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Photocatalytic Degradation of Phenol in Water Solution by Phosphotungstic Acid on TiO_2/ZnO Nanoparticles as Supporting Solid

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Abstract

A Keggin-type heteropolyoxometalate ($H_3PW_{12}O_{40}$) supported on TiO_2/ZnO nanoparticles was used for the degradation of phenol under UV light and H_2O_2 as oxidant. Based on the results, heterogenization of $H_3PW_{12}O_{40}$ on TiO_2/ZnO could improve the photocatalytic process and could be considered an appropriate heterogonous photocatalyst in the removal of phenol from aqueous solutions in the presence of hydrogen peroxide. Degradation of phenol in the presence of the $H_3PW_{12}O_{40}$/TiO_2/ZnO could lead to the disappearance of approximately 95% of phenol under UV irradiation and optimized condition. In the same experiment $H_3PW_{12}O_{40}$ as a homogenous catalyst, removed 70% phenol and the heterogeneous TiO_2/ZnO catalyst removed less than 70% phenol from the water solution in the same conditions.

Keywords: Phosphotungstic Acid; photocatalytic activity; solid supporting; Phenol pollutant.

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Introduction

Phenol and phenolic compounds are organic pollutant in the wastewater of the plastic, petrochemical, pharmaceutical, and pesticidal chemical industries and are considered dangerous materials. Due to their toxicity and low biodegradability can result in serious environmental troubles. Phenol is known as a potential human carcinogen which raises considerable health concern even at low concentrations [1, 2]. phenol is classified as a priority pollutant by the United States Environmental Protection Agency (US EPA) and removing of it from wastewater seems essential. Different processes such as adsorption, coagulation and flocculation, precipitation, biological treatment, distillation, electrocoagulation, solvent extraction, membrane process and advance oxidation are the main techniques used for removing of phenol [3-7]. Photocatalytic degradation is a good technology which can degrade organic pollutants to non-toxic final products such as CO_2 and H_2O and several semiconductors (TiO_2, ZnO, …) are used as photocatalyst for photocatalytic degradation of organic pollutant [8-11] and can be regarded as one of the promising technologies for degradation of phenolic compounds. During the last decade, heteropoly acids (HPA), as green and eco-friendly catalysts, have been considered for the synthesis of organic compounds and degradation of organic pollutants [12-15]. Recently, some researchers found that heteropoly acids (HPA), can modify the surface of semiconductors. Keggin-type HPAs formulated as $H_nXM_{12}O_{40}$ (X = P^{5+} or Si^{4+}) and (M = W^{6+}, Mo^{6+}) are very important heteropoly acids that have supported on semiconductors and used as heterogeneous photocatalysts for environmental remediation. The catalyst could eliminate the difficulties of recycling heteropoly acids and prevent the recombination of hole-electron pairs for both catalysts when heteropoly acids were carried on semiconductors. Thus, an increasing in specific area of heteropoly acid and synergy resulted in enhancing the photocatalytic degradation [16- 18]. In continuation of our works on the catalytic properties of TiO_2/ZnO-supported phosphomolybdic acid and phosphotungstic acid supported on TiO_2 or ZnO nanoparticles for degradation of aniline [19-20]. Here, $H_3PW_{12}O_{40}/TiO_2/ZnO$ was selected as an efficient heterogeneous photocatalyst for degradation of phenol in water solution.

Experimental

Materials and methods

Phenol, $H_3PW_{12}O_{40}$ and other chemicals were purchased from Merck in synthesis grade and used without further purification. In all experiments, distilled water was used for standard and working solutions. The concentration of phenol was determined by 4-aminoantipyrine in the presence of potassium ferricyanide (standard method; 420.1, EPA United States Environmental Protection Agency). The IR spectra were recorded using FTIR Spectra Bruker Tensor 27 spectrometer (KBr pellets, Nujol mulls, 4000–400 cm-1). A Shimadzu UV 160A spectrophotometer with a 1.0-cm quartz cell was used for absorbance measurement.

