Enhanced Photodegradation of Phenol by ZnO Nanoparticles Synthesized through Sol-gel Method
(Peningkatan Fotopenguraian oleh Fenol dengan Sintesis ZnO Nano Zarah melalui Kaedah Sol-gel)

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ABSTRACT

Zinc oxide (ZnO) utilization in advanced oxidation process (AOP) via solar-photocatalytic process was a promising method for alternative treating wastewater containing phenol. The ZnO photocatalyst semiconductor was synthesized by sol-gel method. The morphology of the ZnO nanostructures was observed by using scanning electron microscope (SEM) and the crystallite phase of the ZnO was confirmed by x-ray diffraction (XRD). The objective of this study was to synthesis ZnO nanoparticles through a sol-gel method for application as a photocatalyst in the photodegradation of phenol under solar light irradiation. The photodegradation rate of phenol increased with the increasing of ZnO loading from 0.2 until 1.0 g. Only 2 h were required for synthesized ZnO to fully degrade the phenol. The synthesized ZnO are capable to totally degrade high initial concentration up until 45 mg L^{-1} within 6 h of reaction time. The photodegradation of phenol by ZnO are most favoured under the acidic condition (pH3) where the 100% removal achieved after 2 h of reaction. The mineralization of phenol was monitored through chemical oxygen demand (COD) reduction and 92.6% or removal was achieved. This study distinctly utilized natural sunlight as the sole sources of irradiation which safe, inexpensive; to initiate the photocatalyst for degradation of phenol.

Keywords: Phenol; photocatalyst; photocatalytic; sol-gel; zinc oxide

ABSTRAK

Penggunaan zink oksida (ZnO) dalam proses pengudaraan lanjutan (PPL) melalui proses sinaran suria fotopemangkin merupakan kaedah alternatif untuk merawat air buangan yang mengandungi fenol. Pemangkin semikonduktor ZnO disintesis melalui kaedah sol-gel. Bentuk permukaan struktur nano ZnO dikenal pasti menggunakan analisis SEM dan fasa hablur ZnO disahkan melalui analisis XRD. Objektif kajian ini adalah untuk mensintesis ZnO berstruktur nano melalui kaedah sol-gel bertujuan untuk diaplikasikan sebagai pemangkin dalam proses fotopenguraian fenol di bawah sinaran suria. Kadar fotopenguraian fenol meningkat dengan peningkatan jumlah ZnO bermula daripada 0.2 hingga 1.0 g. Tempoh masa 2 jam diperlukan untuk ZnO sintesis mengurai fenol sepenuhnya. ZnO sintesis mampu untuk menguraikan kepekatan fenol yang tinggi sehingga 45 mg L^{-1} dalam tempoh 6 jam masa tindak balas. Fotopenguraian fenol oleh ZnO sangat sesuai dalam keadaan berasid (pH3), dengan 100% penguraian dicatatkan selepas dua jam masa tindak balas. Penguraian lengkap fenol dikawal menerusi pengurangan keperluan oksigen lengkap (COD) dan sebanyak 92.6% penguraian dicapai. Kajian ini jelas menggunakan sinaran matahari semula jadi sebagai sumber sinaran tunggal yang selamat, murah dan mampu mengaktifkan pemangkin untuk penguraian fenol.

Kata kunci: Fenol; fotopemangkin; fotopemangkinan; sol-gel; zink oksida

INTRODUCTION

In recent years, concerns have been raised by several relevant bodies regarding the green technologies and energy conservation in wastewater treatment in order to reduce the existing environmental problem. The production of photocatalyst and its application in the process treatment are one of the best examples. Photocatalyst was semiconductor metal oxide such as TiO_2, ZnO, and CuO that are safe to be used in the environment during photocatalytic process. These semiconductors are able to utilize sunlight to initiate the photocatalytic reaction and consequently degrade the pollutant (Karunakaran & Dhanalakshmi 2008). The reaction initiates when there is

sufficient energy source radiated on the semiconductor, an electron-hole pair will be produced. Series of chemical reactions will occur and produce hydroxyl radical, superoxide ion and hydroperoxyl radical which are able to destroy the contaminant.

