Characterization and Kinetic Studies on Photocatalytic Degradation of Phenol in Aqueous Solution

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Abstract. Recently, many researchers tend to study the performance of hybrid polyoxometalates (HPOM) as photocatalyst due to its greater performance in photocatalytic degradation. The process that based on the light enhanced generation of reactive OH radical that plays an important role in order to convert organic compound completely into water, CO₂ and inorganic compounds. In this research, the photocatalytic degradation of phenol was studied using HPOM as photocatalyst. The HPOM was synthesized and used to study its effect on photocatalytic degradation of phenol. The synthesized HPOM were characterized using SEM and FTIR. It was found that the surface morphology of the synthesized HPOM displayed an irregular spherical-like shape, granular structure with different size and least distribution of non-agglomerated rod-like nanoparticles. The present of WO₆ octahedral and PO₄ octahedral indicated that Keggin type structure of synthesized hybrid polyoxometalates. The kinetics of photocatalytic degradation of phenol via hybrid polyoxometalates follows pseudo first order kinetic reaction.

1. Introduction
The photocatalytic degradation is a one of effective technique to destroy organic pollutants to CO₂ and inorganic compounds. Titanium oxide (TiO₂) is popular for its excellent photo activity and stability [1]. However technological applications of TiO₂ still be improved especially on the possibility of tuning its photocatalytic related property for a more stringently controlled reaction.

Currently, another photocatalyst have been incorporated known as hybrid polyoxometalates (HPOM) have demonstrated incredible potential in degradation of different organic chemical compound [2]. HPOM is homogeneous photocatalyst, establishing of huge category of well-characterized metal oxygen cluster onion. It is framed basically of tungstate as well as molybdate with or without interest of other elements. It is reported that for the activity of OH radicals appears to be articulated with HPOM than TiO₂. However, issues and difficulties of utilizing HPOM based photocatalysts still stays, for example, understanding the role of iron matching in photocatalyst stability, selectivity and reactivity, and to comprehend the electronic structure of HPOM in their oxidized and diminished ground state and energized state.

Photocatalytic degradation is a common technique with a few clear advantages. But there are still some issues that may need improvements.


TiO$_2$ is considered as noble photocatalyst because of its intrinsic properties but there are some limitations which are critical to photocatalytic technology such as recombination of photo-generated electron or hole pairs. Other than that is its fast backward reaction besides inefficient visible light utilization. Thus the development of new photocatalyst has become a very interesting topic in future research on photocatalytic degradation. One of the good examples is hybrid polyoxometalates.

Hybrid polyoxometalates as a homogeneous photocatalyst has been reported to be an alternative semiconductor of photocatalyst [3]. The stability, combined with extensively alterable molecular properties of HPOM including the heteropoly acids (HPSs) make them as very attractive catalyst. However, there are challenges and problems to be solved. Initially, the application of HPOM is still limited to conventional ones which are acids and oxidants in the production of commodity or specialty chemicals. Another challenge is the understanding of electron structure of HPOM in their oxidized and reduced ground states, exited states and relationship between these states.

The hybrid polyoxometalates can be synthesized to make it unable for specific photocatalytic applications [4]. Besides, the hybrid polyoxometalates characterization can be used as a method to predict and evaluate its performance, efficiency for the reduction of phenolic compounds. Hybrid polyoxometalates may perform better than TiO$_2$ if the synthesizing efforts are properly understood.

The purpose for this paper is to investigate the degradation of phenolic compound by using synthesized hybrid photocatalyst, initiating with the synthesis of HPOM and its characterization. From that point forward, the reaction kinetics is determined through the data analysis. Thorough this research, it is expected that it will contribute significantly towards the essential comprehension on photocatalytic degradation on phenolic compound. The ideally process for phenol degradation is showed in Equation (1) as the end products are gas carbon dioxide and water [5].

$$C_6H_5OH \xrightarrow{UV \text{ Light}} CO_2 + H_2O$$

(1)

2. Materials and Methods

2.1. Materials

Phenol (C$_6$H$_5$O), acetic acids (C$_2$H$_4$O$_2$), methanol (CH$_3$OH), acetonitrile (CH$_3$CN) sulphuric acid (H$_2$SO$_4$), hydrochloric acid (HCL) with the purity (> 95 %) were HmBG. Sodium tungstate Na$_2$WO$_4$, silver acetate (CH$_3$CO$_2$Ag), 4, 4'-bipyridine (C$_{10}$H$_8$N$_2$) and 1,4 -benzotriazole were obtained from Chem Service.

2.2. Synthesis Photocatalyst

The catalyst of HPOM was prepared by mixed of silver acetate (CH$_3$CO$_2$Ag), 1,4-benzotriazole (Hbtz), and 4,4'-bipyridine (C$_{10}$H$_8$N$_2$) and with water. The mixture was stirred the pH value was controlled to pH 2. The mixture was then transferred to Teflon-lined and kept for 3 days at 160 °C. The precipitate obtained was washed with distilled water and dried at room temperature.