Synthesis of $H_3PW_{12}O_{40}$/ TiO_2/ ZnO

Nanoparticles of TiO_2/ZnO and $H_3PWO_{12}O_{40}$/TiO_2/ZnO were prepared according to litterateur procedure, $H_3PWO_{12}O_{40}$ instead of $H_3PMoO_{12}O_{40}$ [21].

Photodegradation of phenol

A stock solution of phenol with a concentration of 1000 ppm was prepared by dissolving an appropriate amount of phenol in distilled water. The working solution was prepared by diluting the stock solution and after pH adjustment (by 0.1N sodium hydroxide and 0.1N hydrochloric acid).

An appropriate amount of catalyst was added to the phenol solution then the mixture was transferred to the Pyrex cell. The photochemical reactor including a wooden box, a Pyrex cell of 100 mL capacity, a magnetic stirrer, a light source on top of the box and two fans for ventilation and cooling the reactor (Figure 1).

The reaction mixture was stirred in a dark condition to ensure adsorption-desorption equilibrium. Then, the appropriate amount of H_2O_2 was added to the solution and the system was irradiated with a 150W mercury lamp.

At the end of each experiment, one sample was taken from the system and centrifuged to remove the catalyst. The progress of the reaction was studied by measuring the adsorption of the solution at 500 λ_{max} nm.

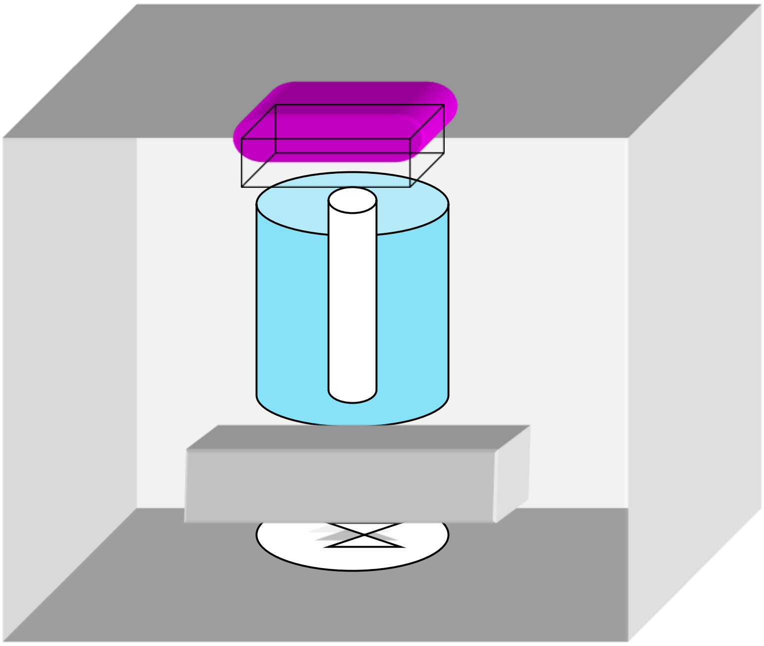

Figure 1. The used photochemical reactor.

Phenol concentration measurement

Phenol degradation efficiency was calculated using the following equation:

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

where C_0 and C_t are phenol concentrations at the initial time and time of t, respectively.

Results and discussion

Characterization of catalyst

Figure 2 shows the XRD pattern of $ZnO/TiO_2/HPW_{12}O_{40}$ catalyst. According to Figure 1, the prepared catalyst is crystalline and the crystalline size is about 80-100 nm. The crystallite size was calculated from the broadening of peaks using Scherer’s formula ($D = 0.891\ \lambda/b \cos 2\theta$, D: average grain size λ: wavelength in nanometers θ = diffraction angle width of half the maximum observed peak).