ZnO has gained attention for its suitability in environmental detoxification. ZnO which also known as the II-IV semiconductor (Bahera 2009) has a wide band energy bandgap (3.3 ev), (Tsay et al. 2010) high photosensitivity and stability (Sakthivel et al. 2003). Several studies have reported that the performances of ZnO as photocatalyst are more efficient compared to the commonly applied photocatalyst which is TiO_2 (Karunakaran & Dhanalakshmi

2008; Sakthivel et al. 2003). Although both semiconductors shared the same energy bandgap, Sakthivel et al. (2003) have proven that the absorption of the solar spectrum is in a larger fraction compare to TiO_2 (Sakthivel et al. 2003). Besides, ZnO has an excellent thermal stability at room temperature (Li et al. 2005) and it is available at low cost. Due to versatile characteristic and studies by others researchers (Li et al. 2005; Pardeshi & Patil 2008; Parida et al. 2006; Sakthivel et al. 2003; Tsay et al. 2010) ZnO is considered as a suitable semiconductor for the photocatalytic process.

Generally, there are various methods for ZnO synthesis that have been carried out such as homogeneous precipitation (Bhattacharjee et al. 2011), hydrothermal synthesis (Hsu & Wu 2005), microwave irradiated (Bahadur et al. 2010), spray pyrolysis (Jang et al. 2005), sol-gel method (Panwar 2009) and wet chemical synthesis (Bahera 2009). In this study, sol-gel method was used for the synthesis of ZnO, as this method is simple, rapid, low cost, which produces high purity end products (Lanje et al. 2013) with low temperature requirement for the synthesis process.

Phenol and its derivatives are one of the most abundant organic contaminants in wastewater and have been extensively used in various industries such as petroleum refining, steel production, pesticides, pharmaceuticals, coal gasification, pulp and paper and food processing (Chowdhury & Viraraghavan 2009). Phenol present as an intermediate in the industrial synthesis of products of adhesive and antiseptics (Alnaizy & Akgerman 2000). The natural degradation rate of phenol could occur through the different process depend on the condition. The natural degradation is usually considered as half-life. Phenol is able to degrade rapidly in air through gas phase radical reaction. The estimated half-life is 14.6 h (ATSDR 2008). In soil, phenol rapidly degrades but is hindered by the high concentrations of phenol and others chemicals. Meanwhile, phenol is persisting in water for a longer period. The half-life biodegradation is estimated less than a day in lake water and 9 days in estuarine water (ATSDR 2008). Typically, half-life for photooxidation by photochemically produced peroxyl radicals is 19 hours (ATSDR 2008). The permissible limit of phenol in water bodies is as low as 0.1 to 1.0 mg L^{-1}. Despite the low concentration limit, phenol treatments are becoming issues due to its toxicity, genotoxicity and extremely high potency of endocrine disrupting (Ahmed et al. 2010). The objectives of this study were to synthesize and characterize ZnO nanoparticles through sol-gel method, followed by evaluation of its photocatalytic activity through photodegradation of phenol.

MATERIALS AND METHODS

ZnO photocatalyst was prepared by sol gel method. Zinc acetate 2-hydrate (Riedel de Haën), oxalic acid (HmbG) and ethanol (HmbG) were used in this synthesis method. Zinc acetate was dissolved in ethanol and refluxed at 75°C for 30 min under vigorous stirring. Another solution was prepared by dissolving oxalic acid in ethanol. Then, the oxalic acid solution was added to precursor solution in drop wise. The final mixture was refluxed for another 1 h at 50°C. The gel formed was aged overnight. Finally, the gel was oven dried at 80°C for 6 h to obtain as-synthesized ZnO and calcined at 400°C for 3 h (Ba-Abbada et al. 2010). Figure 1 shows the flowchart of the ZnO synthesis method. Material characterization was carried out to confirm the properties of the photocatalysts.

Thermogravimetric analysis (TGA) 15 Mettler Toledo (Model: TGA-DSC 1) was used to analyse the as-synthesized ZnO in order to identify the thermal behavior and suitable calcination temperature. The scanning electron microscope (SEM) from JOEL, (Model: JSM- 6301F) was used to analyze the morphology features of the ZnO. The detailed information about the crystallite structure of the ZnO sample was measured by an X-ray diffraction (XRD) from JEOL (Model: JDX-3530M), which used Cu-K α radiation in 2θ range 10-100° at a scan speed of 5°min^{-1}.

