Lacunary Keggin-Type Hetero Polyoxometalate, $K_7PMo_2W_9O_{39}$, Supported on Nano ZnO as an Efficient Photocatalyst for Degradation of Phenol in Water Solution

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ABSTRACT: *In the present research, Lacunary Keggin-type heteropolyoxometalate, ($K_7PMo_2W_9O_{39}$) supported on ZnO nanoparticles was prepared by the impregnation method. Nanoparticle characteristics and the remaining Keggin structure in the nanocomposites were confirmed by FT-IR and XRD analyses. The photocatalytic activity of prepared $K_7PMo_2W_9O_{39}$/ZnO for degradation of phenol under UV light was investigated. H_2O_2 was used as an oxidant in the photocatalytic degradation process of phenol. The results indicated that synthesized nano photocatalyst could be considered an appropriate heterogonous photocatalyst in the removal of organic pollutants from aqueous solutions and heterogenization of Lacunary Keggin-type heteropolyoxometalate on ZnO nanoparticles resulted in the improved light absorption intensity and decreased band gap of nanocomposites. Degradation of phenol in the presence of the $K_7PMo_2W_9O_{39}$/ZnO could lead to the disappearance of approximately 93% of phenol after 60 min. But degradation for the same experiment performed in the presence of the $K_7PMo_2W_9O_{39}$ or /ZnO was less than 60% at the same time.*

KEYWORDS: *Photochemical degradation; Lacunary hetero polyoxometalate, ZnO nanoparticle, Phenol.*

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INTRODUCTION

Pollution of water resources has become a major concern in the last decades. Industrial activities are one of the important sources of pollution which can contaminate ecosystems through the discharge of untreated or inadequate treated wastewater to surface waters. Phenol and phenolic compounds as organic pollutants are frequently found in industrial wastewater [1, 2]. Due to their toxicity, low biodegradability, and ability to build up potential in plants and tissues, these compounds can result in severe environmental troubles. Furthermore, phenol is known as a potential human carcinogen which raises considerable health concerns even at low concentrations. The United States Environmental Protection Agency (USEPA) has classified phenol as a priority pollutant. So, it requires urgent removal of the waste stream before discharge to the environment. Several technologies such as adsorption, biological treatment, coagulation and flocculation, precipitation, distillation, electrocoagulation, solvent extraction, membrane process, and advanced oxidation have developed to remove phenol from water and wastewater [3-7]. However, most of these techniques have some drawbacks including low efficiency, generation of secondary pollutants, high costs, etc. while among these techniques; advanced oxidation is a good technology that can degrade organic pollutants to non-toxic final products such as CO_2 and H_2O. Photocatalytic degradation is an advanced oxidation process that uses semiconductors and a light source to remove pollutants [8]. Among various semiconductors, ZnO has attracted considerable attention as an alternative for TiO_2 due to its remarkable electronic and optic properties [9]. Polyoxometalates (POM) especially has been widely used as catalysts for the synthesis of organic compounds and also for the degradation of organic pollutants [10-13]. Among heteropolyanions, Keggin-type HPAs represented by the formula of $[XM_{12}O_{40}]^{n-}$ when X is the heteroatom (such as P^{5+} or Si^{4+}) and M is the addenda atom (most frequently W or Mo in high oxidation state) are very important heteropolyanions has attracted much interest in catalyst reactions [14]. In recent years, researchers have attempted to immobilization of POM on semiconductors to improve catalytic and photocatalytic activity properties and overcome to drawbacks of both catalysts [15-17]. Recently, photodegradation of aniline by TiO_2/ZnO-supported Keggin-type HPAs nanoparticles has been reported by our group [18-20]. In contrast to the using saturated Keggin-type HPAs as a catalyst, there are a few reports on the catalytic effect of lacunary Keggin compounds. In continuation of our works on the catalytic properties of $[PMo2W9O39]^{7-}$ as a lacunary Keggin-type heteropolyanion [21, 22], in the present work, we selected $K_7PMo_2W_9O_{39}$/ZnO as an efficient heterogeneous photocatalyst for degradation of phenolic compounds in water solution.

EXPERIMENTAL SECTION

Phenol 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 a determination by 4-aminoantipyrine in the presence of potassium ferricyanide (standard method; 420.1). The IR spectra were recorded using FT-IR 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 at a fixed wavelength.

