

Comparison of HPOM and TiO₂ as Photocatalyst for Degradation of Methylene Blue in Aqueous Solution

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ABSTRACT. In this work, the hybrid polyoxometalates (HPOM) (Na₂[PW₁₂O₄₀].nH₂O) photocatalyst has been synthesized by precipitation method and was characterized by SEM and ATR-FTIR techniques. Photocatalytic activity of HPOM was compared with TiO₂ for the photocatalytic degradation of methylene blue (MB) dye. The effect of initial concentration of MB, catalyst dosage and temperature were studied in details. The study found that the HPOM showed the highest photocatalytic activity under UV-vis irradiation and also exhibited remarkable ability to remove MB, suggesting they are promising photocatalyst for wastewater treatment.

Keywords: Polyoxometalates, Photocatalyst, Photodegradation, Methylene blue;

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1. INTRODUCTION

Currently, environmental pollution is the serious problems for human life [1]. The harmful organic pollutants have become one of the major sources of environmental pollution. Therefore, the advancement of economical and green method to treat and purify contamination water has been in the central subject in the technological developments. The conventional treatment methods are physical and chemical methods, such as absorption, oxidation, and so on [2]. Among many methods, photocatalysis is most practicable one, especially for treatment of contaminations, due to its usage of sunlight to decompose organic pollutants [3]. Titanium dioxide (TiO₂) is the most active semiconductor photocatalyst because of its strong oxidizing, long-term thermodynamic stability and relative nontoxicity [4]. Even though TiO₂ with regards to photocatalysis has high band gap energy 3.2 eV, but it has its own limitations which are critical to photocatalytic technology [5], such as: i) recombination of photo-generated electron/hole pairs, ii) fast backward reaction and iii) inefficient visible light utilization. Therefore, studies of new high efficiency photocatalyst are significant.

The syntheses of organic-inorganic hybrid material based on polyoxometalates (POMs) have been paid great attention in the last two decades. Hybrid-POM (HPOM) is a material consisting of three major components, namely POMs, metal ions and organic ligands [6]. HPOM has some potential as a photocatalyst. Generally, HPOM is photo-sensitive activity, which similar to TiO₂. Under UV irradiation, these materials can generate electrons to activate the hydroxyl radicals in water and then degrade the organic dye molecules [7]. Moreover, the diversified structures and topologies of HPOM can be control through different coordination modes and configurations of organic ligands. These make them attractive in applications as diverse as

catalysis, magnetism, photoelectron chemistry, medicine and selective active photocatalyst for the dye degradation [8]. However, the synthesis of HPOM and the research of their photocatalytic performance have seldom been reported so far. So, the study provided a method for the synthesis of HPOM ($\text{Na}_2[\text{PW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$) by nitro aromatic fragments as a ligand. The methylene blue (MB) was used as organic compound to evaluate its photocatalytic activity under UV irradiation in batch photoreactor. Then, the results were compared with the well-known P-25 TiO_2 .

2. MATERIALS AND METHODS

2.1 Materials. Sodium tungstate dihydrate, $\text{Na}_2\text{WO}_4\cdot 6\text{H}_2\text{O}$, p-nitrophenyl phosphate disodium salt hexahydrate, $\text{C}_6\text{H}_4\text{NO}_6\text{P}\cdot 2\text{Na}\cdot 6\text{H}_2\text{O}$ and MB were purchased from Merck, Germany (EMD Millipore Corporation). TiO_2 (99.5%) samples was obtained from Degussa (P-25 TiO_2) Sigma Aldrich. All chemicals used were reagent grade without further purification. Synthesis of HPOM photocatalyst. $\text{Na}_2\text{WO}_4\cdot 6\text{H}_2\text{O}$ was dissolved in distilled water. Then $\text{C}_6\text{H}_4\text{NO}_6\text{P}\cdot 2\text{Na}\cdot 6\text{H}_2\text{O}$ was added to the solution. The reaction was stirred up to dissolution of solids. After that, concentrated H_2SO_4 was added drop wise into the constantly stirring reaction mixture. After some time a yellow precipitate began to form. The solution was kept in dark for 3 days at room temperature. The precipitate was filtered and dried in dark at room temperature for a day. After that, the product was dissolved in ethyl alcohol. The alcohol was evaporated in the oven, and grey-green precipitate is formed. Then, the precipitate was washed with water and dried in the oven at 70°C .

Characterization. The morphology of the samples was observed by using a Scanning Electron Microscope (SEM) on a Zeiss SUPRA 35VP. The elemental content from the samples were observed by using ATR-FTIR. The spectra were obtained on a PIKE MIRacle transform instrument from Perkin Elmer and recorded using a horizontal ATR cell covering the $650\text{-}4000\text{ cm}^{-1}$ spectral range. The ultraviolet-visible (UV-vis) diffuse reflectance spectra were carried out using a spectrophotometer (Shimadzu, Japan/UV-1800 Plus).

