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Degradation of phenol through solar-photocatalytic treatment by zinc oxide in aqueous solution

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ABSTRACT

Phenol-containing wastewater is only allowed in a very small amount either in sewage or industrial effluent due to the hazardous effect towards the environment. The objective of this study was to investigate the photocatalytic degradation of phenol with zinc oxide as photocatalyst under solar light irradiation. The operating parameters such as initial phenol concentration, catalyst loading, pH, effect of aeration, H_2O_2 dosage and effect of solar light irradiation were investigated. The results obtained were fitted well with the Langmuir–Hinshelwood kinetic model. The percentage of phenol removal increased with the increase of irradiation time, catalyst loading, under weakly acidic condition, with the aid of aeration and addition of 0.1 M of H_2O_2. Analysis of UV–vis and chemical oxygen demand attested the complete degradation of phenol concentration and possibility for mineralization.

Keywords: Photocatalytic degradation; Phenol; Zinc oxide; Kinetics study

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1. Introduction

There are increasing concerns on the significance of phenols as an organic contaminant from industrial wastewater such as pesticides, coal conversion, polymeric resin, petrochemical industry, pharmaceutical and oil refinery industries [1]. Phenol can be threatening to human beings and ecosystems due to its biorecalcitrant and acute toxicity behaviour [2]. The effluent wastewater that contains phenol compounds need to be treated until fulfilling the requirement enacted by the Malaysia Department of Environmental Quality Act 1974 (Sewage and Industrial Effluent), which is 0.001 mg/l for Standard A and 1.0 mg/l for Standard B. There are some limitations of phenol treatment via conventional wastewater treatment. For instance, research by Prieto et al. [3] in biological treatment, a longer time which was 40 h required to degrade 200 mg/l of phenol [3]. Previous studies have also shown that the limitation of biochemical treatment which required the suitable temperature and pH to produce an activated sludge at the end of treatment [4]. While, another pollution is tended to occur after treatment with activated carbon as it only involves pollutant phase transfer [5].

Thus, an initiative method for phenol degradation in wastewater was discovered which is through the Advanced oxidation process (AOP) as suggested by Alnaizy and Akgerman [6]. AOP is the aqueous phase oxidation process which involves the generation and

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use of the hydroxyl free radical ($OH^\bullet$) as a strong oxidant to destroy compounds that cannot be oxidized by other conventional oxidants [7]. Among various processes in AOP's, photocatalytic process showed a great potential. Previous study by Fujishima et al. [8] has shown that photocatalytic process occurs when there is an interaction between the solid semiconductor and photons with the appropriate wavelength. Teh and Mohamed [9] reviewed that photocatalytic only involves low-operation temperature, operation cost and energy consumption.

Karunakaran and Dhanalakshmi [10] conducted a series of trial of photodegradation of phenol with different types of semiconductors such as ZnO, TiO_2, Fe_2O_3 and CuO to explore their efficiencies. Thongsuriwong et al. [11] claimed that each of these semiconductors was able to reduce the energy consumption as the light irradiation being utilized to activate their photocatalytic reactions. Each photocatalyst has its unique ability in the environmental detoxification. Titanium dioxide (TiO_2) is the most widely studied photocatalyst for treatment of various pollutant compounds [8,9,12–16]. Recently, ZnO received a lot of attention for further investigation as photocatalyst due to the energy band gap value ($E_g = 3.32$ eV), which is similar to the TiO_2 [16]. Besides that, it also has large free-exciton binding energy (60 mV), wide range of resistivity and high carrier mobility [17]. Zinc oxide is an inexpensive semiconductor with excellent and thermal stability at room temperature [18]. It has a distinctive optoelectronic, catalytic, photochemical properties [19] as well as non-toxic and high transparency in VIS/near IR spectral region [20]. For the above reason, ZnO is considered to be more suitable for photocatalytic degradation of organic pollutants.