Synthesis of $K_7[PMo_2W_9O_{39}]$/ZnO

α-$K_7[PMo_2W_9O_{39}]$ ·$19H_2O$ was prepared according to litterateurs procedure [23]. For the preparation of ZnO containing $K_7[PMo_2W_9O_{39}]$, $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.66 g) was added into an ethanol/H_2O (2:1) solution of $K_7[PMo_2W_9O_{39}]$ (50 mL, 1.0×10^{-4} m). The reaction mixture was placed in a Parr-Teflon lined stainless steel vessel, sealed and heated at 120 °C for 8 h, and then cooled to room temperature. Then the suspension was placed on a hotplate until it completely evaporated and the obtained white precipitate was separated by centrifugation, washed with distilled water and ethanol, and then dried at 60 °C for 8 h.

Photodegradation of phenol

In order to photochemical degradation evaluation of phenol, a stock solution of phenol with a concentration of 1000ppm 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 transferred to the reactor. 0.1N sodium hydroxide and 0.1N hydrochloric acid were used for pH adjustment. The reactor was a Pyrex cell of 100mL capacity on a magnetic stirrer in a wood box with the light

source on top of the box. The box was equipped with two fans for ventilation and cooling the reactor. After preparing a working solution, an appropriate amount of catalyst was added to the phenol solution and it was stirred in dark conditions 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 was analyzed for determining phenol concentration after removal of nano- catalyst using centrifugation.

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 initial and time of t.

RESULTS AND DISCUSSION

Characterization of catalyst

The XRD pattern of the synthesized nanocomposite has been shown in Fig. 1. The XRD patterns demonstrated that the ZnO is crystalline in nature, The diffraction peaks are matched with the hexagonal zincite phase of ZnO and the entire d-line patterns match with reported values (JCPDS Card Pattern: 36-1451).

The surface morphology of synthesized nanocomposites was determined using a scanning electron microscope (SEM). Fig. 2 shows SEM image of synthesized nanocomposites. As seen from Fig. 2, nanocomposites are cubic-shaped particles in nano-size.

Comparison of photocatalytic activity

Some experiments were performed in order to evaluate of photocatalytic activity of the $K_7PMo_2W_9O_{39}$/ZnO nanocomposite in comparison with ZnO and $K_7PMo_2W_9O_{39}$ alone which their results have illustrated in Fig. 3. As it can be seen from Fig. 3, degradation of phenol was occurred at a high rate for all catalysts up to the first 20min of the process. After that degradation of phenol continued at a lower rate. The degradation efficiency was almost reached equilibrium for ZnO and $K_7PMo_2W_9O_{39}$/ZnO catalysts after 80min. However, $K_7PMo_2W_9O_{39}$ as a homogeneous catalyst

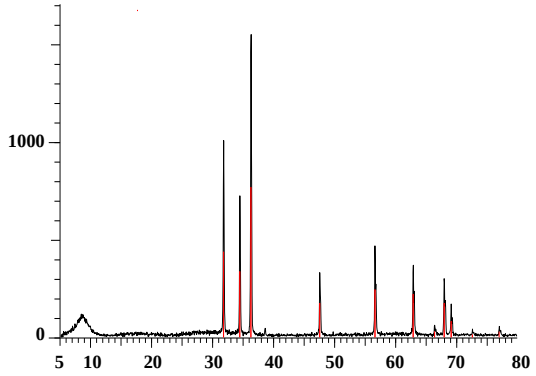

Fig. 1: The XRD pattern of $K_7PMo_2W_9O_{39}$/ ZnO.

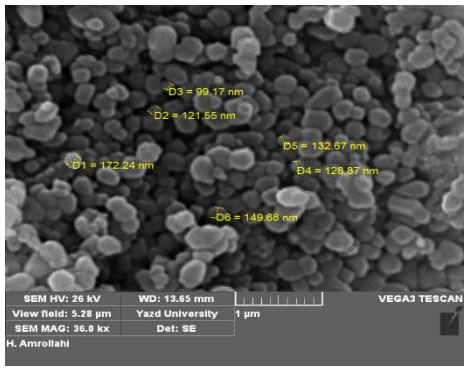

Fig. 2: The Scanning Electron micrographs (SEM) of the $K_7PMo_2W_9O_{39}$/ZnO nanocomposite

showed a relatively high rate of degradation until the end of the process, but the heterogeneous catalyst, $K_7PMo_2W_9O_{39}$/ZnO, showed the highest degradation efficiency and its efficiency reached to 86% at a contact time of 80min. Tabatabaee et al also investigated the degradation of direct blue 71 using $K_7[PMo_2W_9O_{39}].19H_2O$ in the presence of H_2O_2 and reported about 90% removal of direct blue 71 at optimal conditions [21]. In another study, α-$[PMo_2W_9O_{39}]$ was applied as a homogenous catalyst for degradation of aromatic amines in which more than 90 % of aromatic amines (in acetonitrile) were oxidized and converted to nitro products [22].