2.2 Photocatalytic Experiments. Photocatalytic Reactor. The experiments were performed in a batch photoreactor. Light source was offered by a Pen-Ray® Light Source PS-4 (26mA) with emission $\lambda = 254\text{ nm}$. Photoreactor was set-up as shown in Fig. 1.

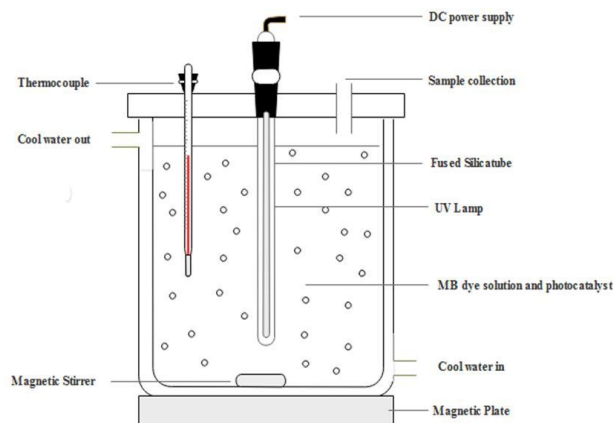


Fig. 1 Schematic diagram of batch photoreactor

2.3 Operating Parameters. Effects of Initial Dye Concentration. In order to investigate the effect of initial MB concentration, various dye concentrations such as 5, 10, 15, 20 and 25 ppm were prepared. 5 ppm MB solution mixed with 0.3 g/L HPOM in the batch reactor and reaction mixture stirred continuously using

magnetic stirrer, at a constant stirring speed of 120 rpm. The temperature of reaction kept constant at 25 °C. After that, 3 ml of sample withdrawn from the flask after the UV light switched on and the absorbance using UV-VIS spectrometer at 664 nm for reaction time at 0, 20, 40, 60, 80, 100 and 120 min. The same procedure were repeated for other initial concentrations and TiO₂ catalyst.

2.4 Effect of Catalyst Dosage. The effect of photocatalyst dosage on photocatalytic degradation of MB using HPOM and TiO₂ were carried out at 0.10, 0.20, 0.30, 0.40, 0.50 g in a room temperature (25 °C). 0.10 g/L of HPOM of 15 ppm of MB solution were added in batch photoreactor. The solution was stirred using magnetic stirrer at constant stirring. 3 ml of reaction mixture drawn after the UV light illuminated to test the absorbance rate at 664 nm in UV-vis spectrophotometer at fixed time interval 0, 20, 40, 60, 80, 100 and 120 min. Later, the experiment were repeated as stated above using different HPOM and TiO₂ dosage.

2.5 Effect of Temperature. 0.3 g of HPOM was added to 15 ppm of dye solution. The temperature of MB solution is varied at 15, 25, 35, 45, and 55 °C using water bath, the solution were stirred at constant stirring speed. The temperature of the reaction mixture was measured using digital thermometer throughout experiment to ensure the temperature of reaction mixture constant from beginning to end of illumination session. However, for temperature that lower than room temperature (25 °C), ice cubes were used to reduce the temperature of reaction mixture. This method is used to let the temperature of reaction mixture reduced in short period of time. Later, 3 ml of sample withdrawn from the flask and absorbance was tested. The experiment were repeated as stated above for TiO₂.

2.6 Analytical Measurement of MB Dye Concentration. The photocatalytic activity of HPOM and TiO₂ samples were evaluated by photocatalytic degradation of MB under UV-vis irradiation ($\lambda = 254$ nm). The samples were analysed after centrifugation (3000 rpm for 3 min). The concentration change of MB determined by the absorbance of the solution at 664 nm, was evaluated with a UV-vis spectrophotometer. Percentage degradation of MB was defined as in Eq. 1.

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

where C₀ is the initial concentration of MB and C is the concentration of MB after photocatalytic reaction.

3. RESULTS AND DISCUSSION

3.1 SEM Analysis. Material morphology was obtained and the micrographs are shown in Fig. 2. SEM micrographs of the HPOM photocatalyst (a) showed large aggregated particles, whereas the TiO₂ (b) particles appeared to be smaller aggregated particles. This results in a high porous volume due to aggregation among tiny particles [9]. Generally, photocatalytic activity of photocatalyst is strongly dependent on its phase structure, crystallize size, surface area, and pore structure. Larger specific area allows more organic reactants to be absorbed onto the surface of the catalyst, while high pore volume results in an improved diffusion of various inorganic products during photocatalytic reaction.