Preliminary studies of phenol photodegradation by Hayat et al. [19], Lee and Chu [21] and Salacies et al. [22] were mostly conducted under the ultraviolet light irradiation. In real application, it is not feasible to supply ultraviolet light irradiation for the huge amount of wastewater containing phenol. Furthermore, it is also not efficient in term of economy, as it will require a huge cost just to supply the irradiation. As in countries where there is sufficient natural sunlight irradiation throughout the year, it has become more preferable and economically efficient to apply the solar-photocatalytic treatment. The objective of this study was to examine the solar-photocatalytic degradation of phenol with ZnO as a photocatalyst. Parameters that promoted the performances of photodegradation of phenol were distinctively studied in this paper. The UV–vis analysis was used to prove the complete degradation of phenol concentration and chemical oxygen demand (COD) for the possibility of mineralization.

2. Materials and methods

2.1. Chemical

Phenol crystallized 99% (detached crystal) (108-95-2) from Panreac and zinc oxide (extra pure) (1314-13-2) was purchased from HmbG Chemical, while hydrogen peroxide (H_2O_2) (7722-84-1) was from Bendosen. The stock solutions of phenol were prepared by dissolving in ultrapure water. Then, the samples for photocatalytic process were from the dilution of the stock solution. All the above chemicals were used without further purification. Ultrapure water was used throughout this work.

2.2. Photocatalytic procedure

The photoreduction of phenol was performed with 500 ml of 50 mg/l of phenol solution in 1,000 ml beaker being contacted with 0.6 g of semiconductor photocatalyst ZnO. The pH of the solution remained at its natural pH around 6.2 for the entire experiment. The solutions were exposed to sunlight. In order to assure the similar sunlight irradiation, the works were carried out at the same time and duration for every experiment. The complete irradiation treatment usually takes about 6 h from 10 am until 4 pm.

The effects of initial concentration on the photocatalytic activity were studied by varying the initial phenol concentration at 10 mg/l, up to 100 mg/l. The solutions were irradiated under sunlight for 6 h. The catalyst loading was maintained at 0.6 g. pH of the solution was not adjusted. Samplings were performed by taking 10 ml of sample at interval time of 0, 0.5, 1.0, 1.5, 2, 3, 4, 5 and 6 h throughout the irradiation process.

Influence of photocatalyst loading on degradation of phenol was investigated by varying the amount of ZnO being added to the phenol solution. The dosages were 0.2, 0.6 and 1.0 g, respectively. The initial concentration of phenol was fixed at 50 mg/l.

Two separate experiments in different places were conducted at the same time in order to identify the effect of degradation with and without sunlight irradiation. By using 50 mg/l of phenol and 0.6 g ZnO, the experiments were placed outside under the sunlight and another one in the room without exposed to sunlight.

To study the effect of pH, solutions at pH 1, pH 3, pH 6 (natural), pH 9 and pH 12 were prepared. The pH of the phenol solutions was adjusted by using 1 M H_2SO_4 and 1 M NaOH.

In order to investigate the effect of aeration in photodegradation of phenol, separated experiment was set-up. One of the set-up was equipped with an air pump to provide extra oxygen via aeration and another one without aeration. Other conditions were remained the same.

The effects of added H_2O_2 on phenol degradation were examined in order to identify the efficiency of photocatalytic oxidation of phenol in aqueous solution in the presence of H_2O_2. The phenol solutions were varied such as phenol/ZnO, phenol/ZnO/H_2O_2 and phenol/H_2O_2. The concentration of phenol and catalyst loading is constant at 50 mg/l and 0.6 g, respectively, while, the concentrations of H_2O_2 were varied at 0.01, 0.1 and 1.0 M of H_2O_2.

2.3. Analytical procedure

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 degradation efficiency was calculated as the following:

$$\text{Photodegradation efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (1)$$

where C_t is the phenol concentration at reaction time t (h) and C_0 is the initial phenol concentration.

COD parameter was measured with HACH DR2800 spectrophotometer.

3. Results and discussion

3.1. Effect of solar irradiation

Solar irradiation plays an important role in the photocatalytic process in order to generate hydroxyl radicals. As shown in Fig. 1, the removal efficiency of phenol was recorded only 3% without exposure to the solar irradiation. The removal of phenol was due to the adsorption mechanism on the surface of ZnO [23]. Since the removals concentration was very low, the adsorption capacity was insignificant. However, in the presence of sunlight, 100% removal was recorded within 6 h of reaction time. Under the sunlight irradiation, more hydroxyl free radical ($OH^{\bullet}$) was produced due to the increasing amount of absorbed photons, Thus, enhanced the photodegradation of phenol [24].