The photocatalytic reactions were conducted in simple experimental set up as shown in Figure 2. Five different concentrations of phenol at 10, 20, 30, 45 and 55 mg L^{-1}, respectively, were prepared in a separate beaker to study effect of different initial concentrations of phenol. The pH of the solution remained at its natural pH around 6
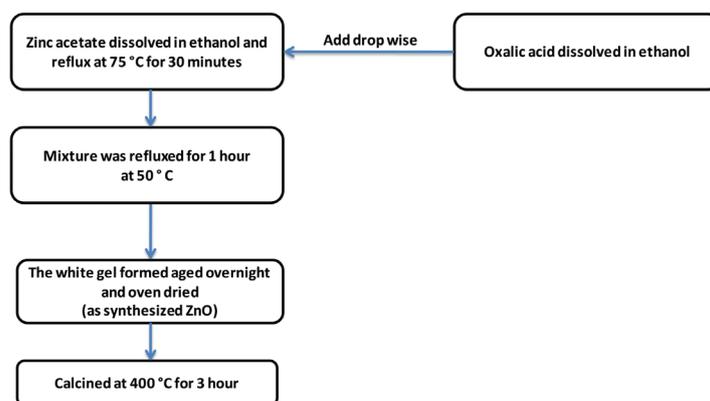
FIGURE 1. Flowchart of ZnO preparation method

for the entire experiment. However, the pH of the phenol solution was adjusted to the require pH value 3 and 12, respectively, in this study of the effect of pH. The effect of photocatalyst loading on the degradation of phenol was studied by varying the ZnO loading to the phenol solution. The dosages were 0.2, 0.4, 0.6 and 1.0 g, respectively. The initial concentration of phenol was fixed at 10 mg L^{-1}.

The photocatalytic degradation of phenol was further interpreted with Langmuir-Hinshelwood kinetic model. The pseudo-first order kinetics with respect to the concentration of the phenol in the bulk solution (C) shown in (1):

$$r = -\frac{dC}{dt} = k_{obs}C \qquad (1)$$

Integrating of this equation (with restriction of C = C$_0$ at t = 0, with C$_0$ being the initial concentrations in the bulk solution and t the reaction time) will become (2):

$$\ln\left(\frac{C_0}{C}\right) = k_{obs}C \qquad (2)$$

In which k$_{obs}$ is the apparent pseudo-first order rate constant and is affected by phenol concentration. Thus, the initial concentration data was utilized for the kinetic study. The values of k$_{obs}$ can be obtained directly from the regression analysis of the linear curve in the plot of ln (C$_0$/C) against t.

UV-Vis spectra of phenol solutions were measured by using UV-Vis spectrophotometer (Hitachi U-2800, Japan) from 200 to 800 nm. The maximum absorbance wavelength (λ_{max}) of phenol is 270 nm. The photocatalytic removal efficiency was calculated as in (3):

$$Removal\ efficiency = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (3)$$

where C$_t$ is the phenol concentration at reaction time t (h); and C$_0$ is the initial phenol concentration. Chemical oxygen demand (COD) parameter was measured with HACH DR2800 spectrophotometer.
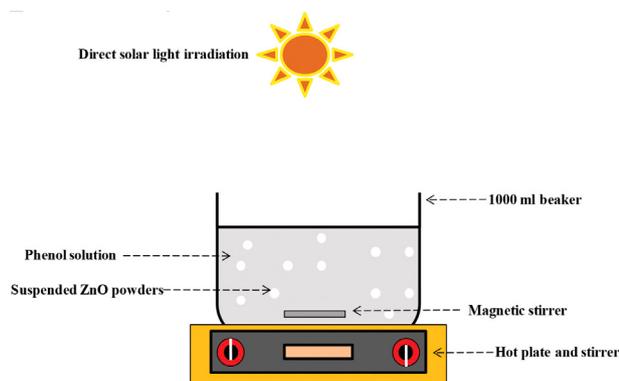

FIGURE 2. The experimental setup for solar photocatalytic treatment

RESULTS AND DISCUSSION

CHARACTERIZATION OF ZNO

Thermal gravimetric analysis (TGA)   Various methods were used to evaluate the synthesized ZnO in this study. Thermal gravimetric analysis (TGA) was applied to identify the thermal decomposition behavior of the as-synthesized sample. Figure 3 shows the TGA curve of the synthesized ZnO before calcination. Figure 3 indicates the weight loss of the synthesized ZnO from 29°C-600°C. The weight loss occurred in three steps. 29°C-160°C, 160°C-230°C and 230°C-370°C. The first step of weight loss was up to 160°C. This indicates the moisture of the sample has evolved and left around 82%.

