

Photodegradation of Phenol Red in the Presence of ZnO Nanoparticles

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Abstract—In our recent study, we have used ZnO nanoparticles assisted with UV light irradiation to investigate the photocatalytic degradation of Phenol Red (PR). The ZnO photocatalyst was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), specific surface area analysis (BET) and UV-visible spectroscopy. X-ray diffractometry result for the ZnO nanoparticles exhibit normal crystalline phase features. All observed peaks can be indexed to the pure hexagonal wurtzite crystal structures, with the space group of $P63mc$. There are no other impurities in the diffraction peak. In addition, TEM measurement shows that most of the nanoparticles are rod-like and spherical in shape and fairly monodispersed. A significant degradation of the PR was observed when the catalyst was added into the solution even without the UV light exposure. In addition, the photodegradation increases with the photocatalyst loading. The surface area of the ZnO nanomaterials from the BET measurement was $11.9 \text{ m}^2/\text{g}$. Besides the photocatalyst loading, the effect of some parameters on the photodegradation efficiency such as initial PR concentration and pH were also studied.

Keywords—Nanostructures, phenol red, zinc oxide, heterogeneous photocatalyst

I. INTRODUCTION

HUGE amount of industrial effluents, as well as life sciences wastewater, have been the major sources of synthetic dyes pollutants that is improperly disposed into the environment and leads to serious water contamination. Even though the environment has its own recovery system, with the extensive released of dyes into the environment they may cause severe ecological problem since most of the dyes are often toxic and also take a long time to degrade. There are many traditional wastewater treatment methods such as adsorption, flocculation and many others which are ineffective on every pollutant. Besides, those treatment methods may not completely neutralize toxic contaminants but instead leaving hazardous substance as residues. Therefore, it is timely to look for a simple yet efficient way to clear up these contaminated water from flowing into our environment

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without treated, which would bring harm in the long run.

Lately, there have been very extensive studies done by researchers around the globe on many photocatalytic systems (UV/semiconductors) since they have been found to be very effective in degrading various organic dyes. They are able to photosensitize the complete mineralisation of a wide range of compounds, like dyes, phenols and pharmaceutical drugs, without producing harmful by-products at near room temperature and pressure [1]–[5]. Most researchers generally considered TiO_2 as the best photocatalyst that has the ability to treat water from a number of organic pollutants [6]–[8]. On the other hand, it has been proven similar efficiency of photocatalytic degradation between ZnO and TiO_2 . ZnO has been reported to be a better substitution to TiO_2 in some application, therefore ZnO can be a suitable alternative for TiO_2 [1]–[3].

In this study, this special feature of ZnO nanomaterial photocatalyst was exploited on the decomposition of organic dye like Phenol Red (PR). Phenol Red possesses wide range of applications, such as bromination catalysts, pH indicator, estrogenic properties and screening test [9]–[12]. Despite its wide range of applications, little is known on the photocatalytic degradation properties of the ZnO nanoparticles on this material. Therefore, present study was aimed at elucidating the effect of different processing parameters, such as concentration of organic dye, photocatalyst loading and the effect of pH on the degradation of this harmful material.

II. EXPERIMENTAL DETAILS

A. Materials

In this study, ZnO nanomaterial was purchased from Sigma-Aldrich, and was used without any further treatment. Phenol Red was purchased from Sigma-Aldrich and was prepared in various solutions in distilled water. The properties of PR are listed in Table 1. In the preparation of different pH value for the solutions, the acid and base precursor materials that have been used were sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH), respectively.

B. Procedures

The photocatalytic degradation was carried out in the UV chamber equipped with five UV tube each producing light source of 254 nm wavelength. The aqueous solutions of PR

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were prepared in the test tube and the study of its photocatalytic degradation was carried out in the immobilized mode. This method was chosen due to its simple apparatus requirement. Besides, few researchers have reported even in aqueous immobilised mode, significant degradation has taken place on the organic compound [13], [14].

