Reusability Performance of Zinc Oxide Nanoparticles for Photocatalytic Degradation of POME

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Abstract. Performance and reusability of different zinc oxide nanoparticles (ZnO-PVP and ZnO-PEG) for photocatalytic degradation of palm-mill oil effluent (POME) has been studied. The nanoparticles properties were characterised with fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The TEM results show that ZnO-PEG nanoparticles exhibit the smaller size than ZnO-PVP with less agglomeration. It was found that ZnO-PEG shows better effectiveness than ZnO-PVP in reducing turbidity, colour and increasing the dissolved oxygen (DO). By using two types of reusability methods: (a) oven drying (b) hot water rinsing, the oven drying method portrayed the most efficient route for POME treatment. This research would be a solution to the palm oil industry for photocatalyst recovering as well as reduction of the chemical usage in order to meet the development of advanced and greener technologies.

1 Introduction

While Malaysia relishes the profitable benefit from the massive production of palm oil, the impact of the production of a large volume of waste has also turn out to be a distressing consequent. Ominously, other than printing and dyeing wastewater, major water pollutants are contributing from the oil palm plantation. POME can be described as a thick brownish effluent which is rich in organic contaminants and discharged at the temperature range 80-90^{o}C[1]. Some approach had been done in order to minimize the environmental threat, which is by using biological treatment. Nonetheless, the brownish colour of the POME still

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cannot be diminished. Therefore, in order to protecting the environment, there were several regulatory controls over by the palm oil mills before they discharge the POME as in-scripted in the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations, 1977 promulgated under the Environmental Quality Act (EQA) 1974 and fallen under the jurisdiction of the Department of Environmental (DOE)[2]. Table 1 showed the standard discharged limit set by DOE and EQA[3].

Table 1. The standard discharged limit set by DOE and EQA.

Parameters	DOE discharged limit (1986 onwards)	Environmental Quality Act
pH	5.0	5.0-9.0
Temperature (^oC)	45	45
BOD_3 (mg/L)	50	100
COD (mg/L)	1000	1000
Total solids (mg/L)	1500	1500
Suspended solids (mg/L)	400	400
Oil and grease (mg/L)	50	50
Ammoniacal nitrogen (mg/L)	100	150
Total nitrogen (mg/L)	200	200

One of the promising approaches that can be implemented in order to degrade the colour of POME is by using photocatalytic degradation process [4]. During photocatalytic degradation process, hazardous organic chemical will be mineralized to become water, carbon dioxide and simple mineral acids [5]. Previously, Mondal & Sharma claimed that photocatalytic degradation is one of the promising methods due to their capability for fully mineralising the organic contaminants under mild conditions such as ambient temperature and pressure [6]. Other than that, Beydoun *et al.,* also reported that the advantage of the photocatalyst used in photocatalysis processes is they can be reused or recycled by their self-generated [7]. In addition, amongst all the methods for the photocatalytic degradation of dyes, ultraviolet (UV) irradiation had been acknowledged for its effectiveness in remove the pollutants and the environmental purification[8].

The performance of the photocatalyst such as ZnO nanoparticles in the photocatalysis process is undeniable especially in the utilization of coupling photocatalytic reactor and membrane. Recently, Desa *et al.,* and Chiranont *et al.,* reported that ZnO-PVP and ZnO-PEG nanoparticles have a great potential as a photocatalyst for industrial dye wastewater treatment [10-11]. Along with its steady wurtzite structure and wide bandgap (3.4 eV) compound semiconductor, ZnO nanoparticles has been generally used as a catalyst for dye wastewater treatment [11] By using ZnO as photocatalyst, Hairom *et al.,* managed to achieve 100% colour removal, 100% turbidity reduction, 100% suspended solid rejection by coupling the photocatalysis and the membrane filtration [12].

There were few researches concerning the reusability of photocatalyst in photocatalysis process. Most of them were succeed to reutilize the photocatalyst back in the remediation of the wastewater with a slightly reduced performance after a few cycle of consecutive run. For instance, Velmurugan *et al.,* had been undergo three consecutive run in order to study the photocatalyst reusability which is the ZnO nanocrystals. The photocatalyst did shown a remarkably photostability by degraded around 85.8% of dye after the third run [13]. Other than that, Gomez *et al.,* had been reutilize the photocatalyst by filtering, washed, and dried in air oven under 70^oC. The result did not portray a large different in term of degradation percentage nor the mineralization for the 1st and the 8th cycle [14]. It is very important for the industries as they can lower their chemical usage besides reducing their cost.