The next step occurred within the temperature range of 160°C until 230°C due to the dehydration. Major weight loss occurred within these steps and the weight remained was 30.52 mg. The destruction of hydrocarbonate (CO$_3^{2-}$) took place at temperature 370°C and 72.41% ZnO weight left. The decomposition of the ZnO precursor was complete at this temperature and can be considered as the optimum calcination temperature for synthesized process. No further weight loss was observed from 430°C until 600°C. This plateau indicates the formation of the ZnO as a decomposition product. This suggested the suitable calcination temperature for ZnO synthesized through sol-gel method is within 400°C and above.
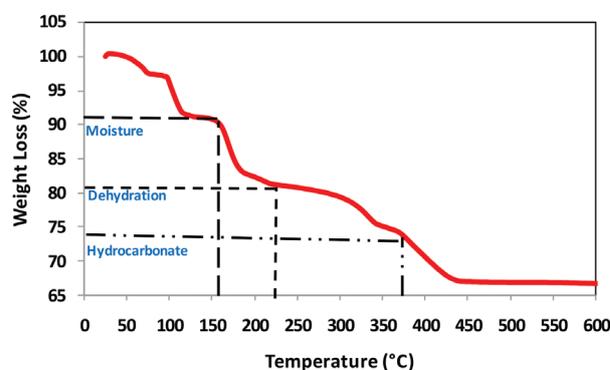

FIGURE 3. TG-DTG curves of ZnO photocatalyst

Crystallite phase of ZnO   The identification of the ZnO from the synthesis process was verified through XRD analysis. Besides, the crystal structure and the physical state of ZnO were also confirmed. Figure 4 shows the XRD patterns of the synthesized ZnO. There are nine diffraction peaks observed between 20° and 80°. The strongest characteristic peak was found at 2θ = 36.32° which corresponds to the plane (1 0 1). Based on phase identification analysis, the peak is indexed as wurtzite with the space group of P63mc (186). Burton et al. (2009) stated that the intensity of characteristic peaks influenced the crystallographic structure of the particles. All the characteristic peaks observed in ZnO are in good agreement

with the pure ZnO standard pattern taken from the Joint Committee of Powder Diffraction Standard (JCPDS) card No. 36-1451 (Raoufi 2013). The XRD results verified that the synthesis method applied in this study are effective in producing pure ZnO photocatalyst since there are no significant peaks that can be related to the impurities in the XRD pattern.
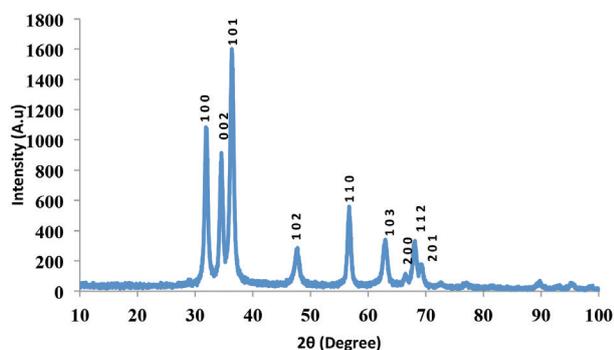

FIGURE 4. XRD pattern for ZnO

Morphology Figure 5(a) and 5(b) illustrates the SEM images of ZnO synthesized through sol-gel method. As shown in Figure 5(b), pseudo spherical shapes of ZnO are observed and some in rod-like shape can be clearly seen. It was also observed that the formation of the particles is not well-ordered in structures. Some of the particles are in long rod-like and others in big, short rod- like shape. The range of particles size for ZnO is 20 - 140 nm. The wide range of the particles sizes may be due to the growth of crystallite. The growth of crystallite on the surface of ZnO will affect the particles size. Thus, the chemical composition utilized for the synthesis of ZnO played important role in determining the size of the obtained ZnO. Larger particle size tends to form due to the viscous solvent used during the synthesis process (Rezapour & Telebian 2011). The viscosity of ethanol (1.074×10^{-3}) is higher that the viscosity of water (8.90×10^{-4}). Ethanol is able to enhance the rapid growth of ZnO nuclei and produces larger particles. Hayat et al. (2010) synthesized nano-ZnO by the modified sol-gel method and the average particles size for ZnO calcined at 400°C is in an average of 105 nm.

