# SYNTHESIS OF TUNGSTEN TRIOXIDE/HYDROXYAPATITE ($WO_3$/HAp) PHOTOCATALYST FOR METHYLENE BLUE DEGRADATION

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**Abstract:** Dyes have toxic properties and complex chemical structures which become a threat to the ecosystem if it exposes to the environment. A photocatalyst is a semiconductor material that can run a photocatalytic process under UV or visible light to degrade most organic molecules, ideally to $H_2O$ and $CO_2$. Tungsten trioxide ($WO_3$) is a visible photocatalyst which could use sunlight irradiation to treat the wastewater pollutant. In this study, $WO_3$ material was hybridized with hydroxyapatite (HAp) through the sol-gel method to degrade methylene blue (MB) synthetic pollutants. The FTIR and SEM-EDX characterization confirmed the presence element of the $WO_3$/HAp hybrid material. The original $WO_3$ and modified $WO_3$/HAp photocatalysts with concentrations of 10, 15, and 20 mg were tested to degrade 15 ppm of 50 ml MB solution under visible light for 4 hours. The highest pollutant degradation was obtained using a 20 mg photocatalyst, which reached the photodegradation efficiency of 73.072% for $WO_3$ and 88.689% for $WO_3$/HAp. The result proved that $WO_3$/HAp hybrid photocatalyst showed higher degradation performance than the unmodified $WO_3$ photocatalyst. The results of this research can be developed for industrial wastewater treatment, including the papermaking, printing and dyeing industries.

**Keywords:** Textile industrial waste; Photocatalytic; Tungsten trioxide-hydroxyapatite ($WO_3$/HAp); Wastewater degradation

**Abstrak:** Zat warna memiliki sifat beracun dan memiliki struktur kimia kompleks yang dapat menjadi ancaman bagi ekosistem apabila terpapar ke lingkungan. Fotokatalis heterogen menggunakan semikonduktor yang memicu proses fotokatalitik dengan bantuan sinar UV atau sinar tampak dalam mendegradasi kebanyakan limbah organik, menjadi $H_2O$ dan $CO_2$. Tungsten trioksida ($WO_3$) merupakan fotokatalis yang dapat menggunakan cahaya matahari untuk mendegradasi polutan pada air limbah. Pada penelitian ini, $WO_3$ dihibridisasi dengan hidroksiapatit (HAp) melalui metode sol-gel untuk mendegradasi polutan sintetik *Methylene Blue* (MB). Hasil karakterisasi FTIR dan SEM-EDX mengkonfirmasi unsur-unsur penyusun material $WO_3$/HAp. Fotokatalis $WO_3$ munri dan $WO_3$/HAp yang dimodifikasi diuji untuk mendegradasi 15 ppm larutan MB 50 ml di bawah cahaya tampak selama 4 jam dengan konsentrasi 10, 15 dan 20 mg. Degradasi polutan tertinggi diperoleh dengan menggunakan fotokatalis

20 mg yang mencapai efisiensi 73,072% untuk $WO_3$ dan 88,689% untuk WO3/HAp. Hasil tersebut membuktikan bahwa fotokatalis hybrid $WO_3$/HAp menunjukkan kinerja degradasi yang lebih baik daripada fotokatalis $WO_3$ tanpa modifikasi.

**Kata kunci:** Limbah industri tekstil; Lotokatalitik; Tungsten trioksida-hidroksiapatit ($WO_3$/HAp); Degradasi air limbah

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## Introduction

In recent years, pollution of water sources has been a severe problem worldwide. Poisonous dyes liquid from textile industrial discard becomes a massive pollutant in natural water bodies. Moreover, the complexity of the dye's chemical structure with long-lasting color makes it challenging to treat (Khor, Khan and Harunsani, 2023) (Hafizah et al., 2019). Various methods have been carried out to remove dyes from wastewater before discharge to the environment, such as adsorption (Hafizah et al., 2019), coagulation (Fagundes-klen and Dotto, 2019), and aerobic degradation (Bharti et al, 2019). However, because of some drawbacks, the water treatment process runs less efficiently (Rajalakshmi and Alagumuthu, 2021). Separating the adsorbent from the dye is a significant problem in the adsorption process. In the coagulation method, sludge will be produced at the end of the process, which requires additional handling. On the other hand, aerobic degradation offers a relatively low price, but the process takes place long time (Moosavi et al, 2020).