Hence, the main objective of this study is to elucidate the performance and reusability of zinc oxide nanoparticles in photocatalytic degradation of POME. The output from this study will help to provide the fundamental understanding of photodegradation process if they are applied within a membrane photocatalytic reactor for industrial wastewater treatment.

2 Materials and chemicals

2.1 Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized by precipitation method in a manner corresponding to Hairom *et al.,*[12]. They were prepared by added 0.15 M of oxalic acid dehydrate solution (obtained from R&M Marketing, Essex, UK) slowly into 0.1 M zinc acetate dehydrate solution (obtained from R&M Marketing, Essex, UK) with the molar ratio 1.5. They were conducted in the room temperature (25°C) under two conditions:

(i) vigorous stirring in the presence of polyethylene glycol (ZnO-PEG)
(ii) vigorous stirring in the presence of polyvinyl pyrrolidone (ZnO-PVP)

For the preparation of ZnO-PVP, 0.015g/L of PVP and 0.025 g/L of PEG (both obtained from R&M Marketing, Essex, UK) were transferred into the mixture respectively after 5 min of reaction. Then, the mixture was stirred for 12 hours under room temperature. The reaction yields precipitate which was filtered and dried at 100°C in oven for 1 hour to remove the excessive water. Subsequently, the precipitate was calcined in furnace under 550°C for 3 hours to remove all the impurities.

2.2 Characterization of ZnO nanoparticles

Chemical bond of the ZnO nanoparticles was characterized by using Fourier transform infrared spectroscopy (FTIR) spectrometer. FTIR spectra was recorded in transmittance mode in an Agilent Technologies Cary 600 series FTIR spectrometer at 4cm-1 of spectral resolution in the range 400-4000cm-1 with 16 scans. The FTIR spectra were obtained directly on the powdery sample repeating the acquisition for 2 times. Next, the purity and crystallinity of the ZnO-PVP and ZnO-PEG samples were analysed with X-ray diffractometer (XRD) (Bruker AXS GmbH model) by using the radiation of Cu Kα with λ = 1.5418Å at 40 kV and 40 mA. The data were collected at room temperature in the range of 2Θ = 10-80°, continuously with the scan rate of 0.025°. High-resolution images for the structural properties of ZnO nanoparticles was analysed by the high resolution transmission electron microscopy (TEM), 200 kV (JEOL JEM-ARM 200F). It offers the ultimate stability for imaging and analysis at the sub-nanometer scale.

2.3 POME sampling and preservation

Raw POME sample wastewater was directly collected from the effluent point of the ponding treatment system of palm oil mill located in Johor. The initial POME characteristics such as pH, dissolved oxygen (DO) turbidity and colour were analysed by using standard methods.

2.4 Photocatalytic degradation of POME

A UV lamp, predominately emit at 365 nm with the definite power of 15 W was employed as the light source. The schematic diagram of the laboratory-scale of this study is shown in Fig. 1. ZnO nanoparticles were added into the POME wastewater. Before starting the photocatalysis process, the mixture was well agitated at 300 rpm for 30 min in the dark to reach adsorption-desorption equilibrium of photocatalyst. The operation temperature was kept constant at room temperature (25°C) by immerse it inside the water bath. The treated POME wastewater was sampled by 5ml at the interval of 5 minutes and the mixed solution (POME and ZnO nanoparticles) was separated by using centrifuge Gyrozen 1736R model for 20 min. The treated wastewater was analysed in term of DO, turbidity and colour intensity. The color intensity was determined with DR 5000 UV-Vis Laboratory Spectrophotometer (Hach). DO was measured by using DO meter (Hach, H280G). The turbidity was analysed using turbidity meter respectively. The percentage of dye removal and DO increment were calculated according to Equation (1) and (2), respectively: C_o and C_t denote the colour intensity at time zero and at time t, respectively whereby DO_o and DO_t represent the dissolve oxygen at time zero and at time t, respectively.

