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Subcritical Water Extraction of Banana Peel Derived ZnO for Photodegradation of Paracetamol

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ABSTRACT

Rapid industrialization and growth have led to the emergence of pharmaceutical compounds in water sources. Therefore, a photocatalytic degradation of paracetamol (PCM) was studied using green catalyst i.e. banana peel extract-based zinc oxide (BZnO) photocatalyst. The catalysts were synthesized by incorporating ZnO with banana peels extract (BPE) extracted using subcritical water (SCW) process at various temperature range between 140-180°C and residence time from 15–45 mins. The produced BZnO photocatalysts were tested for photocatalytic degradation at fixed conditions of 10 ppm of PCM, a photocatalyst dosage of 0.1 g for 120 min. The degradation percentage of PCM was determined using Ultraviolet-Visible Spectroscopy (UV-Vis). The photocatalyst with the highest PCM degradation was then characterized using X-ray Diffraction (XRD) and Brunauer–Emmett–Teller (BET) surface area and pore analyser. Results showed that the highest percentage of PCM photodegradation was 28.20 % using ZnO incorporated with SCW extracted BPE at 140°C for 30 mins. The energy band gap of pure ZnO is calculated to be 3.370 eV, while the energy band gap of the BZnO drops down to 3.290 eV proving that BPE could act as a reducing agent. Further analysis of this BZnO showed the formation of pure nanoparticles with a hexagonal wurtzite crystal structure from its XRD patterns. Additionally, the BET surface area and total pore volume recorded were 20.5702 m2/g and 0.73188 cm3/g, respectively. Hence, green catalyst synthesized by incorporating ZnO and BPE has the potential to be utilized for pharmaceutical wastewater treatment.

1. Introduction

Wastewater contamination poses a significant global challenge, exacerbated by the presence of emerging contaminants (ECs) such as pharmaceutical residues, notably paracetamol (PCM). PCM, ubiquitous due to its household use, enters water sources through effluents from drug factories, hospitals, and households, contributing to environmental pollution as Endocrine Disruptive Compounds (EDCs) according to several authors [1,2]. Khan *et al.,* [3] reported that traditional

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wastewater treatment methods like biological processes and adsorption are often inadequate for PCM removal due to the compound's complex structure and stability, resulting in secondary pollutants like sludge. Photocatalysis using Zinc Oxide (ZnO) has emerged as a promising technology for PCM degradation under sunlight or UV light, offering efficient pollutant removal without generating additional waste based on study conducted by Arumugam *et al.,* [4]. Green synthesis methods such as sol-gel and precipitation are gaining popularity for producing ZnO photocatalysts, minimizing chemical usage and enhancing environmental sustainability in pharmaceutical wastewater treatment according to Sekaran *et al.,* [5].

According to Tan [6], banana peels, abundant yet underutilized, are rich in phytochemicals and phenolics, making them valuable for applications such as nanoparticle synthesis. The disposal of banana peels as waste in landfills based on Vu *et al.,* [7], highlights the need for sustainable utilization strategies to address environmental concerns. Subcritical water (SCW) extraction has emerged as a promising green technology for extracting bioactive compounds from plant sources, including bananas, according to Cheng *et al.,* [8], due to its ability to maintain liquid water at temperatures and pressures below the critical point. Ishak *et al.,* [9] reports that this method offers advantages such as high extraction yields and quality without the use of organic solvents, making it suitable for extracting antioxidants and phenolic compounds from various natural matrices.

This study focuses on harnessing the potential of subcritical water (SCW) extraction for synthesizing zinc oxide (ZnO) nanoparticles using banana peel extract (BPE) as a green precursor. SCW extraction, operating at moderate temperatures and pressures, facilitates the extraction of bioactive compounds from waste biomaterials like banana peels, while also minimizing energy consumption and environmental impact. The synthesized ZnO photocatalysts hold promise for enhancing the photodegradation efficiency of PCM in wastewater, thereby addressing critical gaps in current wastewater treatment strategies. By exploring the synergy between SCW extraction and green synthesis techniques, this research aims to contribute novel insights into sustainable nanomaterial synthesis and advanced water treatment technologies.