Effect of oxidant dosage

In this study, H_2O_2 was used as an oxidant in the photocatalytic degradation process of phenol. The results of the effect of oxidant dosage on the process were presented in Fig.4. The results showed the remarkable effect of the presence

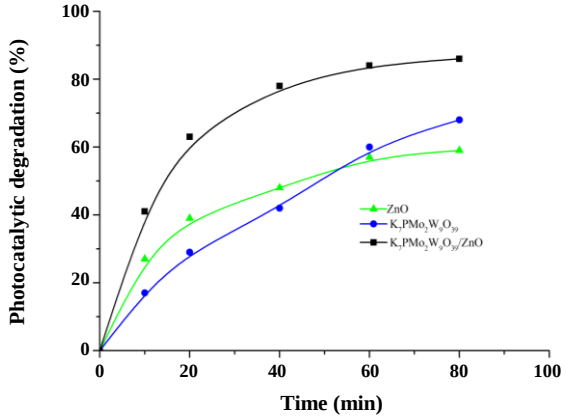

Fig. 3: Photocatalytic activity of catalysts towards phenol.

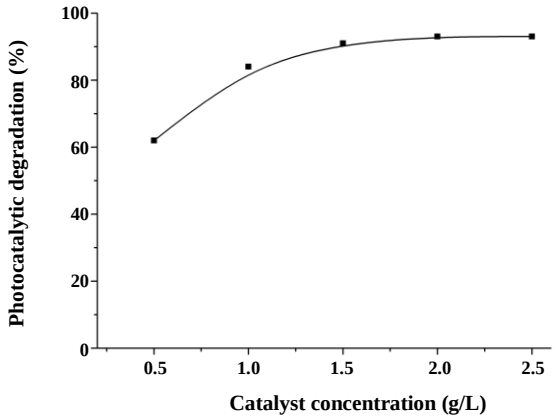

Fig. 5: Effect of catalyst dosage on photocatalytic degradation of phenol using $K_7PMo_2W_9O_{39}$/ZnO nanocomposite.

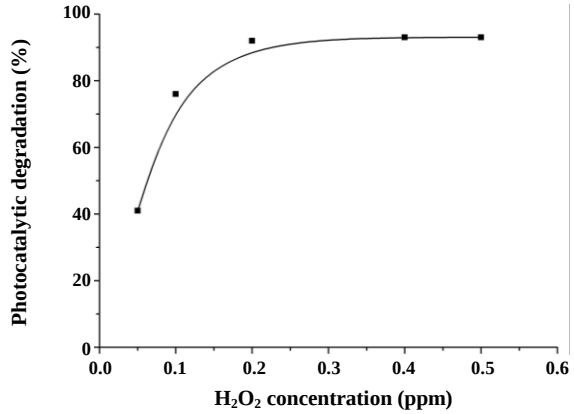

Fig. 4: Effect of oxidant dosage on photocatalytic degradation of phenol using $K_7PMo_2W_9O_{39}$/ZnO nanocomposite.

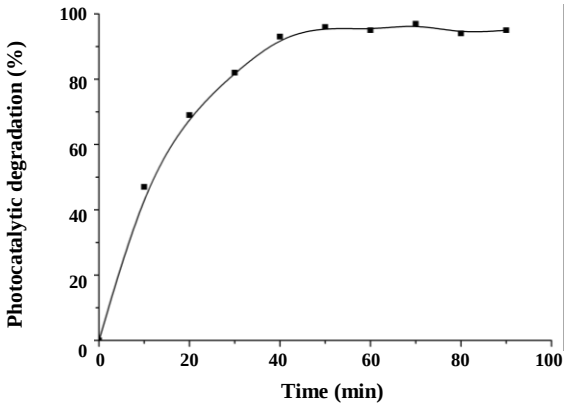

Fig. 6: Effect of contact time on photocatalytic degradation of phenol using $K_7PMo_2W_9O_{39}$/ZnO nanocomposite.

of H_2O_2 as oxidant on the process and this effect was more obvious at lower oxidant dosage. The efficiency of 93% was obtained for photocatalytic degradation of phenol using $K_7PMo_2W_9O_{39}$/ZnO nanocomposite in presence of 0.5ppm H_2O_2 as an oxidant in the system.