3.2 ATR-FTIR Analysis. Infrared spectroscopy was used to detect the presence of functional groups adsorbed on the surface of the photocatalyst. Fig. 3 represents the FT-IR spectra of TiO₂ and HPOM photocatalyst. The infrared band around 3353 cm⁻¹ and 2866 cm⁻¹ are assigned to the stretching and bending vibrations of O-H of TiO₂ and HPOM, respectively. According to Yu and co-researchers [10]. The hydroxyl groups on the surface of samples contribute to enhancement of the photocatalytic activity. This is because O-H can interact with photogenerated holes, which give better charge transfer and inhibit the recombination of electron-hole pairs [11].

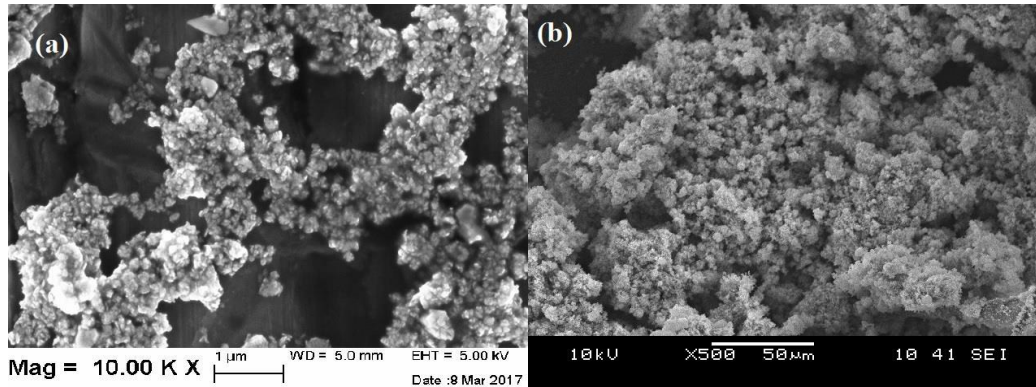


Fig. 2 SEM micrographs of (a) HPOM and (b) TiO₂ photocatalyst

3.3 Photodegradation Study. Effect of Initial MB Concentration. The effect of initial concentration of MB solutions on the percentage removal was investigated at catalyst dosage of 0.3 g and the reaction time of 120 min. Fig. 4 shows the effects of initial concentration of MB from 5 ppm to 25 ppm on percentage degradation of MB. From the result, the percentage of degradation decreased with an increase in the initial concentration of MB. As the concentration increases, more dye molecules are absorbed on the catalyst surface [12]. It causes the penetration of light to the surface of catalyst decreases. Since, the active sites was occupied by dye molecules, the generation of OH• and OH₂• decreased [13]. Moreover, increase in dye concentration shields the UV light. The path length of the photons entering the solution reduced [14]. High concentration requires increment in catalyst surface which needed for degradation. However, the illumination time and the dosage of catalyst are constant in this experiment. Therefore, the relative number of free radicals attacking the dye molecules decreases with increasing amount of dye [15]. At low initial concentration (5 ppm), the MB dye by HPOM giving the highest value of percentage degradation (86.11%) compared to TiO₂ (79.42%) while the percentage was 54.94% by HPOM and 40.56% by TiO₂ for high concentration (25 ppm). This indicates that the photocatalytic activity of HPOM is effective compared to TiO₂.