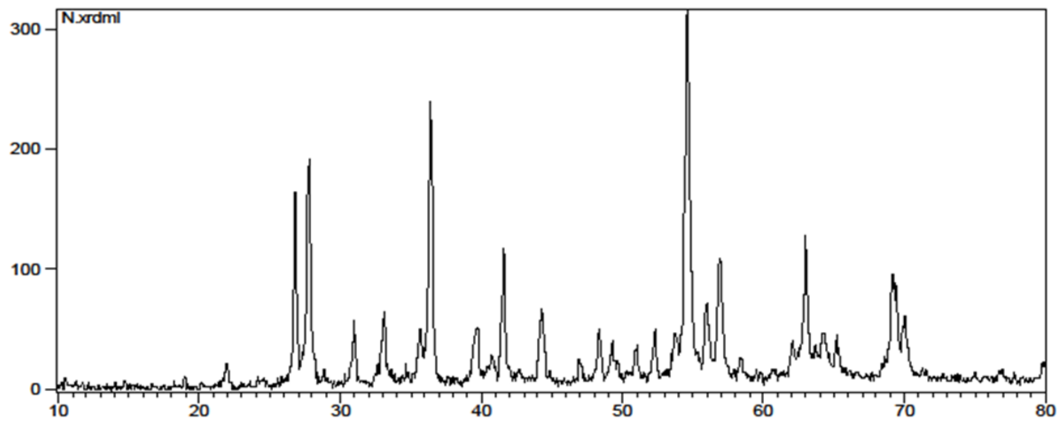

Figure 2. X-ray diffraction pattern of H3PW12O40/ZnO/TiO$_2$ catalyst.

Figure 3 shows the scanning electron microscope (SEM) image of the prepared catalyst nanocomposites. As seen from Figure 2, nanocomposites are spherical -shape particles in nano-size.

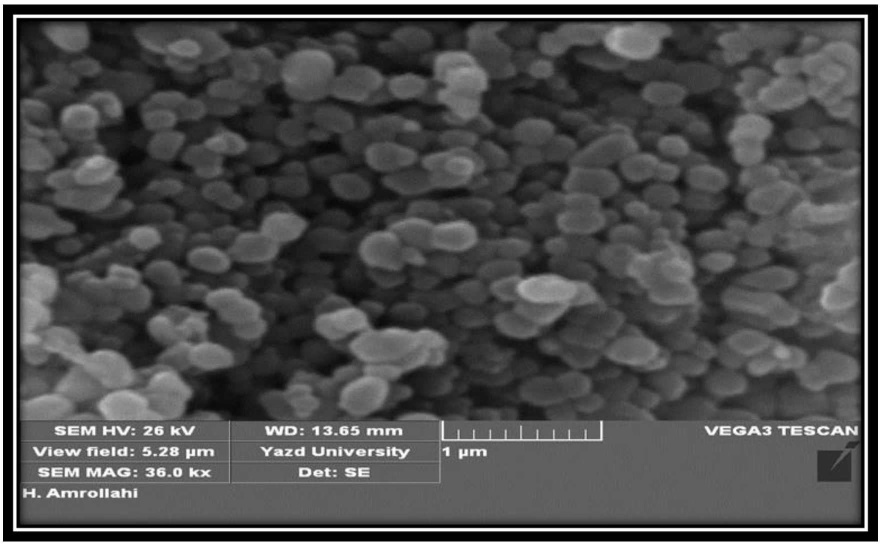

Figure 3. SEM image $H_3PW_{12}O_{40}$/ TiO_2/ZnO catalyst.

Comparison of photocatalytic activity

Some experiments were performed to evaluation of the photocatalytic activity of the $H_3PW_{12}O_{40}/TiO_2$/ZnO nanocomposite in comparison with TiO_2/ZnO and $H_3PW_{12}O_{40}$. The results in Fig. 4, show that the degradation of phenol continued at a lower rate after 20 min. The degradation efficiency almost reached to equilibrium for $P_3W_{12}O_{40}/TiO_2$/ZnO and

$H_3PW_{12}O_{40}$ catalysts after 60min. However, $H_3PW_{12}O_{40}$ as a homogeneous catalyst showed a relatively good rate of degradation until the end of the process, but the heterogeneous catalyst, $P_3W_{12}O_{40}/TiO_2/ZnO$ showed the highest degradation efficiency and its efficiency reached to 97% at contact time of 60min. Tabatabaee et al also investigated the degradation of phenol using $K_7PMo_2W_9O_{39}/ZnO$ in the presence of H_2O_2 and reported about 86% removal of phenol at optimal condition [22]. In another study, $PMo_{12}O_{40}/TiO_2/ZnO$ was applied as a heterogeneous catalyst for degradation of aromatic amines under LED-UV irradiation [21].