$$Percentage\ of\ dye\ removal = C_o\text{-}C_t / C_o \times 100 \quad (1)$$

$$Percentage\ of\ DO\ increment = DO_o\text{-}DO_t / DO_o\ 100 \quad (2)$$

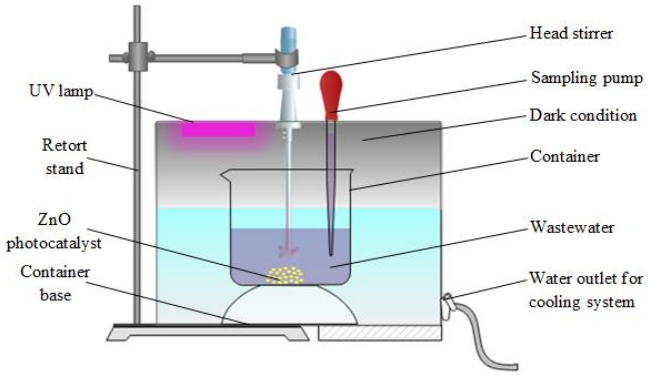

Fig. 1. The schematic diagram of photocatalysis process.

2.5 Reusability method of the ZnO nanoparticles

2.5.1 Oven drying method at 100°C

This method was employed by referring Subash et al. [15]. The photocatalyst was recovered after the photocatalysis process and was run with water. After that, it was dried at 100°C in air oven for 5h. Then, the photocatalyst was ready to use in the next run.

3.2.1 Hot water rinsing method

This method had been studied by Fathy et al. [16]. The catalyst was reutilized by washed it thoroughly using hot distilled water and dried at 80°C overnight for every cycle. Then, the photocatalyst was ready to use in the next run.

3 Results and discussions

3.1 Characterisation of ZnO nanoparticles

3.1.1 FTIR analysis of ZnO nanoparticles

The purity, nature and chemicals bonds of ZnO-PEG nanoparticles were shown in Fig. 2. The first figure, which is Fig. 2(a) indicates the FTIR pattern of ZnO-PEG. Prominent absorption peaks for ZnO-PEG were obtained at 3414.14, 1509, 877.55 and 632 cm^{-1}. The peaks at 3414.14 cm^{-1} and 877.55 cm^{-1} indicates the O-H stretching and deformation due to the adsorption of moisture from surrounding during synthesizing the photocatalyst. The peak observed at 632 cm^{-1} are correspond to Zn-O stretching and deformation vibration while the peak at 1509 cm^{-1} indicates the vibration and stretching of C=O bond. The second figure, which is Fig. 2(b) designates the FTIR pattern of ZnO-PVP. As can be seen in the figures, there were several characteristics absorption bands appearing in the range of 600-4000 cm^{-1} due to covalent bonds of PVP [17]. The peaks that appeared from 1068 and 612 cm^{-1} are attributed as the stretching of C-C rings of breathing of pyrrolidone. The absorption bands at 1634 cm^{-1} due to ZnO stretching and deformation vibration respectively [18].

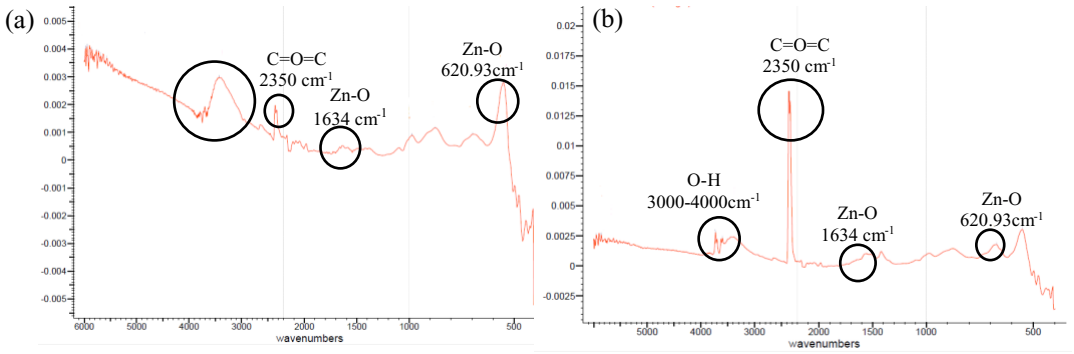

Fig. 2. IR spectra of: (a) 0.015g/L ZnO-PEG and (b) 0.025g/L ZnO-PVP.

The results showed that C=O bond existed in the range from 2327 until 2420 cm^{-1} in the sample as stated by Singh *et al.,* [19]. They also revealed that C=O group carboxylic derivatives present due to residue of zinc acetate used in reaction. It might ensue because of the precursor material and reaction product. The peaks located from 3000 until 4000 cm^{-1} represents as the vibration mode of O–H group of the moisture which make the bond arises and proved that ZnO-PVP samples has absorbed the existence water from surroundings [17].