TABLE I
PROPERTIES OF PHENOL RED

Parameter	Values
Synonym	Phenolsulphonphthalein
Commercial name	Phenol Red
Colour	Yellow to red (pH 6.6 to 8.0) Bright pink (above pH 8.0)
Solvent	Soluble in water (0.77 g/L)
Empirical formula	C ₁₉ H ₁₄ O ₅ S
Formula weight	354.38 g/mol
Absorption maxima	435 nm – 440 nm

Before the degradation processes, ZnO photocatalyst material was premixed with distilled water to obtain different concentration of the catalysts loading. In addition, PR was also premixed with distilled water to obtain the desired concentration. After that, 3.00 ml of PR was added with 0.20 g of premixed catalyst of different concentrations. These samples were then allowed to be irradiated under UV light for varieties of durations in order to observe the time dependence for the degradation processes.

C. Characterization

The ZnO semiconductor material was characterised by X-ray diffraction (XRD) using Bruker AXS-D8 Advance equipped with CuK_α radiation in the scan range 2θ between 4° and 70°. The morphology of the sample was examined by a high-resolution transmission electron microscope (TEM) from LEO 912AB equipped with energy filter. TEM sample was obtained from a suspension of ZnO then was sonicated before it was dropped onto a 300-mesh carbon-coated copper grid and then evaporated the solvent. The specific surface area was determined on the basis of BET instrument using Micromeritics ASAP 2020 V3.01 H. The sample was degassed for 2 hrs at 250 °C prior to the N₂ adsorption analysis.

D. Photocatalytic Analysis

The photocatalytic experiments were conducted to investigate the photodegradation of the PR in photocatalytic aqueous suspension system. After the UV light irradiation for a certain time interval, each samples was centrifuged to separate the suspensions of the ZnO nanoparticles. The concentration of PR was measured by UV-vis spectrophotometer using Cary 50 detector with a scan rate of 120 nm/min in the range of 200 nm to 800 nm. The rate of

degradation was studied in terms of changes of the absorption maximum at the absorption peak of 440 nm. The percentage degradation was calculated from the initial and final absorption of the UV-vis experiments as follows:

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

where C₀ = initial concentration of PR, C = concentration of PR after certain duration of photoirradiation. Similar experimental analysis was carried out for variation of initial concentration of PR, different concentration of the photocatalyst loading (0.25 – 3.5 wt%) and pH of the PR solution (pH 1.36 – 7.18).

III. RESULTS AND DISCUSSION

A. Characterization of the photocatalyst

TABLE II
BET DATA FOR ZnO

Measurement Properties	Values
BET Surface Area	11.90 m ² /g
Pore Volume	0.000599 cm ³ /g
Average Pore Size	6.848 nm

The surface area, particle size, morphology and other characteristics of ZnO catalyst were determined because these characteristics are very crucial in providing the efficiency to degrade the organic compound [14]. The BET surface area for the nanomaterials was found to have a value of 11.9 m²/g, Table 2, indicating the large surface area of the particles. This may contribute to the high photocatalytic activities of the samples since the photocatalytic reaction takes place on the catalyst surface when irradiated with ultraviolet light. From the XRD characterization, as depicted in Figure 1, the 2θ values coincides with those of the standard hexagonal ZnO structures. It is in agreement with the standard hexagonal wurtzite crystal structures with space group P63mc as reported in the literature [15]. Furthermore, there was no distinct peaks observed which indicate the high purity of the nanomaterials.

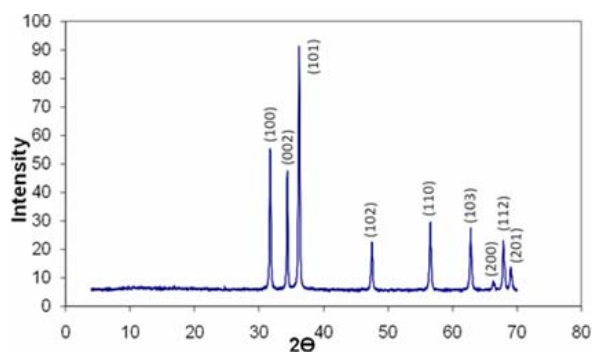


Fig. 1 X-ray diffraction pattern of ZnO nanoparticle photocatalyst

In Figure 2, TEM measurement showed that most of the nanoparticles are spherical to rod-like shape and fairly monodispersed. This shows that current experiment unable to comment on the efficiency of the shape of the photocatalyst in the photodegradation of organic compound if it is to compare with some other samples. On the other hand, the mean diameter of ZnO estimated from the TEM image is 122 nm.