The photocatalytic reaction is initiated when the radiation energy is equal to or higher than the band-gap energy of the semiconductor which causes the electron excited from the valance band to the conduction band, and generated positive hole band (h+) [12]. Excited states electron (e^-) will involve in reduction process [25] to produce superoxide radical anions ($O_2^{\bullet-}$). While, hole band (h+) will diffuse to the surface and react with adsorbed water molecules to form hydroxyl radical ($OH^{\bullet}$).

3.2. Effect of initial concentration

Fig. 2 depicts the effects of initial concentration on the photodegradation of phenol by suspension of ZnO. It is apparent that the degradation of phenol concentration shows identical trend as phenol at different initial concentrations decreased with the reaction time.

Based on the result, the low-concentration ranges indicate more efficient photocatalytic degradation of phenol. The 10 mg/l of phenol recorded 100% removal efficiency within 2 h of reaction time. Chiou et al. [13] also observed the same situation as more than 90% of phenols were photodegraded at the lowest initial concentration in their study (0.13 mM). However, further

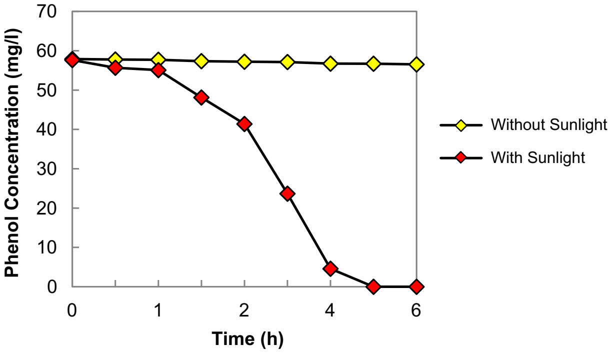

Fig. 1. Photocatalytic degradation of phenol with and without sunlight (phenol initial concentration = 50mg/l, ZnO catalyst loading = 0.6g, initial pH = 6.2).

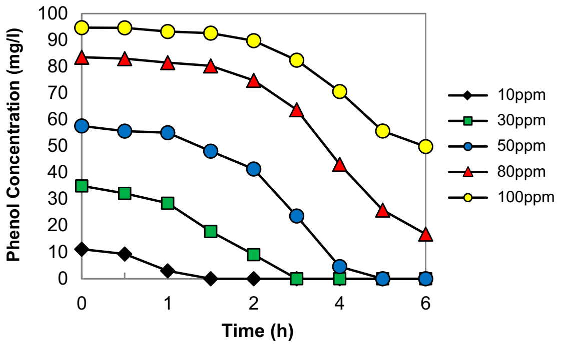

Fig. 2. Photocatalytic degradation of phenol with different initial concentration (ZnO catalyst loading = 0.6g, initial pH = 6.2).

increase in phenol concentration up to 0.7 mM (66 mg/l) inhibited the degradation process [13].

Photocatalytic processes firstly occur with the adsorption of pollutants on the catalyst surface (ZnO). With irradiation of sunlight, hydroxyl radical will form on the surface of catalyst [14]. Phenol molecules will adsorb on the active sites of ZnO surface. Thus, the high adsorption capacity at the surface of the catalyst is important and it promotes photodegradation. In this matter, as the initial concentration of phenol increases, the amount of phenol molecules being adsorbed on ZnO will also increase. However, the irradiation intensity and the total number of hydroxyl radical formed remains the same. Thus, the relative number of hydroxyl radical to the number of phenol molecules decreases and lower the degradation rate [14].

Fig. 3 illustrates the UV–vis absorption spectra of 50 mg/l of phenol using 0.6 g ZnO as photocatalyst during photocatalytic degradation. Only one major absorbance peak can be seen at 270 nm in the UV–vis spectra of phenol. The absorbance peak located at the UV region due to the colourless characteristic of phenol. The intensity of maximum absorbance peaks declined until to the baseline of the spectra within 6 h of solar light irradiation which indicates degradation of the benzene ring by hydroxyl radicals. UV–vis absorption spectra analysis by Ba-Abbada et al. [26] showed that the absorption peak of 2, 4-dichlorophenol gradually decreased at the adsorption peak 285 nm indicated the decomposition of organic compounds.