The photocatalytic method is promising to degrade dye pollutants into clean water and $CO_2$ under ultraviolet (UV) or visible light (Bora *et al.*, 2022). In this process, the catalyst is exposed to light to absorb photons for reactions that occur only through electrons and holes (Azimifar, Ghorbani and Peyravi, 2022). Then, the organic contaminants are destroyed by photogenerated electron-hole ($e^-$-$h^+$) pairs, $^{\bullet}OH$ and $O_2^{\bullet-}$ free radicals in aqueous media (Fulzele, Bhanvase and Pandharipande, 2022; Khor, Khan and Harunsani, 2023). Numerous advantages of the photocatalytic design are high efficiency, green process, inexpensive, reusable, and low possibility of creating secondary contaminants (Zhang et al, 2019) (Azimifar, Ghorbani and Peyravi, 2022). Some researchers have studied the performance of photocatalytic processes to degrade wastewater recently. Seifunnisha and Shanthi (2021) showed the degradation result of malachite green (MG) dye of 88% (UV-light treatment) and 87% (visible light treatment) using ZnO catalyst combined with PEG/Aloe vera. Sadeghzadeh-Attar (2018) examined the photocatalytic activity of $SnO_2$ nanotubes using UV light on methylene blue (MB) dye and obtained the degradation result of MB, reaching 90.7%. In another study, the photocatalytic activity of the $TiO_2$ nanoparticle catalyst on methylene blue (MB) and congo red (CR) dyes was investigated by Sathiyan et al (2020) using UV light. The degradation efficiency was 85% and 99.7% for MB and CR dyes, respectively.

The other semiconductor Tungsten trioxide ($WO_3$) is promoted semiconductor with a small band gap. However, $WO_3$ cannot work effectively as a catalyst because the electrons generated in the conduction band (CB) of $WO_3$ cannot reduce $O_2$. It is due to the redox potential of electrons in tungsten trioxide CB (+0.5 eV) being greater than that of $O_2$ (-0.33 eV) so that electron transfer does not occur. As a result, these electrons can return to the valence band (VB) and the photocatalytic process will be inhibited (Jeevitha et al, 2018). One way to overcome the drawback is to add carriers with good conductivity to increase the transfer of the extracted electrons (Ismail et al, 2017).

Hydroxyapatite (HAp) is a non-toxic inorganic material with good chemical stability. HAp in combination with semiconductors catalyst can improve photocatalytic performance (Piccirillo and Castro, 2017). Hence, it will increase the degradation efficiency of dye molecules in wastewater. HAp promotes dye adsorption due to its positively charged calcium ions and negatively charged phosphate ions. This double charge will attract the ionic dyes and bind to the ions from HAp. Finally, the dye molecules will be drawn to the catalyst surface and degraded. Several other studies have also proven that the adsorption ability and stability of  Piccharillo et al (2016) synthesized HAp-$TiO_2$ material to degrade diclofenac and fluoxetine pharmaceutical waste. The HAp-$TiO_2$ catalyst showed satisfactory performance by successfully degrading 100% fluoxetine and 92% diclofenac. Piccharillo et al (2013) used HAp-β-TCP-$TiO_2$ material to degrade methylene blue dye and obtained a total degradation in just 1 hour. Mohamed and Baessa (2013) tested the photocatalytic activity using a Pd-$TiO_2$-HAp catalyst on potassium cyanide (KCN) pollutants. Get 100% KCN relegation in just 45 minutes.

In sum, $WO_3$ has never been functionalized with HAp, especially for photocatalytic processes. Therefore, a new hybrid material ($WO_3$/HAp) is synthesized as a photocatalyst for dye removal application in an aquatic system in this work. The $WO_3$/HAp hybrid catalyst is potentially owing better photocatalytic performance.

## Methodology

### Materials

All Chemicals, namely tungsten trioxide ($WO_3$) particles, hydroxyapatite (HAp) particles, methylene blue (MB), and absolute ethanol were purchased from Sigma Aldrich and used directly in the experiment.

**Synthesis of $WO_3$/HAp composites**

The $WO_3$/HAp composite was prepared by the sol-gel method under ultrasonication. 10 mg of $WO_3$ was added to 30 ml of ethanol and sonicated for 10 minutes to obtain a homogeneous $WO_3$ solution. Separately, 15 mg of HAp was added to 20 ml of ethanol and sonicated for 10 minutes to obtain the HAp solution. Then, the HAp solution is dropwise into the $WO_3$ solution with continuous stirring. Then the solution was sonicated again for 30 minutes. Then the solution was centrifuged and dried at 60 °C for 24 hours to obtain $WO_3$/HAp composites

**Characterization**

The morphological structure of the composite was analyzed using scanning electron microscopy (SEM, Thermo Fisher Scientific, Series-9951173). The composition of the composites was analyzed using an energy-dispersive X-ray detector (EDX, Thermo Fisher Scientific, Series-9951173). The functional groups were analyzed using Fourier Transform Infra Red (FTIR, IR Prestige-21 SHIMADZU, Series A210048).

**Photocatalytic degradation of methylene blue**

In this study, the methylene blue (MB) dye was prepared as a pollutant model in textile wastewater. The amount of 10, 15, and 20 mg of $WO_3$ and $WO_3$/HAp photocatalysts was added into a batch reactor containing 50 ml of 15 ppm methylene blue solution. Each sample was irradiated by visible light (Osram lamp 100 W) under continue stirred for 4 hours. Then every 30 minutes, 3 ml of the sample was taken and centrifuged to separate the particles from the MB solution. The absorbance value of MB was then measured using a UV-vis spectrophotometer to determine its concentration.