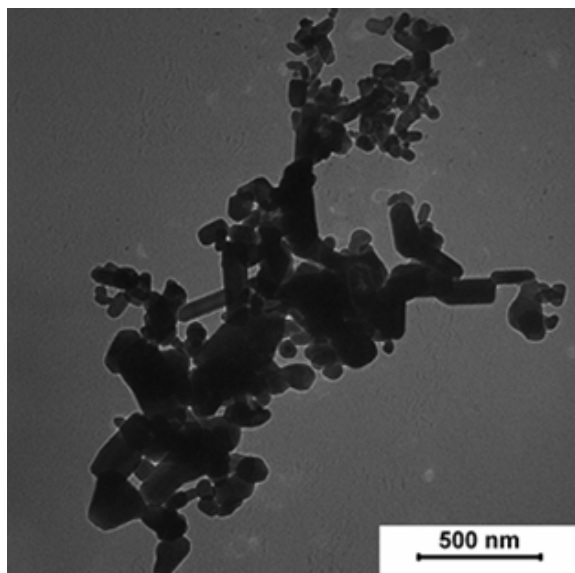


Fig. 2 TEM picture of nanoparticles ZnO photocatalyst

B. UV-vis spectra for initial dye concentration

Initial investigation was conducted with the PR solutions were irradiated without the presence of catalyst under direct illumination of UV light. It was irradiated in a 15 minutes interval for one and a half hours to observe if there is any degradation effect. This was carried out because there are various dyes which were degraded when exposed to direct UV light in a short period of time even without the presence of catalyst. However, there were insignificant changes observed for the duration of 1½ hours (< 1%). This showed that the organic compound in the solution was very stable and do not have self-destruct mechanism even it was radiated under UV light for one and a half hours. This was in agreement to the previous study where PR is not degraded in a short irradiation period as compared to some other dyes, especially when PR is mixed with Lauryl Sulfate Broth [16].

Figure 3 shows the UV-vis spectra measurement for different concentration of PR solution. The absorption peak was observed at 440 nm. The peak gradually decreases as the concentration decreased. This is in agreement with the knowledge that the amount of organic compound contained is less for solution with lower concentration.

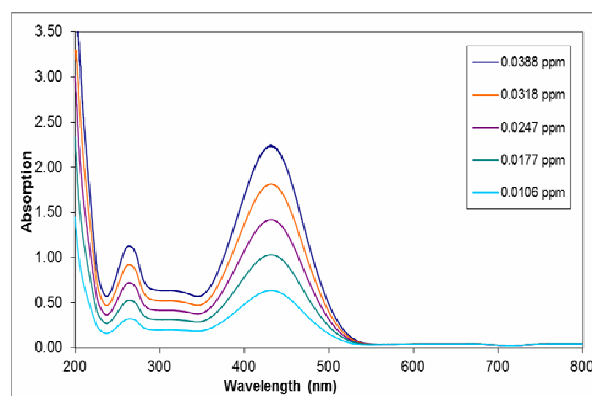
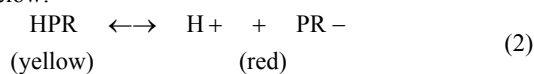


Fig. 3 UV-vis absorption spectra for different concentration of PR

C. Effect of initial dye concentration

As mentioned earlier, without ZnO substitution, no effect was recorded on the degradation of PR. However, after ZnO was added into the solution, the absorption peak at 440 nm dropped significantly, whereas a new peak was observed at 565 nm as depicted in Figure 4. These two absorption peaks represent the absorption spectra for proton donor (HPR) and proton acceptor (PR⁻) forms of the phenol red with the inclusion of ZnO photocatalyst. Since PR is a weak acid, therefore the proton donor form dissociates reversibly in solution into a proton donor and proton acceptor form, as shown below:



The decreasing of the absorption peak at 440 nm indicates that the decomposition of organic compound in the solution has taken place, whereas the new absorption peak was also decreased with time.

