Synthesis of Tungsten doped Titanium dioxide nanofibers for the degradation of paraquat by photocatalytic process

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Abstract. In this research, tungsten doped titanium dioxide nanofibers were prepared by the hydrothermal method and used as a photocatalyst in the photocatalytic process. The prepared samples were investigated by XRD, FESEM, and UV-vis spectrophotometer. The experimental results show that the prepared samples have an anatase phase and absorb UV light. In addition, it was found that the increased amount of tungsten resulted in larger crystal size. For the efficiency of paraquat degradation by the photocatalytic activity of the prepared nanofibers, it was found that the W:15TiO₂ nanofibers had the highest efficiency of paraquat degradation. It can degrade 73.97% of paraquat in 120 min.

1. Introduction

Paraquat is a highly toxic herbicide. If chemicals are absorbed into the body, it will have serious consequences. Paraquat is highly soluble in water, so it is easily washed away by rainwater or watering plants and can flow into natural water sources. Currently, the removal of paraquat contaminated water is commonly used for physical adsorption and chemical adsorption. The adsorbents commonly used are rice husk [1], soil [2], activated carbon [3], and Goethite [4].

The photocatalytic process is a process that has attracted attention among researchers in the degradation of dyes and heavy metals such as mercury, lead, and cadmium [5]. The most popular photocatalyst is Titanium dioxide (TiO₂) because it is stable to chemicals, no toxicity, and low cost. However, TiO₂ has a wide energy bandgap of 3.2 eV; therefore, it can only react in the range of ultraviolet. Coupling TiO₂ with other metal oxides is a method for improving photocatalytic properties of TiO₂ [6]. The electron - hole recombination rate is a key factor affecting the efficiency of the photocatalyst. This influences the production of photo - excited sites on the surface of the catalyst. When TiO₂ is doped with WO₃, a semiconductor with a smaller energy gap band, charge separation is improved. In addition, WO₃ can increase the acidity of TiO₂ affects the adsorption equilibrium and photooxidation activity of the catalyst.

In this research, synthesize tungsten doped TiO₂ (W doped TiO₂) nanofibers with a hydrothermal method, which is easy and environment friendly. The characteristics of the prepared sample were investigated using field emission scanning electron microscope (FESEM), X-ray diffractometer (XRD)
and UV-VIS Spectrophotometer. The degradation efficiency of paraquat by photocatalytic processes was also studied.

2. Experimental methods

2.1. Preparation of W doped TiO$_2$ nanofiber

In a typical synthesis, TiO$_2$ and Na$_2$WO$_4$$\cdot$2H$_2$O powder in the ratio of W: TiO$_2$ 1:1, 1:5, 1:10, and 1:15 were dissolved in 100 ml of 10 M NaOH. The solution was well mixed by stirring with magnetic stirrer for 20 min and then kept at room temperature for 24 h. The resulting solution was then transferred into a Teflon-lined stainless-steel autoclave, sealed and heated for 48 h 30 min in an oven at 150 °C. The final product was washed with de-ionized water until pH = 7, dried for 24 h at 120 °C, and calcined for 2 h at 500 °C. The prepared samples were analyzed for crystalline structure, morphology, and absorption of light by XRD, FESEM, and UV-vis spectrophotometer, respectively.

2.2. Photocatalytic activity

The photocatalytic degradation of paraquat was measured by monitoring the absorption of paraquat solution at 258 nm. The photocatalytic process was performed using a 10 W UV reactor. The samples for photocatalysis were prepared by mixing 100 mg of prepared samples with in 60 ml of 100 ppm paraquat aqueous. This solution was stirred in darkness for 30 min to obtain the adsorption/desorption equilibrium of the paraquat molecules on the surface of the prepared samples. Oxygen was bubbled continuously through the mixture during the reaction process to prevent a change in the concentration of dissolved oxygen. At regular intervals, 3 mL of suspension was sampled and centrifuged with 6000 rpm for 15 min. The residual concentration of paraquat solution was monitoring using UV-vis spectrophotometer at a wavelength of 258 nm. Percentage degradation of the initial paraquat concentration was calculated using equation (1)

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\% \text{ degradation} = \frac{C_0 - C_t}{C_0} \times 100
\]

where $C_0$ is the initial paraquat concentration, $C_t$ is the concentration of paraquat at irradiation time $t$.

3. Results and discussion

![Figure 1. XRD patterns of prepared samples.](image-url)
Figure 1 shows the XRD pattern of TiO$_2$ and W doped TiO$_2$ nanofibers. The anatase and rutile mixed phases are observed in all samples. The XRD patterns show anatase peak at $2\theta = 24.75^\circ$ 48.34$^\circ$ and 75.48$^\circ$ and rutile peak at $2\theta = 28.86^\circ$. The XRD peak at 10.44$^\circ$ indicates the occurrence of nanofibers. However, no W-derived peak is detected for W doped TiO$_2$ nanofibers and the (101) diffraction plan shows that the peak position of W doped TiO$_2$ nanofibers shift slightly to lower $2\theta$, because the ionic radius of W$^{6+}$ (41 pm) is smaller than that of Ti$^{4+}$ (53 pm).

The morphology of the prepared sample is shown in figure 2. Figure 2 (a) shows that pure TiO$_2$ has a distinctive fiber shape. Figure 2 (b) - (e) shows that tungsten content affects the fiber growth of the prepared samples.

**Figure 2.** SEM images of (a) pure TiO$_2$, (b) W:TiO$_2$, (c) W:5TiO$_2$, (d) W:10TiO$_2$, and (e) W:15TiO$_2$. 
Figure 3. UV-vis spectra of prepared samples.

Figure 3 shows the UV-vis spectra of the prepared sample. Pure TiO$_2$ show absorption peak at 253 nm. When tungsten was doped, it was found that the optical absorption peak of the prepared sample shifted towards longer wavelength. Absorption at wavelengths below 400 nm derives from the transition of electrons from the valence band to the conduction band of TiO$_2$. The photocatalytic activity of the prepared samples was measured by the degradation of the paraquat solution under UV irradiation. The relationship between the degradation efficiency of the paraquat solution and irradiation time is shown in figure 4. The first 30 min of radiation is evident that the degradation efficiency increases significantly with an increase in the irradiation time. After that, the degradation efficiency will be stable in every prepared sample. The results show that W: 15TiO$_2$ can degrade paraquat up to 73.97% in 120 min, which is still considered low efficiency. For paraquat content analysis to be accurate, it should be analyzed by GC-MS, which must be further studied.

Figure 4. Relationship between the degradation efficiency of the paraquat solution and irradiation time.
4. Conclusion

W doped TiO$_2$ nanofibers were synthesized by the hydrothermal method. The prepared samples show the mixed-phase between anatase and rutile phases of TiO$_2$. All prepared samples can absorb UV light. When the prepared samples were used as photocatalysts for paraquat degradation, it was found that W:15TiO$_2$ had the highest paraquat degradation efficiency, followed by W:10TiO$_2$ and pure TiO$_2$. This shows that the amount of tungsten affects the photocatalytic activity.

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