2. Methodology

All chemicals used in the research were of analytical grade without the need for further purification, Aqueous solutions for all chemicals were prepared using deionized (DI) water. The cultivar of banana, Pisang Nangka were obtained from a banana fritters stall in Kuala Lumpur, Malaysia.

a) Materials: Banana peels (Pisang Nangka), 99% purity of zinc nitrate hexahydrate ($Zn(NO3)2.6H2O$) and 500 mg of paracetamol (PCM).

b) Banana peel preparation: The cultivar of banana was selected based on its skin color intensity, rated as C3 (more green than yellow) on the Von Loesecke scale (1950). After washing each banana peel with distilled water and peeling the remaining pulp, the peel was further rinsed with distilled water, was cut into pieces measuring approximately 1 cm by 1cm, and subsequently dried at 60°C for 15 hours.

c) Subcritical water (SCW) extraction: The sample-to-water ratio of 1 to 2 was experimented where 50 g of banana peel was loaded with 100 mL of distilled water into the SCW reactor. The sample was heated at various temperatures (140, 160 & 180 °C) at different residence times (15, 30 & 45 minutes). The reactor was cooled once the extraction was completed.

Banana peel extract (BPE) was collected from the vessel and filtered. The supernatant was collected, dried at 60°C for 15 hours and stored in a zip-lock bag for further test.

d) Green synthesis of zinc oxide: Green synthesis of ZnO via BPE followed a simple sol-gel and combustion technique. 15 mL of BPE was mixed with 3 g of Zn(NO3)2.6H2O at 80 °C and stirred at 400 rpm until a gel-like formation produced. Then, the gel was calcined in a furnace for 1 hr at 600 °C and 50 °C/min. The produced white-colored ZnO powder was kept in sample vials for further use at room temperature.

e) Photocatalytic degradation of paracetamol: A 10 ppm PCM solution with pH value of 6 was prepared. The initial concentration of the PCM solution was determined using UV-Vis. 0.1 g of the synthesized BZnO was mixed with the PCM solution and sonicated for 5 minutes. The resulting mixture was placed in a photocatalytic reactor and stirred in the dark for 40 minutes to achieve absorption-desorption equilibrium. Then, the UV light was activated for 2 hours, with samples taken every 10 minutes to be centrifuged and analyzed using UV-Vis. These steps were replicated for all the BZnO photocatalysts. The photodegradation percentage of PCM was calculated by using Eq. (1), where C and C0 are final PCM concentration and initial PCM concentration respectively.

$$\text{Percentage Degradation } (\%) = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

3. Results

3.1 Green Synthesis of Banana Based Zinc Oxide Nanoparticle

Interestingly, the green method of synthesis using plant sources have been found appropriate for the production of ZnO NPs dues to its numerous health, environmental, economic, and medicinal benefits according to Hamrayev *et al.,* [10]. The green synthesis approach via a straightforward sol-gel method using banana peel extract (BPE) resulted in an effective fabrication of ZnO. The interaction of BPE with an aqueous solution of zinc nitrate hexahydrate results in the formation of a complex involving zinc ions (Zn^{2+}) and a hydroxyl group within BPE. Subsequent heating of the mixture until evaporation takes place leads to the formation of a gel-like substance. The gel was then exposed to thermal decomposition at elevated temperature and Khorsand Zak *et al.,* [11] said that it is to facilitate the conversion of Zn^{2+} complexes to ZnO NPs. The chemical equation pathway for the green synthesized BZnO is shown in Eq. (2) and Eq. (3).