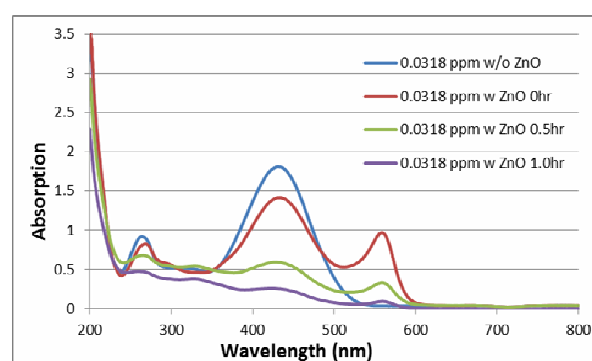


Fig. 4 UV-vis absorption spectra for 0.0318 ppm of PR

D. Effect of irradiation duration

In Figure 5, the percentage degradation of PR increases with the decreased of its initial concentration for both 0.5 hr

and 1.0 hr irradiation time. This was in agreement with the understanding that even though the concentration of the organic compound is high, however the amount of organic compound that able to interact with the catalyst was limited. This is because photocatalytic degradation process takes place only on the surface of the catalyst [17]. It is also shown that with the addition of ZnO into the solution, more than 20% of the organic compound has been decomposed, even before irradiated with UV light.

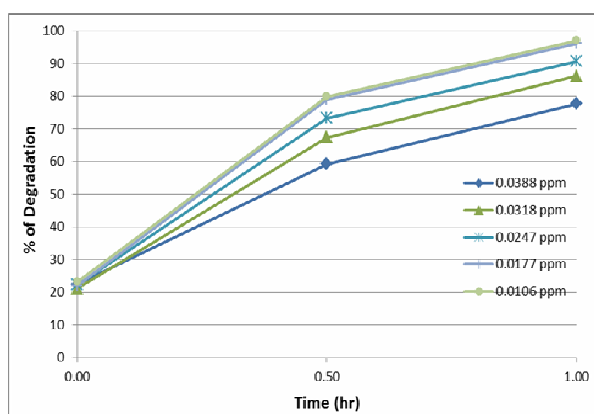


Fig. 5 Photodecomposition efficiency on the effect of initial concentration of PR

For 0.50 hr irradiation, almost 60% and 80% of the organic substances have been degraded from the 0.0388 ppm and 0.0106 ppm solutions, respectively, whereas when irradiated for 1.0 hr the percentage degradation were 78% and 97%, respectively. Figure 5 clearly shows that the highest percentage degradation is 0.0106 ppm solution. This can be seen that the degradation is more achievable when the concentration is lower. When the initial concentration of PR is higher, it will have inhibitory effect on the photodegradation due to the photons interception before they can reach the catalyst surface, decreasing the absorption of photons by the catalyst. This phenomenon can be explained due to the increase of incidental photonic flux irradiating the catalyst in the dilute PR solution. Therefore, the rate of hydroxyl radical ($\text{OH}\cdot$) production increases which would allow the degradation to be faster [18].

E. Effect of photocatalyst loading

The amount of ZnO in the solution is an important parameter that can affect the photodegradation rate of PR. It is found that the degradation value increases with the catalyst loading, but to a certain concentration. The concentration of the catalyst loading was varied from 0.50 to 3.50 wt% (w/v) to study the effect on the photodegradation of the PR. The photodegradation efficiency of PR for different concentration of ZnO was shown in Figure 6. This experiment was carried out under the UV light of wavelength 254 nm. In Figure 6, the percentage of degradation generally increases as the concentration of the ZnO catalyst was increased. With the

increased of the catalyst concentration, the number of active sites on the photocatalyst surface increases, which in turn, increase the number of hydroxyl, and superoxide radicals. However, when the concentration of ZnO catalyst increases above certain value, the degradation rate seems to reach equilibrium value and decreases slightly. The equilibrium value is reach due to the concentration of PR while the decrease is probably due to the photon interception of the light rays by the suspension.

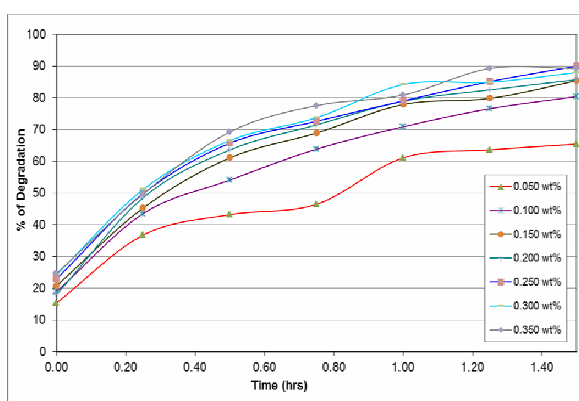


Fig. 6 Photodecomposition of PR with photocatalyst loading

F. Effect of pH

Most semiconductor oxides are amphoteric and therefore an important parameter governing the rate of reaction taking place on semiconductor particle surfaces is the pH of the dispersions, since, it influences the surface-charge-properties of the photocatalyst [19]. The effect of pH on the rate of degradation needs to be considered since industrial effluents may not be at neutral pH.