2.3. Characterization

Polyoxometalates is prepared according to literature methods [6]. The morphology of the particles will be characterized using scanning electron microscopy (SEM). Crystallization and HPOM structure is analyzed using Fourier Transform Infrared Spectroscopy (FTIR).

2.4. Photocatalytic Study

As the effect of pollutant concentration is importance in any process of water treatment so it is necessary to investigate its dependence. For this study, the concentration of phenolic compounds
concentration will be varied from 20 to 100 ppm with constant dosage of catalyst is applied at 0.1 g.

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM)

The surface morphology and topography properties of the hybrid polyoxometalates (HPOM) was observed by using the Scanning Electron Microscopy (SEM) (Figure 1).

Figure 1. SEM image of the synthesis the synthesized HPOM of magnification at x3000

The configuration of the surface morphology of the synthesized hybrid-polyoxometalates is illustrated in Fig. 1. From this figure, the synthesized hybrid-polyoxometalates sample displayed an irregular spherical-like shape, granular structure with different size and least distribution of non-agglomerated rod-like nanoparticles.

According to Grama [7], the rod-like nanoparticles were observed in their study for synthesized silver tungstate. The samples also displayed aggregation among major and minor particles which resulted in high porous volume. The sample showed a smooth surface area. The samples exhibit least contrast size distribution with average size range at 0.31 nm.

3.2. Fourier Transform Infrared Spectroscopy (FTIR)

The functional group of synthesized hybrid polyoxometalates was recorded by using FTIR around the wavelength range 4000-400 cm\(^{-1}\) by applying potassium bromide (KBr) pallet method. The present of WO\(_6\) octahedral and PO\(_4\) octahedral indicated that Keggin type structure of synthesized hybrid polyoxometalates. Four W\(_3\)O\(_9\) was surround PO\(_4\) formed edge sharing octahedron.
Figure 2. FT-IR spectra of synthesis hybrid-polyoxometalates

Table 1 shows the wavelength values of hybrid polyoxometalates and was distinguished by comparing the values from other researchers. Various types of oxygen atom responsible for the fingerprint of FTIR bands between 1121.19 cm\(^{-1}\) – 728.51 cm\(^{-1}\) of synthesized hybrid polyoxometalates. The main peaks were observed at 1058.83 cm\(^{-1}\), 954.85 cm\(^{-1}\) and 796.41 cm\(^{-1}\). The peak of 1058.83 cm\(^{-1}\) and 796.41 cm\(^{-1}\) showed the vibration of W-O bonds. For the peak of 954.85 cm\(^{-1}\), it indicates the bonding of (W-O-W).

| Wavenumber (cm\(^{-1}\)) | Interpretation | Reference (cm\(^{-1}\)) |
|---------------------------|----------------|-------------------------|
| 1058.83                   | (P-O)          | 1080.39                 |
| 954.85                    | (W-O)          | 982.60                  |
| 796.41                    | (W-O-W)        | 796.18                  |

The peak at 500 cm\(^{-1}\) - 400 cm\(^{-1}\) is due to the metal-oxygen transition bond where the silver-oxide stretching vibration is responsible to indicate strong band at range 499.10 cm\(^{-1}\). This finding of a metal–oxygen region band was also similar obtained from Yang & Wang [8]. A series of band in the region range in between from 1185.67-1593.37 cm\(^{-1}\) are regarded as the bands of organic ligand 1H-Benzotriazole (Hbtz) and 4,4’-Bpyridine (Bpy). The similar of an organic ligand series region finding was also obtained according to previous researcher at the similar range. The band at 3500.39 cm\(^{-1}\) and 1593.37 cm\(^{-1}\) region of the synthesis hybrid-polyoxometalates are due to the stretching vibration of the O-H and N-H hydrogen bonded. The similar finding region band of attribute water molecule was also obtained from Yang & Wang [8].

3.3. Effects of initial concentration

The photocatalytic degradation of phenol was conducted for 60 minutes by adding 0.1 g of HPOM as photocatalyst assist with UV light. In order to study the effect of initial concentration of phenol, various phenol solution was prepared with differ concentration from 20 to 100 ppm. From the result obtained, as the concentration of initial phenol increased, the percentage of phenol degradation also decreases as illustrated in Figure 3. It was found that the 20 ppm of phenol has the highest percentage of phenol degradation meanwhile 100 ppm is the lowest. It can be concluded that the higher the initial concentration will resulted the lowest of percentage degradation.
As the initial concentration of phenol increase, significant amount of UV light is absorbed by the phenol molecules rather than the particles of catalyst of HPOM [9] and affect the decrease penetration of light to the catalyst surface [10]. The big amount of phenol adsorbed on the surface of catalyst reduced the generation of hydroxyl radical [11] as the number of active sites for the adsorption of hydroxyl ion reduced [12]. And these cause least number of the hydroxyl radical attact the phenol compound and cause the efficiency of the degradation decrease [13].