$$\text{BPE} + H_2O + Zn^{2+} = [BPE/Zn^{2+}] \quad (2)$$

$$[\text{BPE}/Zn^{2+}] + O_2 = [BPE/ZnO] \quad (3)$$

3.2 Photocatalytic Degradation of Paracetamol

ZnO photocatalysts with different SCW extraction conditions of temperature (140, 160 & 180 °C) and residence time (15, 30 & 45 minutes) were successfully synthesized using BPE. Results show that all the BZnO has better performance compared to the chemically synthesized ZnO as illustrated in Figure 1. Among all the samples, Z14-30 has the highest photodegradation of PCM (28.20%) where the BPE was extracted at SCW conditions of 140 °C for 30 minutes. Z14-15 to Z14-30 shows an increasing trend of photodegradation percentage but Z14-45 decreases down to 21.88%, indicating

the most optimum photocatalysts is Z14-30 at 140 °C. Another study by Yu *et al.,* [12] on the subcritical water extraction of phenolic compounds from XiLan olive fruit dreg reported that the phenolic yield increased with longer residence times up to 30 minutes, after which it started to decrease. This suggests that there is an optimal residence time for maximizing the extraction of phenolic compounds.

As for ZnO extracted at 180 °C, there is a gradual increment in the photodegradation percentage, showing potential for the subsequent residence time of 60 minutes to possess a higher percentage. This suggests that longer the residence time, higher concentration phytochemicals are being extracted out from sample. A study conducted by Zullaikah *et al.,* [13], on the subcritical water extraction of phenolic compounds from Moringa oleifera leaves found that increasing the residence time from 5 to 20 minutes resulted in a significant increase in the total phenolic content of the extracts. The authors concluded that longer residence times allowed for more efficient extraction and recovery of the phenolic compounds.

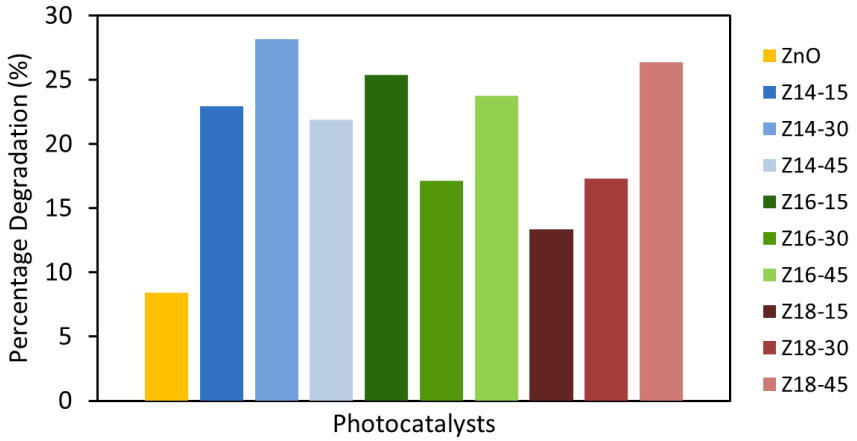

Fig. 1. Photodegradation of PCM with various photocatalysts

3.2 Ultraviolet-Visible Spectroscopy

The optical properties of the green synthesized BZnO were analysed by using UV-Vis spectroscopy. The optical band gap energy was evaluated for the photocatalysts, Z14-15, Z14-30 and Z14-45 by plotting Tauc's plot using the following Eq. (4).

$$(\alpha hv)^2 = A(hv - E_g) \tag{4}$$

where α, h, v, Eg and A are the absorption coefficient, Planck's constant light frequency, band gap energy and a constant respectively. Through extrapolation of the linear of the linear portion (Figure 2), the intercept at x-axis will give the band gap value which are 3.285, 3.290 and 3.310 eV for Z14-15, Z14-30 and Z14-45 as reported in Table 1, respectively. The band gap indicates an increasing trend with the increase of residence time. This suggests that the synthesis reaction is time dependent. Previous study by Mokhtar *et al.,* [14] has reported band gap values for BZnO to be 3.230 eV. In comparison, commercial ZnO has a band gap energy of 3.370 eV according to Jafarova & Orudzhev, [15].