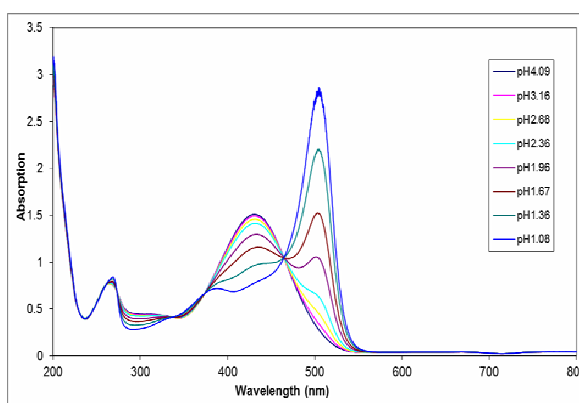
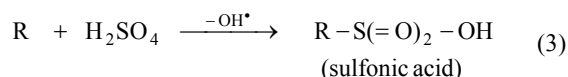


Fig. 7 UV-vis absorption spectrum of PR in acid solution

As can be observed from Figure 7, with the absence of ZnO, the main peak (440 nm) decreases with the increased of the acidity of the suspensions. However, this leads to the

formation of new peak at 502 nm. The formation of this 502 nm absorption peak is believed due to the sulphuric acid undergone electrophilic aromatic substitution with aromatic compounds to give the corresponding sulfonic acids. The production of the sulfonic acids could possibly be explained as below:



where R is the hydrocarbon side chain (aromatic compounds). Figure 8 shows the sample with pH = 2.36, with the addition of ZnO, the main absorption peak decreases and lead to the formation of new absorption peak at 560 nm whereas the absorption peak formed at 502 nm was totally disappeared. This showed that the production of sulfonic acids substance were in temporary basis. On the other hand, for sample with pH 1.67 its main absorption peak increased by 16.59% when ZnO was added into the solution. This showed that ZnO was more reactive in the interaction with sulfonic acids which caused the breaking of the aromatic compounds of the sulfonic acids. Subsequently, when these samples were exposed to UV light source, the main peak and the new peak started to degrade by 29.46% and 51.46% when the suspensions were irradiated for 0.5hr and 1.0hr, respectively.

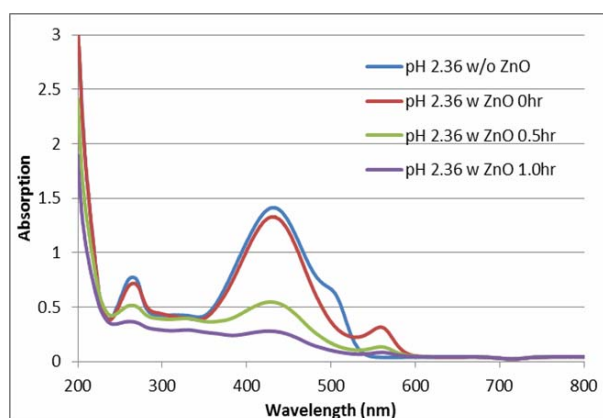


Fig. 8 UV-vis absorption spectrum for acid solutions for pH 2.36

When ZnO was added into the solutions of very high acidity (pH < 1.50), the main absorption peak start to increase, while the new absorption peak at 502 nm was degrading. However, when these samples were irradiated with UV light source, the main peak and the new peak didn't show any significant changes. It is believed that at a very high acidity, ZnO itself has been dissolved [20].

IV. CONCLUSION

From the observation above, it can be concluded that the photocatalytic degradation of PR has only taken place with the presence of the photocatalyst, which without catalyst it might

take a very long time to photodegrade. Experimental results showed that, with the existence of ZnO nanoparticles, the photodegradation of PR was significantly enhanced which implies the great potential of this material in the waste water treatment system, except for a very acidic solution (pH < 1.36). For different initial concentration of dyes, it can be deduced that the percentage degradation is higher when the concentration of the solution is lower. For samples solution within the pH range of 3.16 to 7.18, there is no definite result to conclude if photodegradation of PR is more favour to be degraded in the acidic or bases solutions.

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