BET analysis Figure 6 shows the nitrogen adsorption-desorption isotherm of ZnO with a general type IV, and hysteresis loop resembled to type H3. The loop between 0.9 and 1.0 relative pressure indicate that the synthesized ZnO has a definite mesoporous structure. This suggests that most of the pores are mainly slit-pores (Zaki et al. 1987). Insert Figure 6 here

Based on the BJH analysis in Figure 7, the pore size distribution of the sample depicts a maximum at 2.03 nm indicating that majority of the pore size is 2.03 nm and the rest are above 2.03 nm. This result agrees well with the nitrogen adsorption-desorption isotherm which indicates that the ZnO obtained in this study is a mesoporous
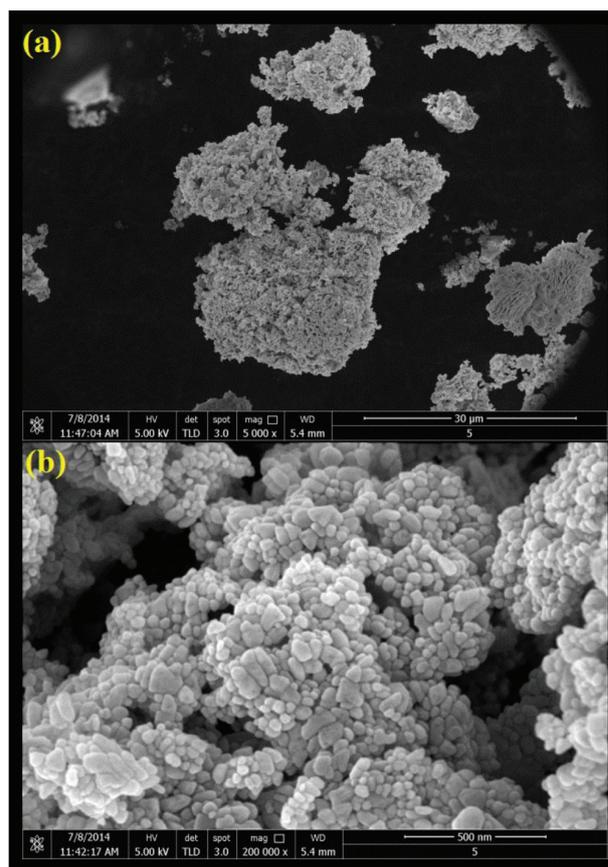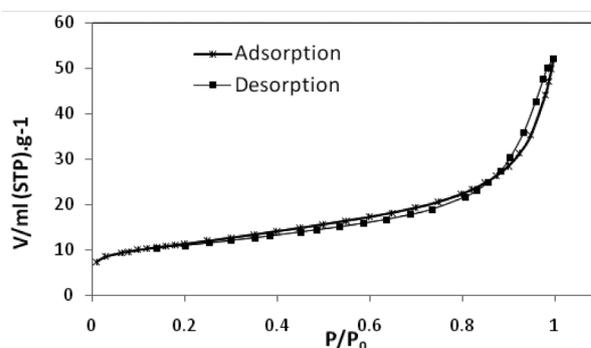

FIGURE 5. SEM micrograph for ZnO (a) 5000× (b) 200000×

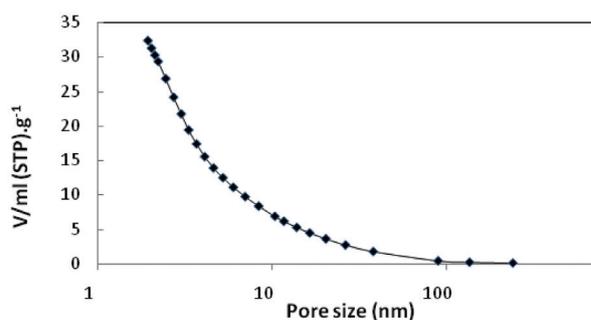FIGURE 6. Nitrogen adsorption-desorption isotherm of ZnO