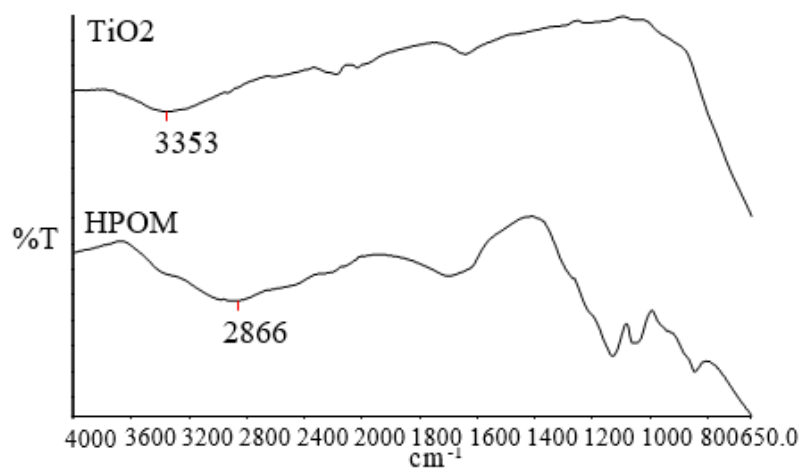


Fig 3 FT-IR spectra of TiO₂ and HPOM photocatalyst

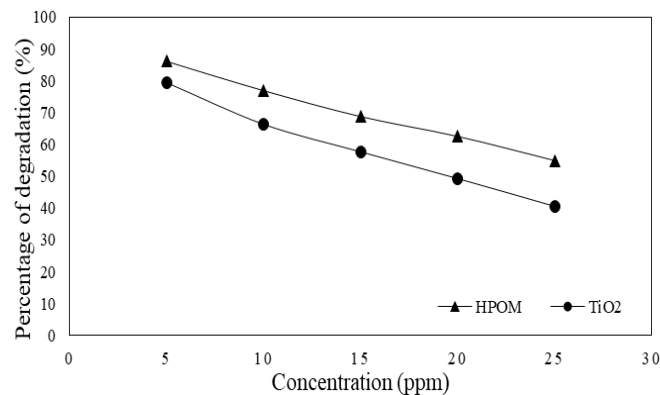


Fig 4 The effect of initial concentration on the photocatalytic activity of MB dye at 120 min. Photocatalyst dosages: 0.3 g, reaction temperature: 25 °C

3.4 Effect of Catalyst Dosage. Fig. 5 shows the degradation of MB in the range of 0.1-0.5 g/L catalyst dosage. From this figure, it is confirm that for HPOM by increasing the dosages, the percentage of MB removal is increase to 81%. Initially, when the catalyst dosages increase, it will increase the number of active sites on the photocatalyst. This will increase the number of hydroxyl and superoxide radical [16] and the amount of photons accelerated become larger in this the process [17]. Thus, it lead to higher degree of degradation of MB was observed.

In contrast, this not happened to TiO₂ when excessive the catalyst dosage. Some of the catalyst effect the solution opacity (transparency or translucency) when the catalyst dosage increased and it causes the reduction in the photon flux in the reaction mixture [18]. Thereby, it decreases the photocatalytic degradation rate. Moreover, increment of catalyst dosage beyond the optimum may also results a loss in surface area by agglomeration (particle-particle interaction) of catalyst particles, hence the part of catalyst surface become unavailable for photon absorption and the rate of degradation decrease [14]. The suspended particles in the reaction mixture cause the excessive light scattering which also progressively reduces the rate of degradation [19]. Therefore, degradation of MB by TiO₂ was reduce after exceed 0.3 g.

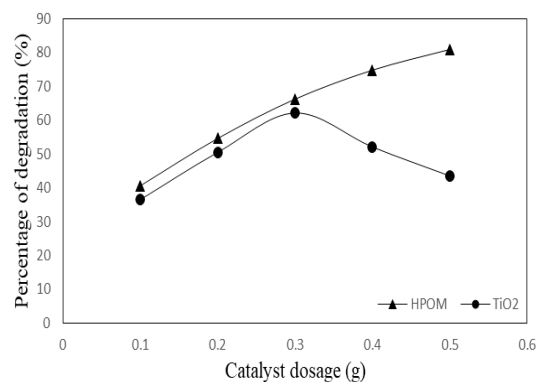


Fig. 5 The effect of catalyst dosage on the photocatalytic activity of MB dye at 120 min. Reaction conditions: MB Concentration: 15 ppm,

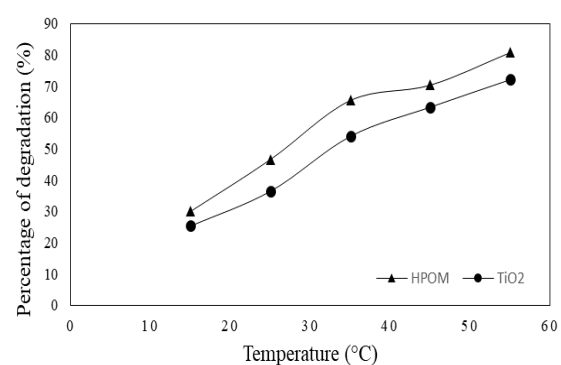


Fig. 6 The effect of temperature on the photocatalytic activity of MB dye at 120 min. Reaction conditions: MB concentration: 15 ppm, photocatalyst dosage: 0.3 g

temperature: 25 °C

3.5 Effect of Temperature. Fig. 6 illustrates the effects of temperature by reaction mixture of MB from 15 °C to 55 °C while other parameters were fixed at 0.3 g catalyst dosage and 15 ppm of MB concentration. HPOM shows the highest degradation rate compared to TiO₂. The percentage degradation of reaction mixture for HPOM and TiO₂ at 55 °C is 81% and 72% respectively. The overall results show that, the increase in the reaction temperature results in an increase in the photodegradation rate. The enhancement of the photooxidation is probably due to the increasing collision frequency of molecules [20].

4. SUMMARY

The HPOM was synthesized by precipitation method with nitro aromatic fragments as a ligand. The degradation behaviour of the MB dye under UV-vis light irradiation was studied. Multiple factor affect the degradation rate of the photocatalyst on the MB removal. High MB removal is achievable with HPOM compared to TiO₂.

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