3.3. Effect of catalyst loading

Another critical parameter to identify the photocatalytic degradation capability is the catalyst loading. The dosage of ZnO was varied from 0.2 to 1.0 g in this study.

As shown in Fig. 4, degradation of phenol increased as the amount of catalyst loading increased. The increase of catalyst loading would provide a more active site and this led to higher adsorption of the phenol molecule onto the surface of ZnO. Therefore, higher degradation rate was observed in higher catalyst loading as all the phenol molecules were able to occupy at the surface of ZnO [14]. The overall photodegradation rate increased with an increase in the weight of catalyst load. According to Lathasree et al. [27], the degradation rate of o-chlorophenol increased as the loading of ZnO increased up to optimum amount varied in the range of 1.0 g/l up to 3.0 g/l.

3.4. Effect of pH

Fig. 5 shows the reduction of phenol concentration in different pH conditions (pH 1–12) under solar-photocatalytic degradation process. As shown in Fig. 5, photocatalytic degradation of phenol was almost zero in the solution with pH 1 because ZnO was dissolved under acidic condition. It was observed that the removal efficiency of phenol under solar-photocatalytic degradation was higher in weakly acidic solutions compared to alkaline solutions. From the reaction of oxygen (O_2) with excited states electron (e^-) in conduction band, $O_2^{\bullet -}$ was produces and consequently will react with hydrogen ion (H^+) to produce $^{\bullet}HO_2$ [25]. Amount of $^{\bullet}HO_2$ will increase as the pH of the phenol solution lower than the pK_a of $^{\bullet}HO_2$ (pKa = 4.88). As the increase of $^{\bullet}HO_2$, more $OH^{\bullet}$ will formed which promoted the degradation of phenol [28].

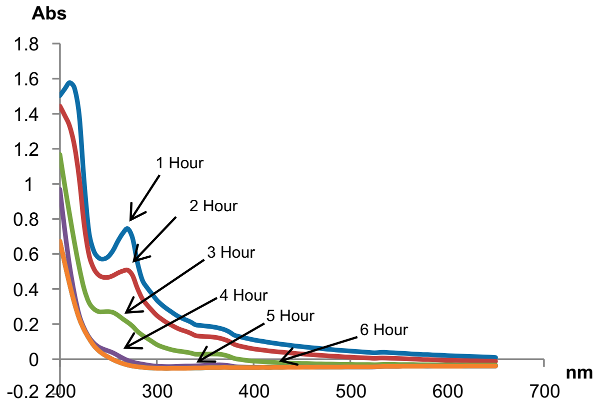

Fig. 3. UV–vis spectrum analysis of photocatalytic degradation of phenol (phenol initial concentration = 50mg/l, ZnO catalyst loading = 0.6g, initial pH = 6.2).

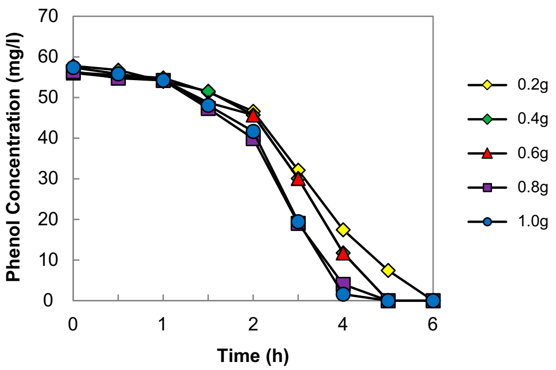

Fig. 4. Photocatalytic degradation of phenol with different catalyst loading (phenol initial concentration = 50mg/l, initial pH = 6.2).

