H$_3$PW$_{12}$O$_{40}$ and Nano-sized Titania Supported on Urea Formaldehyde Resin for Photo catalytic Decolorization of Dye Pollutants in Aqueous Solution

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Abstract

In this work, H$_3$PW$_{12}$O$_{40}$ (PPT) and nano-sized titania supported on urea formaldehyde (UF) resin was prepared via an impregnation method. The prepared sample was characterized by X-ray diffraction (XRD), UV-Vis spectrophotometer, Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The photo catalytic activity of the PPT/TiO$_2$/UF sample was evaluated by the decolorization of Bromothymol Blue (BB), Direct Yellow12 (DY) and Texas Red (TR) dye solutions under UV-Vis and visible light irradiation. The optical property of the PPT/TiO$_2$/UF sample was evaluated by UV-Vis spectrum. The effect of photocatalyst dosage and dye concentration on photo catalytic decolorization of dyes was investigated. Photo catalytic efficiency of the PPT/TiO$_2$/UF sample was compared with TiO$_2$/UF sample. Moreover, the reusability of the sample was examined.

Keywords: Composite, H$_3$PW$_{12}$O$_{40}$, Photo catalyst, TiO$_2$, Urea formaldehyde.

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Introduction
Textile wastewaters are an important source of environmental contamination. The dye removal in environmental systems was carried out by adsorption, coagulation, ozonation and photo catalytic degradation method. Photo catalytic reaction based on UV and visible irradiated semiconductor provides electrons in the conduction band and holes in the valence band. Finally, this leads to the destruction or decolorization of many organic dyes in aqueous solutions [1-3]. Nowadays, preparation of photo catalyst materials by combining organic and inorganic components has received intense attention due to their improved properties [4-6]. For various reasons such as higher efficiency, better accessibility of the active sites and lower cost, depositing the catalyst on a support is currently favored [7, 8]. Polymeric materials have been widely used in chemical reactions as supports or catalysts [9-12]. Urea-formaldehyde (UF) resin has good properties such as good adhesion, high curing rate, good performance and low cost [13], and H₃PW₁₂O₄₀ is an excellent candidate for improving the photo catalytic activity. Supporting H₃PW₁₂O₄₀ via various supports has been investigated, too [14-17]. Among the photo catalysts, TiO₂ has been most widely used because it is easily available, inexpensive, non-toxic, and photo stable. Generally, combination leads to preparation of more active catalysts which can be more easily handled for recycling and reuse [18, 19]. In this work, the PPT/TiO₂/UF composite was synthesized and characterized. Then, photo catalytic decolorization of dye pollutants such as (BB), (DY) and (TR) was investigated.

Experimental
Materials
In this work, UreaFormaldehyde (37%), sulfuric acid (98%), TiO₂, H₃PW₁₂O₄₀, NaOH, Texas Red (TR), Direct 12 yellow (DY), and Bromothymol Blue (BB) were purchased from Merck Company.

Instrumentation
The product was characterized by using XRD (Holland Philips Xpert, X-ray diffractometer with Cu-Kα radiation), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM, EDX, Vega 2 Tscan). The progress of adsorption experiments was measured by UV-Vis spectrophotometer (Shimadzu UV-2550).

Synthesis
The urea-formaldehyde (UF) preparation
The traditional method of synthesizing urea formaldehyde resin (UF) is condensation polymerization with formaldehyde and urea [20, 21]. 5 g urea and 6 mL formaldehyde (37%) were
heated at 80°C under vigorous stirring. After that, 6 drops of sulfuric acid (98%) were added. Then, the solution was converted to a milky color, and the product was separated and dried at room temperature.

*The TiO$_2$/UF nanocomposite preparation*

First, the prepared urea formaldehyde was dispersed in 100 mL distilled water. Then, TiO$_2$ was added into the urea formaldehyde suspension. The weight ratio of the urea formaldehyde and TiO$_2$ was chosen 7:3 (w/w). After stirring the mixture for 11 hours at 80°C, the product was dried.

*The PPT/TiO$_2$/UF preparation*

The PPT/TiO$_2$/UF was synthesized using the impregnation method. First, the prepared urea formaldehyde was dispersed in 100 mL distilled water. Then, TiO$_2$ and PPT were added into the urea formaldehyde suspension, and the weight ratio of the urea formaldehyde, TiO$_2$ and PPT was chosen to be 7:2:1 (w/w). After stirring the mixture for 11 hours at 80°C, the product was dried.

*Evaluation of photo catalytic activity*

In this research, a high pressure mercury 400 W lamp manufactured by Philips, Holland, and a filament tungsten linear J118 mm, with the power of 500 W, from Long Life Lamp Company, was used as the UV-Vis and visible light sources, respectively. The dye solutions of (BB), (DY) and (TR) with 40, 25 and 20 mgL$^{-1}$ concentrations were prepared as an environmental pollutant model, respectively. The structure of the dyes was showed in scheme 1.