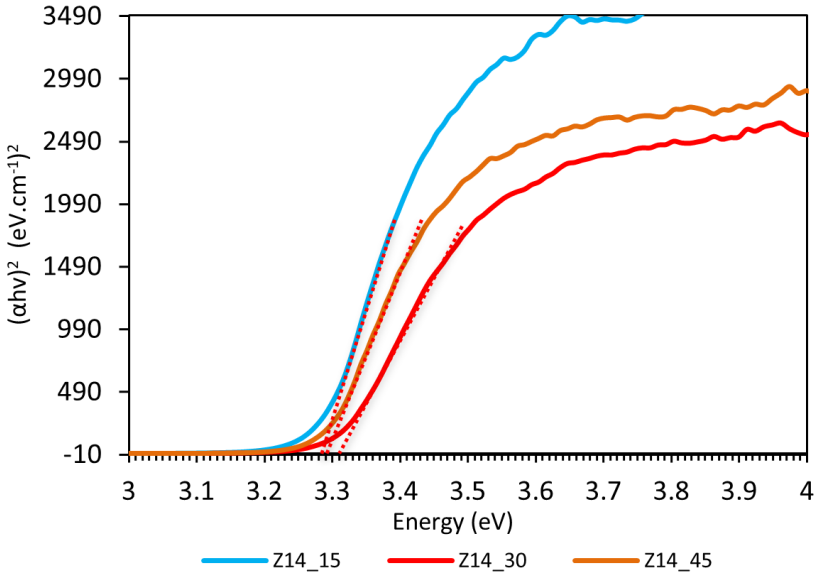

Fig. 2. Optical band gap energy

Table 1
Band gap energy of the green synthesized photocatalysts

Photocatalysts	Band gap energy (eV)
Z14-15	3.285
Z14-30	3.290
Z14-45	3.310

3.3 X-Ray Diffraction

The XRD pattern for Z14-30 is shown in Figure 3. Diffraction peaks of hexagonal wurtzite phase of Z14-30 represented at 31.72° (100), 34.54° (002), 36.21° (101), 47.46° (102), 56.72° (110), 63.89° (103), and 68.05° (201) planes corresponded to Joint Committee on Powder Diffraction Standards (JCPDS) card no. 36-1451 as per reported by Samuel *et al.,* [16]. However, there were two additional peaks observed (as indicated in blue) and this indicates that the synthesized ZnO NP are contaminated with impurities based on the study conducted by Gupta *et al.,* [17]. It can be deduced that the crystallinity of the sample is poor due to the broadness of the peaks and the intensity of the peaks were low. The crystallite size of Z14-30 can be calculated using the Scherrer formula as explained by Mursal *et al.,* [18] which is shown in Eq. (5), where D, k, λ, β and θ are denoted as average crystallite size, constant, full-width at half maximum (FWHM), wavelength and Bragg angle respectively.

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{5}$$

By using the formula, the average crystallite size obtained for Z14-30 is 46.45 nm. According to Mohamed Isa [19], the increase of peak intensity reveals enhancement of crystallinity.