FIGURE 7. BJH pore size distributions

material. The BET surface area obtained is 40.04 $m^2.g^{-1}$. This value is compatible with the surface area of the commercial 10 nm ZnO nanoparticles (Wang et al. 2007). Moreover, ZnO synthesized through sol-gel method has higher surface area compared to other method such as hydrothermal which is 4.5 m^2 g^{-1} (Pudukudy & Yaakob 2013).

PHOTOCATALYTIC OF PHENOL

Effect of catalyst loading   In order to evaluate the photocatalytic activity of the synthesized ZnO in this study, it was used as a photocatalyst in the photodegradation of phenol under solar light irradiation. Effect of different catalyst loading was investigated. The dosage of ZnO was varied from 0.2 to 1.0 g in this study. In order to verify the role of the photocatalyst in the photocatalytic process, phenol solution alone was evaluated under the same condition without the addition of ZnO (0.0 g). Based on Figure 8(a), the photodegradation of phenol increased as the catalyst loading increased. For high catalyst loading at 0.8 and 1.0 g, the reaction time required for the total removal to achieve was 1.5 h. Meanwhile, for 0.2 and 0.4 g catalyst loading, 2 h were needed for total removal of phenol. The increase of catalyst loading would provide more active site and this condition will lead to higher adsorption of the phenol molecule onto the surface of ZnO. This could be due to the photocatalytic processes firstly occur with the adsorption of pollutants on the catalyst surface. The hydroxyl radical will then form on the surface of the catalyst after received the irradiation of sunlight (Zulfakar et al. 2011). Phenol molecules will adsorb on the active sites of ZnO surface. Thus, the high adsorption capacity at the surface is important and it promotes photodegradation (Yusoff et al. 2014). Without the photocatalyst (ZnO), the photocatalytic process does not occur. The presence of sunlight only allowed the photolytic process to occur. It was observed that the photolytic that occurred for 2 h are not enough to degrade the phenol molecules. Thus, this proved that photocatalyst played a crucial role in the degradation of phenol through photocatalytic process.

Figure 8(b) shows that the kinetic model followed the pseudo- first order of Langmuir-Hinshelwood kinetic model. From Figure 8, the photodegradation rate at 0.2, 0.4, 0.8 and 1.0 g catalyst loading is 8.53, 12.44, 14.10 and 14.92 mg L^{-1} h^{-1}, respectively. Therefore, higher photodegradation rate was observed in higher catalyst loading as all the phenol molecules were able to occupy at the surface of ZnO. Lathasree et al. (2004) stated that the degradation rate of o-chlorophenol increased as the loading of ZnO increased.

Effect of phenol concentration   The results obtained from the photocatalytic degradation of phenol by ZnO at different initial concentration are presented in Figure 9(a). Interestingly, the degradation efficiency of phenol by ZnO is excellent. From Figure 9(a), it shows that only within 6 h of contact time, phenol molecules are able to be totally degraded at the initial concentration of 45 mg L^{-1}.

Rapid degradation was recorded in 10 mg L^{-1} of phenol concentration. Only 2 h are needed for the phenol molecule to be totally degraded. This result is comparable with previous studies reported by Rezapour and Telebian (2011) where total degradation of 10 mg L^{-1} of phenol was able to achieve in less than 3 h under UV light irradiation. Moreover, it can be observed that, after 3 h under solar irradiation, more than 50% of phenol is removed except for 50 mg L^{-1}. The average removal percentage recorded after 3 h for 20, 30 and 40 mg L^{-1} are 86.4%, 60.25% and 51.5 %, respectively.