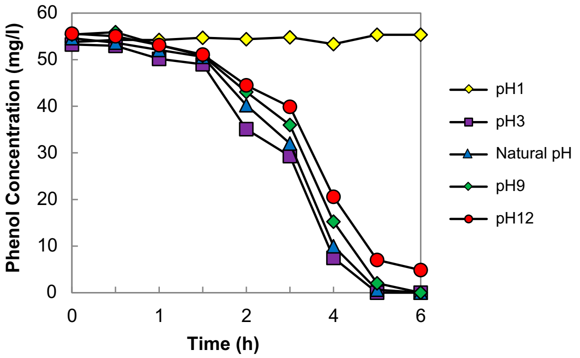

Fig. 5. Photocatalytic degradation of phenol with different pH (phenol initial concentration = 50mg/l, ZnO catalyst loading = 0.6g).

The degradation of phenol performed better in the solution without pH adjustment (basic pH solution) compared to alkaline solution. Complete removals were recorded for solution of pH 3, 9 and basic condition at the end of reaction time (6 h). However, during the 5th hour of solar irradiation, the degradation at natural pH solution were higher which was, 99%, compare to 97% for pH 3 and 96% for pH 9. According to the research conducted by Wang et al. [15], 0.1 mM of 2-chlorophenols decomposition was above 95% efficiency in 140 min at acidic and neutral conditions. Only about 60% removal efficiency recorded at pH 11. A previous study by Wang et al. [28] using TiO_2 as catalyst also reported that the decomposition of o-nitrophenol and p-nitrophenol was better under acidic conditions.

3.5. Effect of aeration

Effect of aeration on photocatalytic degradation of phenol also studied and the result is shown in Fig. 6. It was observed that higher removal efficiency in all of the studied concentrations with the aid of aeration compared to non-aeration. Although the difference was not as high as without aeration but it is still improving the performances with the aid of aeration. The photocatalytic degradation rates with aeration enhanced removal efficiency as with the aid of aeration. With the aid of aeration, the superoxide ion ($^{\bullet}O_2^-$) was formed through the reduction process on the surface of ZnO [29]. The superoxide ions may act as oxygen nucleophile agents [21] that able to attack phenol and produce reduction products [22]. Through aeration, more oxygen is available as electron acceptor and more superoxide ions are produced. Thus, the degradation rate of phenol increased.

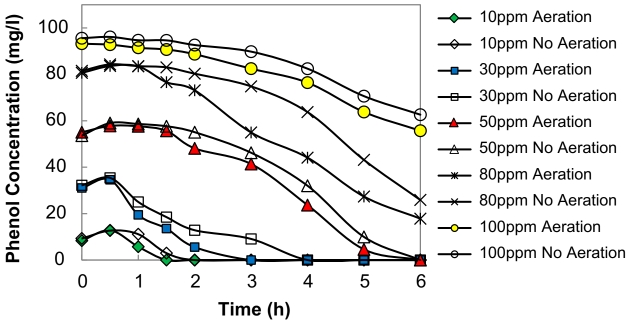

Fig. 6. Photocatalytic degradation of phenol with and without aeration (ZnO catalyst loading = 0.6g, initial pH = 6.2).

3.6. Effect of added H_2O_2 dosage

The addition of H_2O_2 to photocatalytic treatment with ZnO can be applied to increase the effectiveness of the process. Fig. 7 presents that the reduction of phenol concentration was more rapid through the combination of H_2O_2 at a concentration of 0.1 M. Only 4 h were required for phenol degradation of phenol in 0.1 M of H_2O_2, and then followed by photodegradation in 0.01 M of H_2O_2.

During 4 h of reaction, the removal efficiency for 0.01 M H_2O_2 was 84%, while 62% for that without H_2O_2. The result shows that the addition of H_2O_2 could enhance the degradation rate of the phenol compound in solution. Chiou et al. [13] reported the increase of degradation with the addition of H_2O_2. The removal efficiencies of phenol in 3 h reached 58% to 84% with the addition of H_2O_2 from 1.77 to 8.82 mM. Compare to oxygen, H_2O_2 is a more powerful oxidant which can generate a mass number of electrons. Consequently, it will prevent the recombination of electron-hole pairs. H_2O_2 is also an electron