3.1.2 XRD analysis of ZnO nanoparticles

The crystallinity of the ZnO nanoparticles had been shown by the XRD pattern in Fig. 3. The crystalline regions of the ZnO nanoparticles had been clearly observed at the range 30° to 40° (2θ values). The results of the XRD patterns corresponded well with the standard wurzite structure at planes ⟨1 0 0⟩, ⟨0 0 2⟩ and ⟨1 0 1⟩ [20]. Furthermore, it was found that the less intense peak at the range 40° to 80°, which indicates the high crystallinity of the different forms of ZnO.

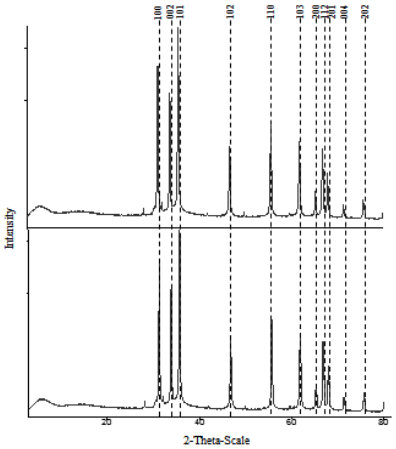

Fig. 3. XRD patterns of: (a) ZnO-PEG and (b) ZnO-PVP.

3.1.3 TEM analysis of ZnO nanoparticles

The morphology and size of the ZnO-PEG and ZnO-PVP nanoparticle were studied using TEM as shown in Fig. 4 The result showed a less agglomerated particle between two types of the ZnO nanoparticle. However, it was observed that the particle size of ZnO-PEG provided the smaller size compared to ZnO-PVP nanoparticles. The particle size of ZnO-PEG ranged from 60 to 150 nm and particle size of ZnO-PVP ranged from 80 to 150 nm respectively. According the result, ZnO-PEG give a smallest particle due to the high performance of the PEG as capping agent compared to PVP during the synthesis of the ZnO nanoparticle. The smaller size of the ZnO-PEG is due to the PEG capped performance during the synthesize of the zinc oxide nanoparticles as proven by Tshabalala *et al.,* and Rahim *et al.,* [22-23]

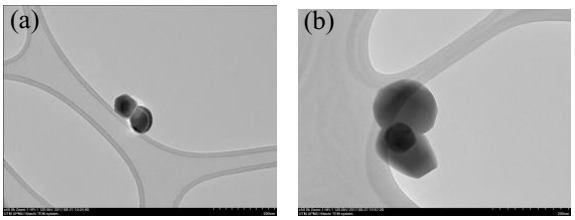

Fig.4. TEM image of: (a) ZnO-PEG and (b) ZnO-PVP.

3.2 Reusability performance of ZnO nanoparticles for photocatalytic degradation of POME

3.2.1 DO increment percentage analysis

From Fig. 5, the graph represented the maximum DO increment percentage of photocatalysis by ZnO nanoparticles. Based on the graph, it can be clearly observed that, there were enormous different between DO percentage for the 1st cycle and 2nd cycle. For the reusability methods, the oven drying method succeeded to demonstrate a higher performance compared than hot water rinsing method for both type of ZnO nanoparticles. This is might be the hot water could damage the chemical structure of the ZnO while

reutilizing it back. Despite to the fact that the performance of the ZnO nanoparticle had been reduced for the second time usage, they manage to increase the DO to the standard, which can be legally discharge to the environment, which is at the range 0.9-1.5 mg/L. Therefore, the treated wastewater could be discharged to environment and safe to aquatic life. From the analysed results, it could be deduced that the treated wastewater is safe to discharge to environment since their DO value is in the acceptable range [24].

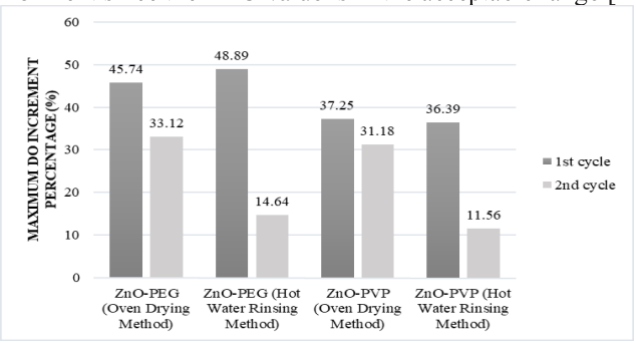

Fig. 5. Maximum DO increment percentage of photocatalysis by ZnO nanoparticles.