For the highest phenol concentration (55 mg L^{-1}), although total removal could not be achieved after 6 h, it could reach 84.2% of degradation. As a comparison, the degradation of 2, 4-dichlorphenol was studied by Ba-Abbad et al. (2010) with ZnO prepared by sol gel method. With the optimum loading of ZnO (2 g/l), 50 mg L^{-1} of 2, 4-dichlorophenol was able to be degraded within 60 min. In general, therefore, it seems that an extra reaction time is required in order, for all the phenol molecules to react with the hydroxyl radical therefore the total degradation
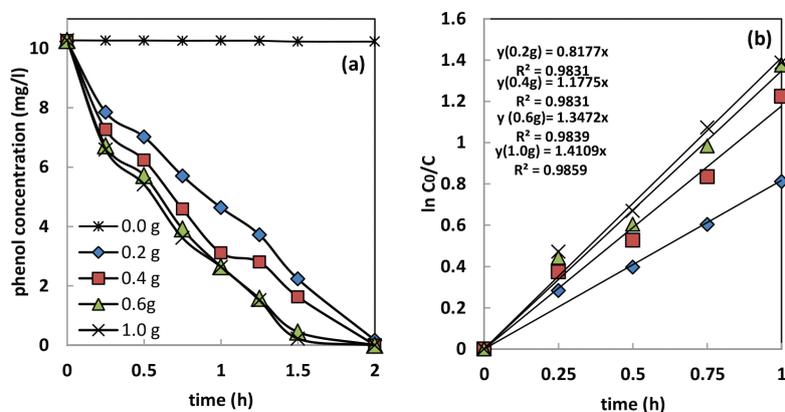

FIGURE 8. (a) Photocatalytic degradation of phenol by ZnO with different catalyst loading and (b) Kinetic studies for effect of catalyst loading

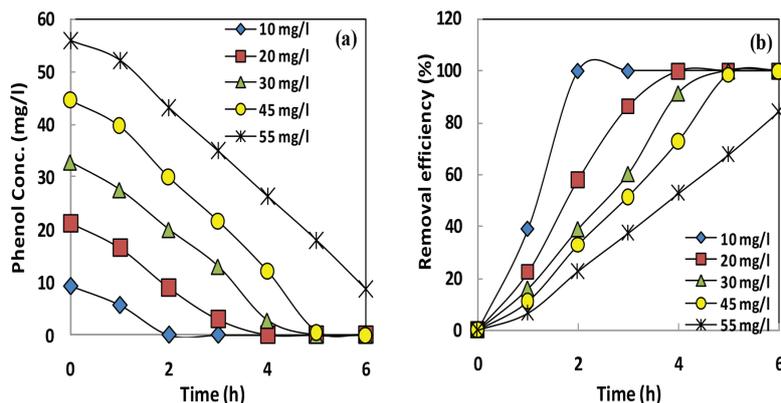(Phenol concentration = 10 mg L^{-1}, Initial pH= 6.2)

FIGURE 9. (a) Photocatalytic degradation of phenol by ZnO at different initial
concentration and (b) Percentage removal of phenol

(Catalyst loading = 0.6 g, Initial pH = 6.2)

can be achieved in higher concentration. Benhebal et al. (2013) studied the degradation of phenol and benzoic acid by ZnO synthesized through sol-gel method. After 120 min under irradiation of UV light, 69.75% of phenol and 67.98% of benzoic acid were degraded.

Effect of pH Figure 10(a) shows the photocatalytic degradation of phenol under different pH conditions. The most effective pH condition is pH3 and unadjusted pH (pH6). The phenol molecules required only 2 h to achieve total degradation in pH3 and unadjusted pH (pH6). Figure 10(b) indicates the percentage of phenol degradation at different pH conditions. After 1 h, around 88% of degradation was recorded in acidic condition (pH3) and 60.7% in natural condition. This can be explained by the ZnO surface which is positively charge based on point of zero charge and the existing of phenol in neutral species at pH3-7. In this condition, phenol molecules are not dissociated or formed aggregates (Pardeshi & Patil 2008). Thus, maximum numbers of phenol molecules are able to absorb on ZnO photocatalyst and consequently increase the photodegradation of phenol.

Besides, the effective photocatalytic degradation occurred in pH3 and pH6 is due to the electrostatic interaction ZnO and phenol molecules (Ahmed et al. 2010). When the pH of the phenol is lowered than the point zero charges of the ZnO, the surface of ZnO will be more positively charged. Thus, the attractive forces are stronger between the surface of ZnO and phenol molecules and consequently degraded it faster.