![Scheme 1. Structure of (BB), (DY) and (TR) dyes.](image-url)
Air was blown into the dye solutions with an aquarium pump to maintain the solution saturated with oxygen. In each experiment, 0.5 g L\(^{-1}\) of the prepared nanocomposite was used. The adsorption experiments were examined in the dark. For adsorption and decolorization experiments, the suspension was sampled at regular intervals of 15, 30, 45, 60, 90, 120 and 180 minutes, and was immediately centrifuged to completely remove catalyst particles. Then, the concentration of dye as a function of time was calculated by the following Eq. (1).

\[
X = \frac{C_0 - C_t}{C_0} \text{Eq. (1)}
\]

Where \(C_0\) is the initial dye concentration and \(C_t\) is the dye concentration at time \(t\).

**Results and discussion**

In Figure 1(a and b), the XRD pattern of the TiO\(_2\)/UF and PPT/TiO\(_2\)/UF samples can be seen, respectively. In Figure 1(a and b), the pure TiO\(_2\) diffraction patterns can be observed. From the XRD patterns, it was found that the H\(_3\)PW\(_{12}\)O\(_{40}\) was hardly observed in PPT/TiO\(_2\)/UF sample. Figure 1b shows the weak peak at \(2\theta=34.4^\circ\) that was related to the H\(_3\)PW\(_{12}\)O\(_{40}\)[18].

![XRD patterns of the samples](image)

**Figure 1.** XRD patterns of the samples, (a) TiO\(_2\)/UF, (b) PPT/TiO\(_2\)/UF.

In order to investigate, the FT-IR and UV-Vis were carried out. The FT-IR and UV-Vis spectra of the H\(_3\)PW\(_{12}\)O\(_{40}\), pure TiO\(_2\), TiO\(_2\)/UF and PPT/TiO\(_2\)/UF are depicted in Figure 2(a-e) and Figure 3(a-
e), respectively. Corresponding to Figure 2a, the peaks of 520 and 670 cm\(^{-1}\) were detected for the stretching vibration of Ti-O-Ti bonds. The FT-IR spectrum, as shown in Figure 2b, revealed that the four characteristic peaks of 840, 890, 990 and 1080 cm\(^{-1}\) were related to \(\text{H}_3\text{PW}_{12}\text{O}_{40}\), which could be assigned to W-O-W, W=O and P-O bonds, respectively [21]. Figure 2d shows the FT-IR spectrum of PPT/TiO\(_2\)/UF sample. The bands of 520, 670, 840, 890, 990, and 1080 cm\(^{-1}\) were attributed to the vibration mode of Ti-O, W-O-W, W=O, and P-O, thereby confirming the existence of TiO\(_2\) and \(\text{H}_3\text{PW}_{12}\text{O}_{40}\), respectively. Figure 2e shows the FT-IR spectrum of TiO\(_2\)/UF sample. Comparison of Figure 2(a and e) illustrates the existence of TiO\(_2\).

Figure 2. FT-IR spectra of the samples, (a) TiO\(_2\), (b) \(\text{H}_3\text{PW}_{12}\text{O}_{40}\), (c) UF, (d) PPT/TiO\(_2\)/UF and (e) TiO\(_2\)/UF.

Figure 3(a-e) presents the UV-Vis spectra of the TiO\(_2\)/UF, PPT/TiO\(_2\)/UF, PPT, TiO\(_2\) and UF. As shown in Figure 3b, TiO\(_2\) sample had a peak at about 243 nm. As shown in Figure 3a, for TiO\(_2\)/UF sample, there was a peak at about 243 nm. This peak was related to the presence of TiO\(_2\). Figure 3(d and e) show the absorption peaks of the UF and PPT samples at about 206 and 268 nm,
respectively. The absorption peaks of the PPT/TiO$_2$/UF sample at about 206, 268 and 469 nm were observed (Figure 3c). The peak at about 268 nm was related to the presence of H$_3$PW$_{12}$O$_{40}$.

**Figure 3.** UV-Vis spectra of the (a) PPT, (b) PPT/TiO$_2$/UF, (c) TiO$_2$, (d) TiO$_2$/UF and (e) UF.

Figure 4(a-c) shows the SEM images of the pure TiO$_2$, TiO$_2$/UF and PPT/TiO$_2$/UF samples. Figure 4a shows the TiO$_2$ sample is nanoparticles with diameters of about (24-200) nm. For the TiO$_2$/UF and PPT/TiO$_2$/UF nanocomposites, UF is micro-spheres with diameters of about (2.6-4.7) µm, and the TiO$_2$ and PPT nanoparticles are dispersed around the UF (Figure 4(b and c)). Figure 4d illustrates the EDX analysis of the PPT/TiO$_2$/UF composite. The result of the EDX shows the presence of Ti, W and P elements for composite.