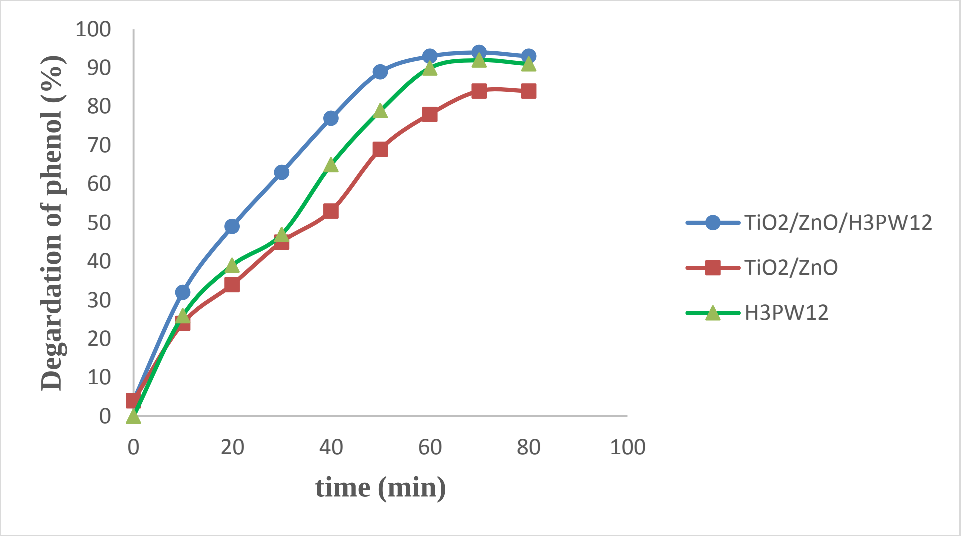

Figure 4. Comparison of photocatalytic activity (phenol 10 ppm, catalyst 2 g/L, H_2O_2 0.7 ppm, pH = 3).

Evolution of different parameters on photocatalytic degradation of phenol

pH effect study

pH is one of the most significant factors in removing organic pollutants. We tested how the pH level of the solution affected the efficiency of removing phenol. We investigated pH levels of 3, 5, 7, and 9 by using HCl and NaOH to adjust the pH. The study found that as the pH increased from 3 to 9, the degradation efficiency decreased, and removal efficiency was higher at acidic pH. Therefore, pH = 3 was chosen for continuation experiments. $H_3PW_{12}O_{40}$ is stable in acidic pH and it is changed to lacunary ions ($PW_{11}O_{39}^{7-}$ or $PW_9O_{34}^{9-}$) in pH> 3 [23] and phenol is changed to phenolate ion in basic pH. Therefore, according to results strong acidic pH is more efficient in photocatalytic degradation.

Effect of catalyst amounts

We investigated how different amounts of catalysts, ranging from 0.5 to 3.0 g/L, affect the efficiency of phenol degradation. As observed from Fig. 5, photocatalytic degradation of phenol using the $P_3W_{12}O_{40}/TiO_2/ZnO$ was increased from 61% to 88% with an increase in nanocomposite dosage from 0.5 g/L to 2.0 g/L. The increase in degradation efficiency is negligible from a catalyst dosage of 2.0g/L to 3.0g/L. The nanocomposite dosage of 2.0 g/L was considered as the optimum catalyst amount.

Effect of oxidant dosage

In this study, H_2O_2 was used as an oxidant in the photocatalytic degradation process of phenol. Figure 6 shows that H_2O_2 is an efficient parameter in the advanced oxidation of phenol. An efficiency of 92% was obtained for photocatalytic degradation of phenol using 2g/L $P_3W_{12}O_{40}/TiO_2/ZnO$ nanocomposite in the presence of 0.7 ppm H_2O_2 as oxidant in the system.