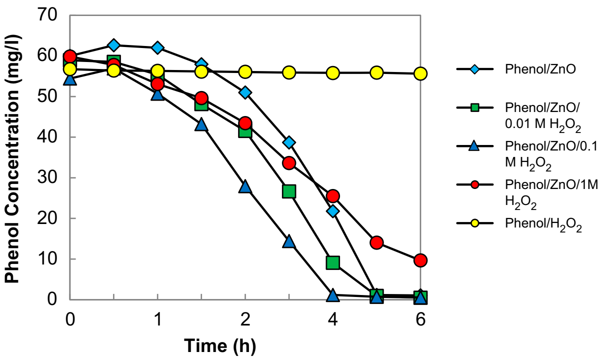

Fig. 7. Photocatalytic degradation of phenol with different concentration of H_2O_2 (phenol initial concentration = 50mg/l, ZnO catalyst loading = 0.6g, initial pH = 6.2).

acceptor and it is able to react with electrons in the conduction band and generates radicals to attack phenol molecules [30]. However, the result showed shown that the addition of 1 M H_2O_2 inhibited the degradation of phenol. Obviously, this indicates that the concentration of H_2O_2 plays an important role in photodegradation process. This attributed to the auto decomposition of H_2O_2 to oxygen and water and possibly the recombination of hydroxyl radical [31]. Higher concentration of H_2O_2 acts as free radical scavenger itself. Thus, decrease the concentration of hydroxyl radical and reduce the removal efficiency [32].

3.7. Mineralization of phenol

Mineralization of phenol should be considered, as the intermediate products possibly can be more toxic that the phenol itself such as hydroquinone [6]. Therefore, COD monitoring was conducted for phenol after photocatalytic degradation under solar irradiation. As shown in Fig. 8, the COD removal efficiency for initial phenol concentrations of 10, 30, 50, 80 and 100 mg/l was recorded as 89, 90, 89, 77 and 71%, respectively. According to Zhang et al. [33] that at high initial COD, the COD removal rates were higher with the same amount of reagent used [34]. It was found that the COD level was still above zero, although complete removal of phenol was recorded. The phenol molecules may fully degrade within 6 h of reaction, but not totally mineralized which could ascribe to the formation of the intermediate product that required more irradiation time to be fully mineralized. Priya et al. [35] reported that mineralization of phenolic wastewater in the presence of catalyst was possible in 4 h, but much longer time of photocatalytic degradation was required in order to mineralize the phenolic wastewater completely [35].

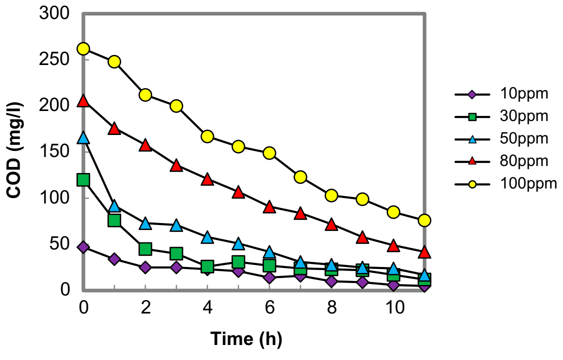

Fig. 8. COD monitoring in photocatalytic degradation of phenol (ZnO catalyst loading = 0.6g, initial pH = 6.2).

There are various intermediates formed during or after the photodegradation of phenol as a mineralization byproduct [36]. Sobczyński et al. [37] detected three main intermediates which are catechol, resorcinol and hydroquinone [37]. It was observed that the colour of the phenol solution during reaction were changed from milky white to slightly brown. A similar observation was reported by Pardeshi and Patil [5]. The formation of intermediates depends on the initial concentration of phenol [13]. Chen and Ray [38] discovered that the intermediates will only form in high phenol concentration and consequently affect the degradation rate. In higher concentration of phenol, the light brown colour remained after 8 h of irradiation. This may be due to the formation of coloured intermediates such as hydroquinone [5]. Besides aromatic intermediates, there are probabilities of aliphatic intermediates and polymeric compound formed in the reaction solution. Based on the literature studies [37], compounds that may be detected are formic acid, acetic acid and biphenols.