Effect of nanocomposite dosage

The effect of nanocomposite dosage in the range of 0.5 to 2.5g/L on the degradation efficiency of phenol was also investigated. As observed from Fig.5, photocatalytic degradation of phenol using the $K_7PMo_2W_9O_{39}$/ZnO nanocomposite was increased from 63% to 93% with an increase of nanocomposite dosage from 0.5 g/L to 2.5 g/L. Although, the increase of degradation efficiency was negligible from catalyst dosage of 1.5g/L to 2.5g/L. Therefore, the nanocomposite dosage of 1.5g/L was considered as the optimum nanocomposite dosage.

Effect of contact time and degradation kinetic

The optimum contact time of reaction is one of the most important parameters in the applicability evaluation of advanced oxidation processes. Effect of contact time on photocatalytic degradation efficiency of phenol using $K_7PMo_2W_9O_{39}$/ZnO nanocomposite was investigated. Fig. 6 indicates that the photocatalytic degradation efficiency of phenol has increased along with the increase of contact time. As previously mentioned, the results showed photocatalytic degradation process of phenol is fast at initial contact time. As it is obvious from Fig.6, the photocatalytic degradation process nearly reached equilibrium at 60min. So, the contact time of 60min was accepted as the optimum contact time for the photocatalytic degradation process of phenol using $K_7PMo_2W_9O_{39}$/ZnO nanocomposite. Similar results were achieved in the study of phenol degradation using UV/ZnO process by *Saeedi et al.*

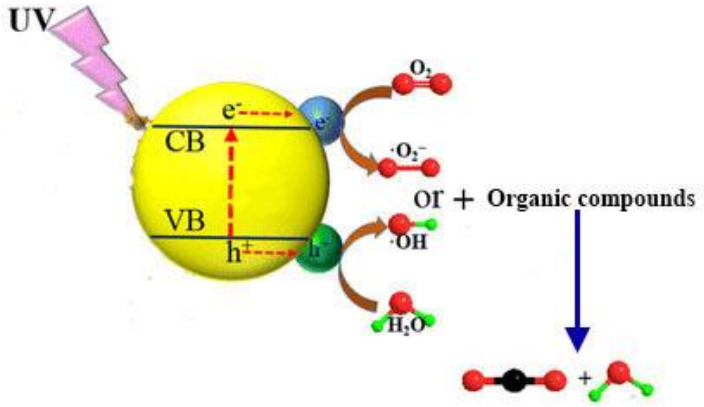

Fig. 7: Mechanism for photocatalytic degradation of organic compounds by semiconductors as a photocatalyst under the UV irradiation.

They reported a removal efficiency of 94.7% for 5mg/L at a contact time of 90min. The reported trend for phenol degradation with contact time in this study also is consistent with the results of the present study [24].

Mechanism of photodegradation using $K_7PMo_2W_9O_{39}$/ZnO

The process of generation, transfer, and consumption of the photogenerated carriers are important elements in photocatalytic reactions. In the photocatalytic process, when photocatalyst absorbs photons with energy higher the semiconductor's band gap energy, electrons from its filled Valance Band (VB) are promoted to its Conduction Band (CB) and valance band holes h^+ are formed (Fig. 7). The electron would reduce any available species, including O_2, water, and hydroxide ion to form hydroxyl radicals. The OH □ ¯ radicals are very strong oxidizing agents and can easily attack the organic molecules and leading finally to their complete mineralization. According to literature, in the photodegradation of organic compounds by ZnO and TiO_2 superoxide and hydroxyl radicals are the main reactive species during photocatalytic degradation. Hydroxyl radicals can be originated from the reaction between holes and H_2O in the presence of semiconductors such as ZnO and TiO_2 [25-28] and the case of $PMo_2W_9O_{39}$/ZnO radicals of OH □ ¯ derived from the electroreduction of dissolved oxygen or H_2O_2 with electrons *via* chain reactions [29].

CONCLUSIONS

A nano photocatalyst of Lacunary Keggin-type heteropolyoxometalatby on ZnO nanoparticles was successfully synthesized. The nano photocatalysts nearly indicated a good photocatalytic activity toward phenol as an organic pollutant model.

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