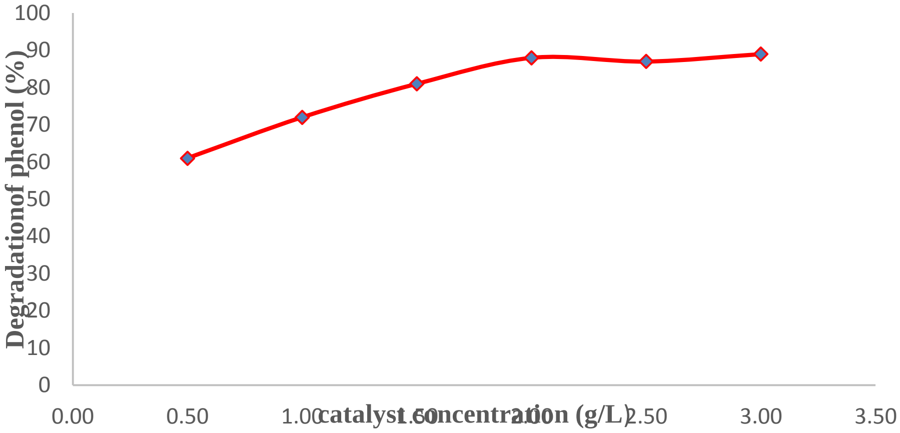

Figure 5. Effect of catalyst amounts (phenol 10 ppm, H_2O_2 0.5 ppm, time 60 min).

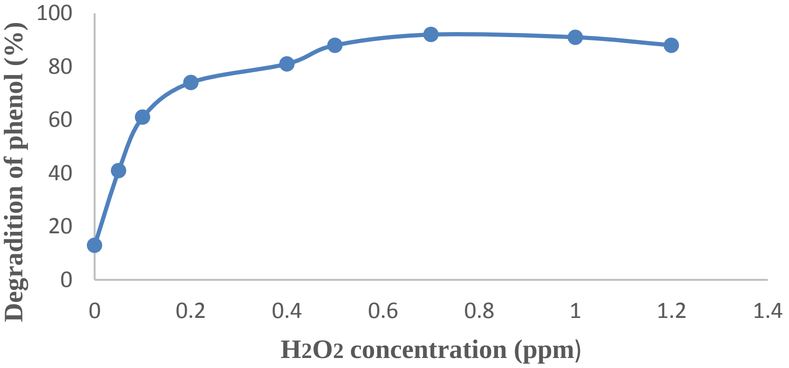

Figure 6 Effect of H_2O_2 concentration (phenol 10 ppm, catalyst 2.0 g/L, pH=3, time 60 min).

Effect of contact time for degradation of phenol

Effect of contact time as an important parameter was investigated in the applicability evaluation of advanced oxidation processes on photocatalytic degradation efficiency of phenol (Fig. 4). Fig. 4 indicates that the photocatalytic degradation efficiency of phenol has increased along with the increase of contact time and it has been reached to equilibrium at 60min. Saeedi et al. reported a removal efficiency of 94.7% for 5mg/L at contact time of 90min in the presence of UV/ZnO [24]. Comparing the results of this research with their results shows that $P_3W_{12}O_{40}/TiO_2/ZnO$ is more efficient for advanced oxidation of phenol.

Effect of phenol concentration

The effect of phenol concentration was investigated with 4, 6, 10, 12, 15 and 20 mg/l of phenol under optimal conditions (Fig. 7). Increasing the initial concentration of phenol up to 12 ppm does not significantly affect the removal efficiency of phenol. But after that, the efficiency is decreased significantly.