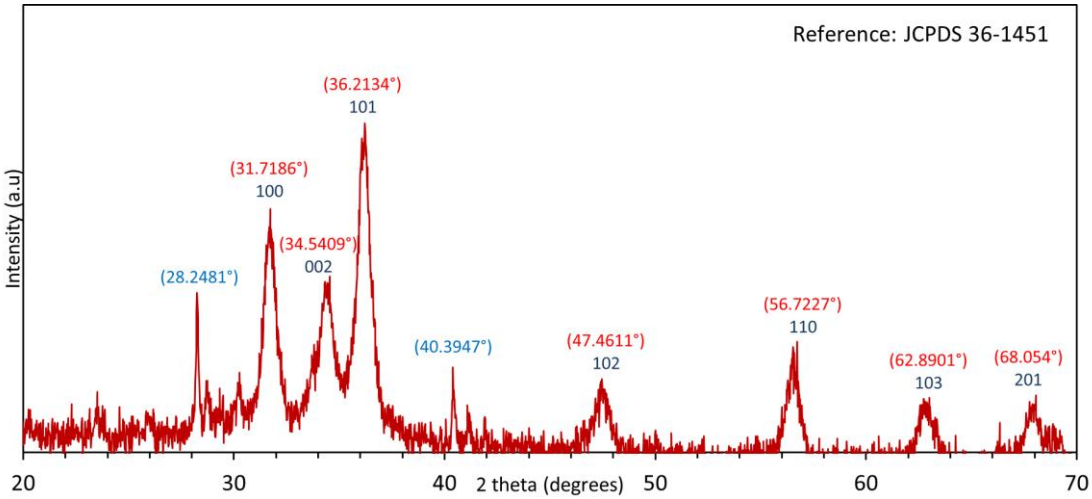

Fig. 3. XRD Pattern of synthesised Z14-30 photocatalysts

3.4 Surface Area and Pore Volume Analyzer

The surface area and pore characteristics of Z14-30 sample was determined using the Quantachrome Instrument Novatouch, with the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models employed for surface area and pore volume calculations, respectively. According to the IUPAC classification, the isotherm exhibited by the sample, as presented in Figure 4 indicates Type IV isotherm and this shows the sample is mesoporous as reported by Thommes *et al*., [20]. The condensed state interactions between molecules as well as the adsorbent-adsorptive interactions dictate the adsorption behaviour in mesopores. Pore condensation occurs in this instance after the first monolayer-multilayer adsorption on the mesopore walls, which follows the same path as the comparable portion of a Type II isotherm. The process by which a gas in a pore condenses to a liquid-like phase at a pressure p, that is lower than the bulk liquid's saturation pressure p_0, is known as pore condensation based on Thommes & Cychosz [21]. The surface area and pore volume results are 20.5702 m^2/g and 0.73188 cm^3/g respectively.

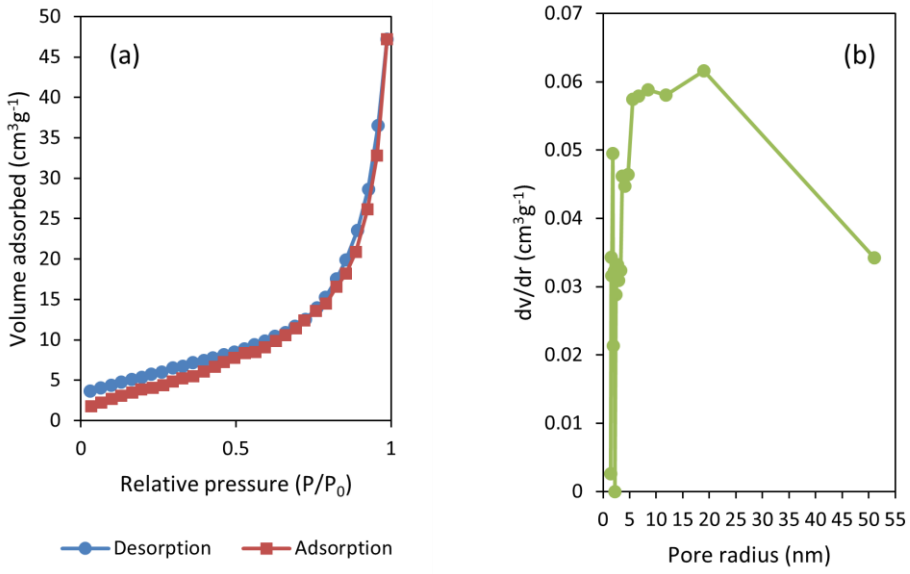

Fig. 4. Surface area and pore radius analysis for Z14-30. (a) Nitrogen adsorption-desorption isotherms. (b) Pore size distribution

4. Conclusions

The present study reveals that BPE-based zinc oxide was successfully synthesized at various SCW extraction conditions of temperature (140, 160 & 180 °C) and residence time (15, 30 & 45 minutes). The residence time shows more significant impact on the photocatalytic properties to degrade PCM under UVC light with the highest photodegradation percentage of 28.20% for BPE at 140 °C for 30 minutes which is much higher than the chemically synthesized ZnO. Therefore, the SCW extraction method proposed in this study has promises to be used for the green synthesis of BZnO NPs in the utilization of paracetamol photocatalytic degradation in wastewaters.

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