3.8. Photocatalytic degradation kinetics

Several researchers reported that the photocatalytic degradation of phenol illuminated by catalyst followed the Langmuir–Hinshelwood kinetic model [5,38–41]. The initial concentration of phenol has the fundamental effect on the degradation rate. The photocatalytic degradation by solar irradiation of phenol by ZnO suspension follows the pseudo-first-order kinetics with respect to the concentration of the phenol in the bulk solution (C) as shown below:

$$r = -\frac{dC}{dt} = k_{\text{obs}}\, C \tag{2}$$

Integrating of this equation (with the same restriction of $C = C_0$ at $t = 0$, with C_0 being the initial concentration in the bulk solution and t the reaction time) will lead to the expected relation:

$$\ln\left(\frac{C_0}{C}\right) = k_{\text{obs}}\, C \tag{3}$$

in which k_{obs} is the apparent pseudo-first-order rate constant and is affected by phenol concentration. 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) vs. t. The value which corresponds to different initial concentrations, along with the regression coefficients are listed in Table 1.

Table 1
Pseudo-first-order apparent constant values for the different initial concentration of phenol (ZnO catalyst loading = 0.6 g, initial pH = 6.2)

C_0 (mg/l)	K (h^{-1})	R^2
10	1.4927 ± 0.172	0.9027 ± 0.007
30	0.6333 ± 0.193	0.9052 ± 0.013
50	0.3954 ± 0.008	0.9182 ± 0.005
80	0.1306 ± 0.002	0.9328 ± 0.003
100	0.0946 ± 0.0002	0.9871 ± 0.002

Table 1 shows the pseudo-first apparent constant values for concentration 10 mg/l until 100 mg/l. The k value reduced as the concentration of phenol increased. Phenol with the lowest concentration gave higher k value compare to the phenol with concentration 80 mg/l and 100 mg/l. This may due to the photocatalytic degradation at lower concentration was faster than high concentration. At low concentration, the competition for reactivity and catalytic sites on the surface of ZnO was not high as there were only a few phenol molecules in lower concentration. The degradation rate of 10 mg/l was about 16 times higher than the degradation rate in 100 mg/l of phenol solution. This indicates more rapid and easier photodegradation at lower concentration. This observation indicates that the initial phenol concentration significantly affected the rate of phenol photocatalytic degradation. The correlation coefficient is relatively lower (less than 0.99) in low phenol concentration. This can be described to the irradiation intensity. Since sunlight was fully utilized in this research, the intensity of sunlight might be inconsistent during the photocatalytic reaction. Thus, the result obtained might slightly fluctuate. In order to overcome the problem, the experiments were repeated three times and the standard deviation were calculated. However, all the correlation coefficient value obtained was above 0.9000.

3.9. Economical evaluation

The evaluations in terms of the economy are also crucial to verify whether this treatment is suitable to be applied in real application in industries and for its sustainability. An overall cost estimation, will depend on the full scale system and it is majorly relied on the characteristic and concentration of pollutant, effluent flow rate and reactor configuration. However, one obvious factor that will drastically reduce the treatment cost is the solar light. In countries where the natural solar light can be obtained everyday during daylight, solar photocatalytic became more economical and preferable. It is unreliable to supply an ultraviolet light in a big scale application. Besides, the effective photocatalyst ZnO used are far cheaper than other, usually applied catalyst TiO_2. ZnO is 12 times cheaper than TiO_2 which is also more efficient in visible light. Furthermore, this treatment does not produce any sludge and the photocatalyst can be re-used up to five times without any further treatment [5].

4. Conclusion

The solar-photocatalytic degradation of phenol was studied with ZnO as a photocatalyst. With phenol concentration less than 50 mg/l, complete removal of phenol was observed within 6 h of photocatalytic reaction. The optimum photocatalyst loading and pH were 0.6 g and pH 3, respectively. The addition of aeration and hydrogen peroxide (H_2O_2) with adequate concentration (0.1 M) increased the photodegradation rate. The solar-photocatalytic degradation rate of phenol with ZnO as catalyst followed Langmuir–Hinshelwood kinetics model and the photocatalytic degradation rate was more rapid at lower phenol concentration. The COD and UV–vis analysis attested partial mineralization of the phenol solution under solar-photocatalytic process.

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