3.2.2 Turbidity reduction percentage analysis

The turbidity of treated wastewater is very relative to the percentage of dye degradation. Fig. 6 showed the maximum percentage of turbidity reduction on two different types of ZnO nanoparticles and two different types of reusability methods. It can be deduced that, by using oven drying method, it can provide a better performance in reducing turbidity of the wastewater for the ZnO-PEG and ZnO-PVP. In 2012, Carre *et al,* also claimed that UV photons excite ZnO, which then reacts with water molecules or hydroxide ion to produce hydroxyl radicals [25]. Then, colours were absorbed at the surface of ZnO; which then be degraded. Consequently, the degradation leads the breaking at least one of the conjugated bonds since the colour of wastewater formed by conjugated molecules. However, the turbidity might increase if the photocatalysts use beyond the optimum dosage resulting in fewer catalyst active sites available for photon absorption to generate $\square OH$ and O_2^- radicals [27–29].

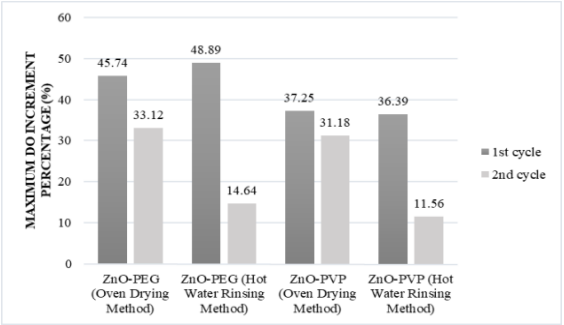

Fig. 6. Maximum turbidity reduction percentage of photocatalysis by ZnO nanoparticles.

3.2.3 Colour removal percentage analysis

Fig. 7 portrayed the comparison of experimental data of the colour removal percentage of POME by using two different types of ZnO nanoparticles by using two different types of reusability methods. The color removal results for both nanoparticles were exhibited the oven drying method could be applied as a method to reutilize back the nanoparticles. Even though the performance was reduced, it still managed to remove the colour almost 40%. Moreover, the method for the oven drying method was much simpler compared to the hot water rinsing method. The results portray the ability of the both photocatalyst to recover event though there might be slightly different of their performance. In addition, The smaller size of the ZnO-PEG really affected its capability in degrading the colour of POME due to higher effective surface area [11].

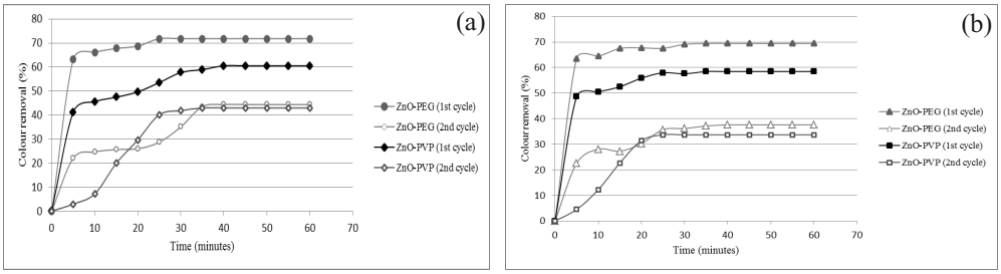

Fig. 7. Colour removal percentage by: (a) Oven drying method at 100°C and (b) Hot water rinsing method.

4 Conclusions

Both ZnO-PEG and ZnO-PVP were successfully synthesized and characterized. Their morphology, crystallinity, purity and chemical bond has been revealed by using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and transmission electron microscopy (TEM). ZnO-PEG exhibit smaller size of nanoparticles compared to ZnO-PVP at range 60-150nm. And the presence of capping agents; PEG and PVP obviously reduced the agglomerations and could be seen in their performance of reducing colour of POME. Comparing for both type of ZnO-nanoparticles, both of them have capability to be reused in the next run. However, ZnO-PEG still showing its effectiveness after the second cycle compared to ZnO-PVP. For the reusability method, it can be concluded that the most suitable method that can be apply for the reutilize the ZnO-nanoparticle is by using oven drying method at 100°C.

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