Mineralization of phenol The mineralization of phenol can be monitored through chemical oxygen demand (COD) in order to totally mineralize the molecules into water and carbon dioxide. The complete mineralization is crucial to ensure the end product of the treatment is clean and non-hazardous. This is due to the some of the intermediates by-product formed through the mineralization of phenol is harmful such as resorcinol, catechol, and hydroquinone (Valtierra et al. 2005). With the present of irradiation, the phenol molecules react with photogenerated holes or with photoinduced •OH radicals which resulted in producing a number of hydroxylated reaction intermediates (Sobczyński et al. 2004). Several researchers have studied the mineralization of phenol (Chen & Jay 1999; Pardeshi & Patil 2008); however the pathways subjected to the full mechanism and its derivatives have yet been established (Sobczyński et al. 2004).
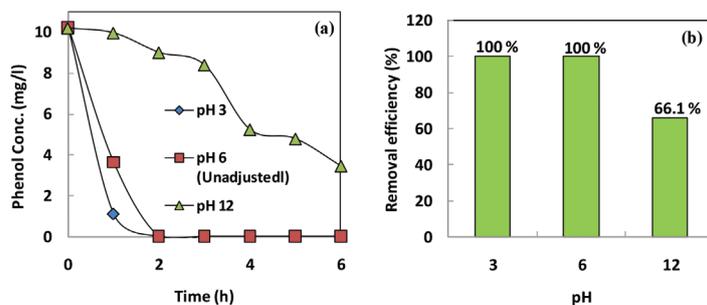

FIGURE 10. (a) Photocatalytic degradation of phenol in different pH and
(b) Photodegradation percentage

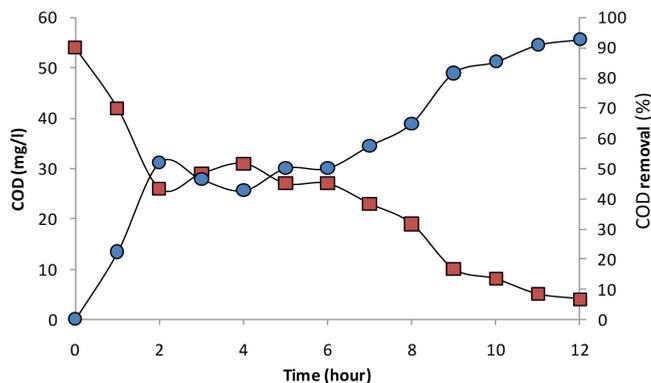(Phenol concentration = 10 mg L^{-1}, Catalyst loading = 0.6g)

FIGURE 11. (a) COD monitoring in photocatalytic degradation of phenol and percentage of degradation

(Phenol concentration = 10 mg L^{-1}, Catalyst loading = 0.6 g)

Based on Figure 11, it was observed that the COD value of the phenol are decreased which indicates the mineralization of the phenol molecules and intermediates. The formation of phenol intermediates is observed when the colour of the phenol solution changed from milky solution to slightly brown solution. This occurred during the 3rd until 8th hour of reaction time. The brown colour indicated the formation of the benzoquinone and hydroquinone which are colored intermediates (Pardhesi & Patil 2008). Besides, it was also due to the mixture of other various intermediates such as catechol. This observation supports the slightly increasing of COD value during the 3rd and 4th hour. Consequently, the COD continued to decrease and reached 92.6% of removal until the 12th hour of reaction time.

CONCLUSION

ZnO photocatalyst was successfully synthesized through sol-gel method. The particles shape formed are in rod-like shape with different diameter. The size range of ZnO was within 20 -140 nm. The synthesized ZnO showed enhanced photocatalytic activity in the photodegradation of phenol. Catalyst loading is directly proportional to the photodegradation rate of phenol within 2 h of reaction. The solar-photocatalytic study followed Langmuir-Hinshelwood kinetic model. ZnO is capable to achieve total degradation of phenol until 45 mg L^{-1} of initial phenol concentration. The fastest degradation was achieved in acidic condition (pH3) followed by unadjusted condition (pH6). In alkaline condition, the percentage degradation recorded was 66.1%. Higher concentration of phenol can be totally mineralized by sol-gel synthesized ZnO, where the removal of the COD value is 92.6% after 12th hour reaction.

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