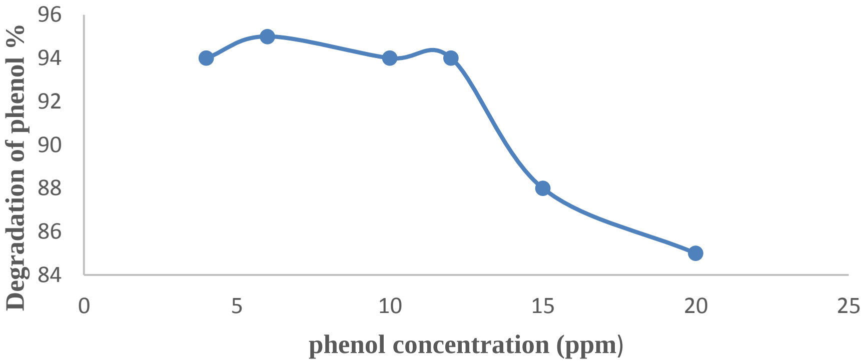

Figure 7. Effect of phenol concentration (catalyst 2.0 g/L, pH=3, H_2O_2 0.7 ppm, time 60 min).

Mechanism of photodegradation using $H_3PW_{12}O_{40}/TiO_2/ZnO$

In the photocatalytic process, after absorbing photons with energy higher than the semiconductor’s band gap energy (E_g), electrons from the filled valance band (VB) are promoted to the conduction band (CB) and the valance band holes h^+ are formed (Fig. 8). Valence band electrons convert available substances such as water, hydroxide ions, and O_2 molecules into hydroxyl radicals. The OH ◌̇ ¯ radicals are powerful oxidizing agents that can easily attack organic molecules, ultimately leading to their complete mineralization. According to literatures, in the photodegradation of organic compounds by ZnO and TiO_2 superoxide and hydroxyl radicals are the main reactive species during the photocatalytic degradation [25-27] and in the case of $H_3PW_{12}O_{40}/TiO_2/ZnO$ radicals of OH $^{\cdot -}$ derived from the electroreduction of dissolved oxygen or H_2O_2 with electrons *via* chain reactions [28].

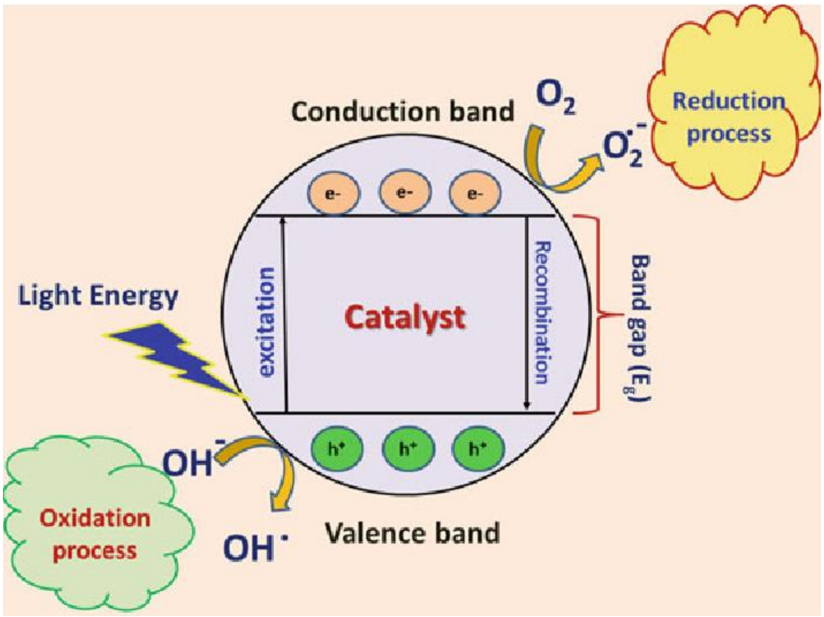

Figure 8. Mechanism for photocatalytic degradation of organic compounds by semicondutors as a photocatalyst under the UV irradiation.

Conclusion

The Keggin-type heteropolyo acids (HPAs) are good homogeneous catalyst for oxidation reaction. Supporting of HPAs on solid semiconductors can enhance the photocatalytic properties of semiconductors. Phosphotungstic acid supported on TiO_2/ZnO ($H_3PW_{12}O_{40}/TiO_2/ZnO$) nanoparticles were successfully synthesized and was uese for degradation of phenol in water solution. The synthesised catalyst is a good photocatalyst for degradation of phenol and can remove nearly 95% of phenol in optimaized condition.

Acknowledgements

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