In this work, (BB), (DY) and (TR) dye solutions were chosen as the environmental pollutant model for the photo catalytic evaluation of the prepared samples. First, the adsorption degree of dye solutions on the surface of the UF sample was measured in the dark. Then, the photocatalytic activity of the UF sample for the decolorization of dye solutions was examined under UV-Vis irradiation. The adsorption experiments indicated that 3, 14 and 20% of (BB), (DY) and (TR) dye solutions were adsorbed on the surface of the UF sample after 180 min. Photo catalytic experiments also showed that 5, 16 and 25% decolorization of (BB), (DY) and (TR) dye solutions had occurred. The comparison of these experiments showed that the UF had poor photocatalytic activity (Figure 5).
Figure 4. SEM images of the samples: (a) TiO$_2$, (b) TiO$_2$/UF, (c) PPT/TiO$_2$/UF and (d) EDX analysis of the PPT/TiO$_2$/UF composite.

Figure 5. Comparison of photo catalytic decolorization and dye adsorption of (BB), (DY) and (TR) on surface of the UF under UV-Vis irradiation and dark condition.

The comparison of the photo catalytic activity of the TiO$_2$/UF and PPT/TiO$_2$/UF composites for the decolorization of (BB), (DY) and (TR) dye solutions has been depicted in Figure 6 (A-C). Photo catalytic results showed that the PPT/TiO$_2$/UF composite had high photo catalytic activity as compared to the TiO$_2$/UF composite.
Figure 6. Photo catalytic decolorization of BB, DY and TR dye solutions in the presence of the (a)TiO$_2$/UF and (b) PPT/TiO$_2$/UF samples under UV-Vis irradiation.
The photo catalytic experiments showed that 56% (BB), 97% (DY), 96% (TR) and 42% (BB), 59% (DY) 67% (TR) decolorization of dye solutions had occurred in the presence of the PPT/TiO$_2$/UF and TiO$_2$/UF composites under UV-Vis irradiation and after 180 min, respectively. Until now, some efforts have been made to develop an efficient visible light photo catalyst for wastewater treatment [22-24]. In this work, the photo catalytic activity of the PPT/TiO$_2$/UF composite was examined under the visible light. The photo catalytic results showed that 48%, 73% and 87% decolorization of BB, DY and TR dye solutions had occurred under visible light and after 180 min, respectively (Figure 7a). For PPT/TiO$_2$/UF sample the photo catalytic activity under visible and UV-Vis irradiation was compared in Figure 7b. These results showed that the PPT/TiO$_2$/UF sample could degrade dye pollutants under visible light. The effect of (TR) dye concentration from 10 to 100 mgL$^{-1}$ was studied in presence of the PPT/TiO$_2$/UF composite under UV-Vis irradiation (Figure 8).

![Figure 7](image-url)

**Figure 7.** (a) Photo catalytic decolorization of (BB), (DY) and (TR) dye solutions in presence of the PPT/TiO$_2$/UF sample under visible irradiation, (b) Comparison of photo catalytic activity under visible and UV-Vis irradiation for PPT/TiO$_2$/UF sample.
It was found that the decolorization efficiency of the (TR) dye solution was decreased when increasing the initial dye concentration. By increasing the dye concentration, more dye molecules could be adsorbed on the surface of the PPT/TiO$_2$/UF sample, and the active sites of the catalyst would be reduced. The influence of photocatalyst dosage to the decolorization extent of (TR) dye solution was investigated from 0.25 to 4.5 g/L of the PPT/TiO$_2$/UF sample. According to results effective decolorization was occurred with 0.5 g/L of catalyst concentration (Figure 9).

It should be noted that at higher doses of catalyst, the scattering effect and the aggregation of particles may reduce the catalyst efficiency [25]. The reusability of the PPT/TiO$_2$/UF sample for
decolorization of (TR) dye solution was also investigated. The results after four runs experiment 93, 92 and 92 %, were obtained (Figure 10).

As shown, the PPT/TiO$_2$/UF sample could be an efficient photo catalyst for degradation of dye pollutants under UV-Vis and visible irradiation. Coupling and supporting homogeneous and heterogeneous photo catalysts with different band gap energies can lead to an increase in photo catalytic efficiency. Generally, under UV-Vis and simulated sunlight irradiation, the electrons were generated by exciting TiO$_2$. After that, H$_3$PW$_{12}$O$_{40}$ could accept these electrons and form its reduced state, the H$_3$PW$_{12}$O$_{40}$ was then re-oxidized by O$_2$, yielding ·O$_2$ and H$_3$PW$_{12}$O$_{40}$. The reactive species such as h$^+$, ·O$_2$, ·HO$_2$, ·OH etc. generated in the system finally resulted in the pollutants decolorization [14].

**Conclusion**

Summary, a new type of heterogeneous photo catalytic material for removal of organic pollutants was prepared. Urea formaldehyde (UF), as a support, was used for TiO$_2$ and PPT. High photo catalytic activity of the sample is attributed to the synergistic effect between the PPT and the TiO$_2$/UF.

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**References**

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