3.4 Kinetic Study

Usually, the kinetics of photocatalytic degradation has often been modelled by Langmuir-Hinshelwood equation that covers the properties of the adsorption on the photocatalyst surface [14]. The Langmuir-Hinshelwood is used to describe the degradation process kinetics and to assume the reaction that will take place on the surface of the catalyst [15]. In this model, the rate of reaction, \( r \) is proportional to the fraction of surface of the substrate, \( \theta \). The model is expressed as Equation (2) where the \( r \) is the reaction rate (mmol. L\(^{-1}\) min\(^{-1}\)) \( k_r \) the reaction rate constant (mmol. L\(^{-1}\) min \(1\)), \( K \) the adsorption equilibrium constant of phenol (1 mmol\(^{-1}\)), and \( C \) the concentration of phenol (mmol L\(^{-1}\)). The relationship between the initial degradation rate \( (r) \) and the initial concentration of organic substrate for a heterogeneous photocatalytic degradation process can be described by Langmuir-Hinshelwood (L-H) [16] model by assuming that the kinetic degradation of phenol is pseudo order at condition \( t=0 \) and \( C=C_0 \), so the equation can be expressed as Equation (3).

\[
\begin{align*}
 r &= -\frac{dC}{dt} = k_r \theta \\
 r_o &= \frac{1}{k_r K C_o} \left( \frac{1}{1 + K C_o} \right)
\end{align*}
\]

(2) (3)

These Equation (3) can be rearranged into linear form as Equation (4)

\[
\frac{1}{r_o} = \frac{1}{k_r K} \left( \frac{1}{C_o} \right) + \frac{1}{k_r}
\]

(4)

Where \( 1/r_o \) is the dependent variable, \( 1/C_o \) the independent variable, \( 1/k_r \) is the linear coefficient and \( (1/k_r K) \) the angular coefficient of the straight line. From this model, the L-H adsorption constant and the rate constant were obtained by plotting \( 1/r_o \) versus \( 1/C_o \) as shown in Figure 4.
The representation of $1/r_0$ versus $1/C_0$, as shown in Equation (4) in the presence of different concentrations of phenol versus initial phenol concentration yields a straight line indicating a pseudo-first order reaction [17]. From Figure 4, the graph was plotted based on five different initial concentration from 20 to 100 ppm with the correlation coefficient, $R^2$ value above 0.99. Therefore it is fitted to Langmuir-Hinshelwood model.

4. Conclusions
The effective degradation of phenol is possible by using photocatalytic degradation method using hybrid polyoxometalates (HPOM) as photocatalyst and assist by UV-light for the photo radiation in this study. From the characterization results, HPOM was successfully been synthesized. By using Scanning Electron Microscopy (SEM) the image show the rod-like nanoparticle shape of sodium tungstate which is the major part in the formation of HPOM. While the result from Fourier Transform Infrared Spectroscopy (FTIR) show the peak of significant bonds of P-O, W-O and W-O-W that proved the structure of HPOM. In this work, the initial concentration of phenol affect the efficiency of phenol degradation. The higher initial concentration of phenol will decrease the percentage of degradation. As the result showed that 20 ppm of phenol have a higher degradation rate instead of 100 ppm which has lower rate of degradation. In order to evaluate the photocatalytic degradation, the kinetic rate was study. The linearization of Langmuir-Heinshelwood plotted showed that the degradation of phenol follows the pseudo first order kinetic reaction.

References
[1] Kormali P, Triantis T, Dimotikali D, Hiskia A and Papaconstantinou E 2006. *Appld. Catal. B: Environ.* **68**(3) 139-146.
[2] Ivanova S 2014 *ISRN Chem. Eng.* 2014 ID 963792.
[3] Kormali, P., Troupis, A., Triantis, T., Hiskia, A., and Papaconstantinou E 2007 *Catal. Today*, **124**(3) 149-155.
[4] Aldred E M, Buck C and Vall K 2009 Chap. 21 - Phenols. In Aldred, Buck, & Vall (Eds.), *Pharmacology* (pp. 149-166). Edinburgh: Churchill Livingstone.
[5] Ammam M 2013 *J. Mater. Chem. A* **1** 6291-6312.
[6] Ling H, Kim K, Liu Z, Shi J, Zhu X and Huang J 2015 *Catal. Today* **258** 96-102.
Acknowledgments
The authors acknowledge the research grant provided by Universiti Malaysia Perlis under the Fundamental Research Grant Scheme ((FRGS/1/2015/Tk02/Unimap/02/2) and RMIC UniMAP that resulted in this article.