag/DZH; pH: 9; Temperature: 30 °C]

3.2.3   Effect of Ag Loading on DZH The photodegradation performance of Ag and various Ag loading on DZH catalyst was evaluated using 0.03 g/L catalyst dosage at pH 9 for 5 mg/L PCT concentration. As demonstrated in Figure 7, 10 wt.% Ag/DZH shows the highest degradation rate (0.01197 mg/L.min). The different photocatalytic efficiencies were achieved for each catalyst, which most likely due to the effect of the Ag dispersion and composition in the DZH surface. Similar trend was reported by Shen et al.(2008) during deposition of ZnO on the silica nanoparticles where well dispersion of ZnO resulted in high photodegradation of methylene blue [22]. 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.
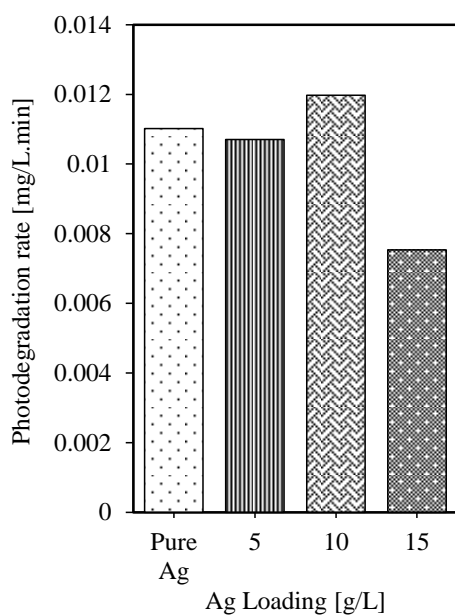

Figure 7. Effect of Ag loading on degradation of paracetamol [Initial Concentration: 5 mg/L; Catalyst dosage: 0.03 g/L; pH: 9; Temperature: 30 °C]

4. Conclusion

This study focused on simple electrochemical approach to synthesis Ag and series of Ag loaded on ZH (Ag/DZH). Their physicochemical properties were studied in detail with XRD, SEM, FTIR and XPS. This report verified that smaller particle size was obtained when Ag loaded to DZH catalyst support. The synergistic effect between particle size and nature of DZH enhanced the photodegradation towards Paracetamol. In summary, 10 wt.% Ag/DZH poses highest degradation rate compared to pure Ag and other Ag/DZH catalysts.

Acknowledgment

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