## Results and Discussion

**SEM and EDX analysis**

The morphological structure of the tungsten trioxide ($WO_3$), hydroxyapatite (HAp), and $WO_3$/HAp composites are shown in Figure 1. Furthermore, the EDX spectra of the $WO_3$/HAp were also performed in Figure 2 and Figure 3 to confirm the presence of element composition of the material after hybridization. SEM results show that the $WO_3$ particles have an almost round shape with uniform sizes; similar results were also reported by (Nandiyanto et al., 2018). Meanwhile, HAp particles are described as having a crystal-like shape (Mirela et al., 2020). On the other hand, $WO_3$/HAp shows a crystal-like shape that clumps together to form spheres. These results indicate the formation of a composite between tungsten and hydroxyapatite.

The chemical composition of each composite is presented in Table 1. It can be seen that the composition of the $WO_3$/HAp composite contains tungsten which is derived from $WO_3$. Furthermore, EDX analysis of the composite also contains phosphate and calcium, which are the core components of hydroxyapatite. Therefore, this result proves the successful hybridization of $WO_3$/HAp material.

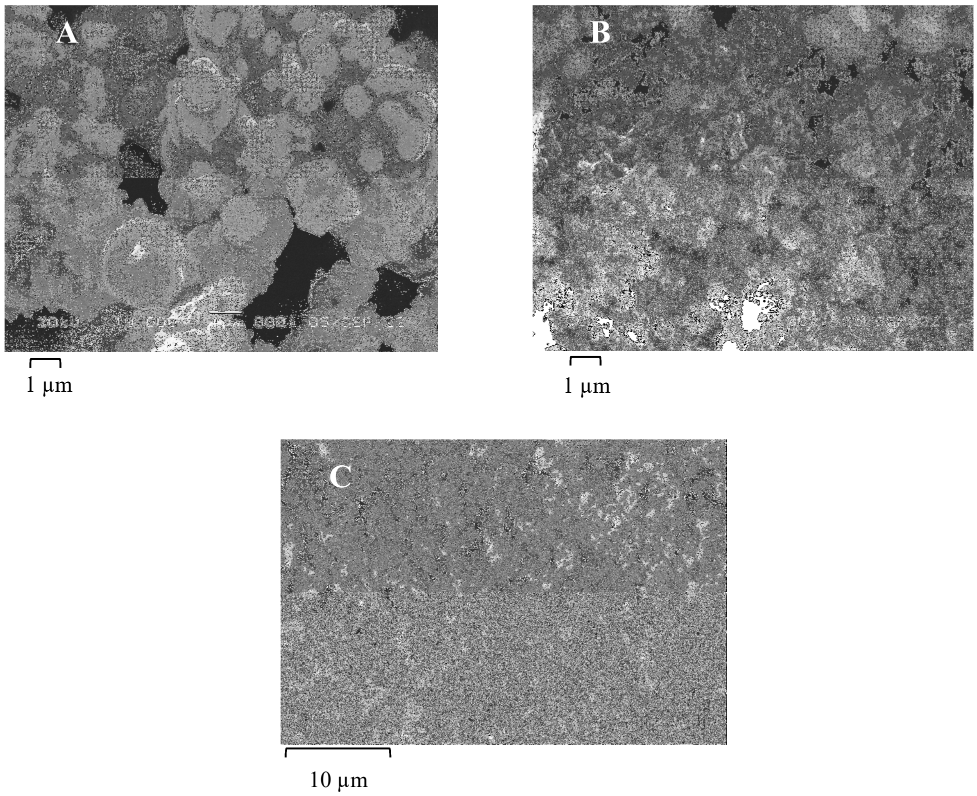


Figure 1. The SEM images of composite: (a) $WO_3$, (b) HAp and (c) $WO_3$/HAp

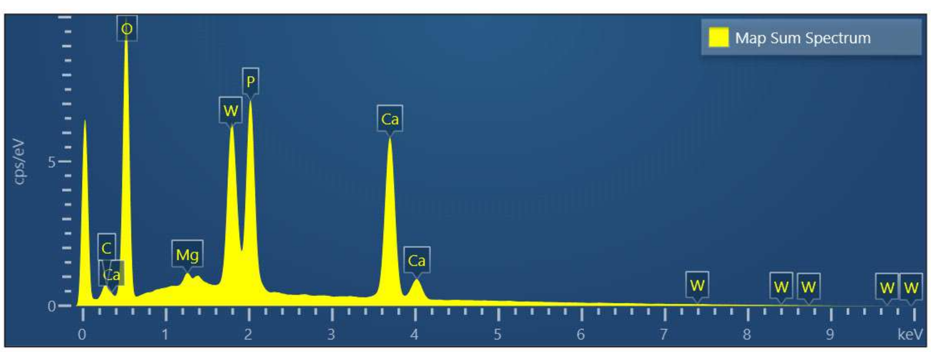


**Figure 2**. The EDX spectra of $WO_3$/HAp

**Table 1.** Chemical composition (%) of $WO_3$/HAp from EDX analysis

| Composition (%) | | | | | |
|---|---|---|---|---|---|
| Carbon | Oxygen | Tungsten | Phosphate | Calcium | Magnesium |
| 1,7 | 30,6 | 24,2 | 13,1 | 29,9 | 0,5 |

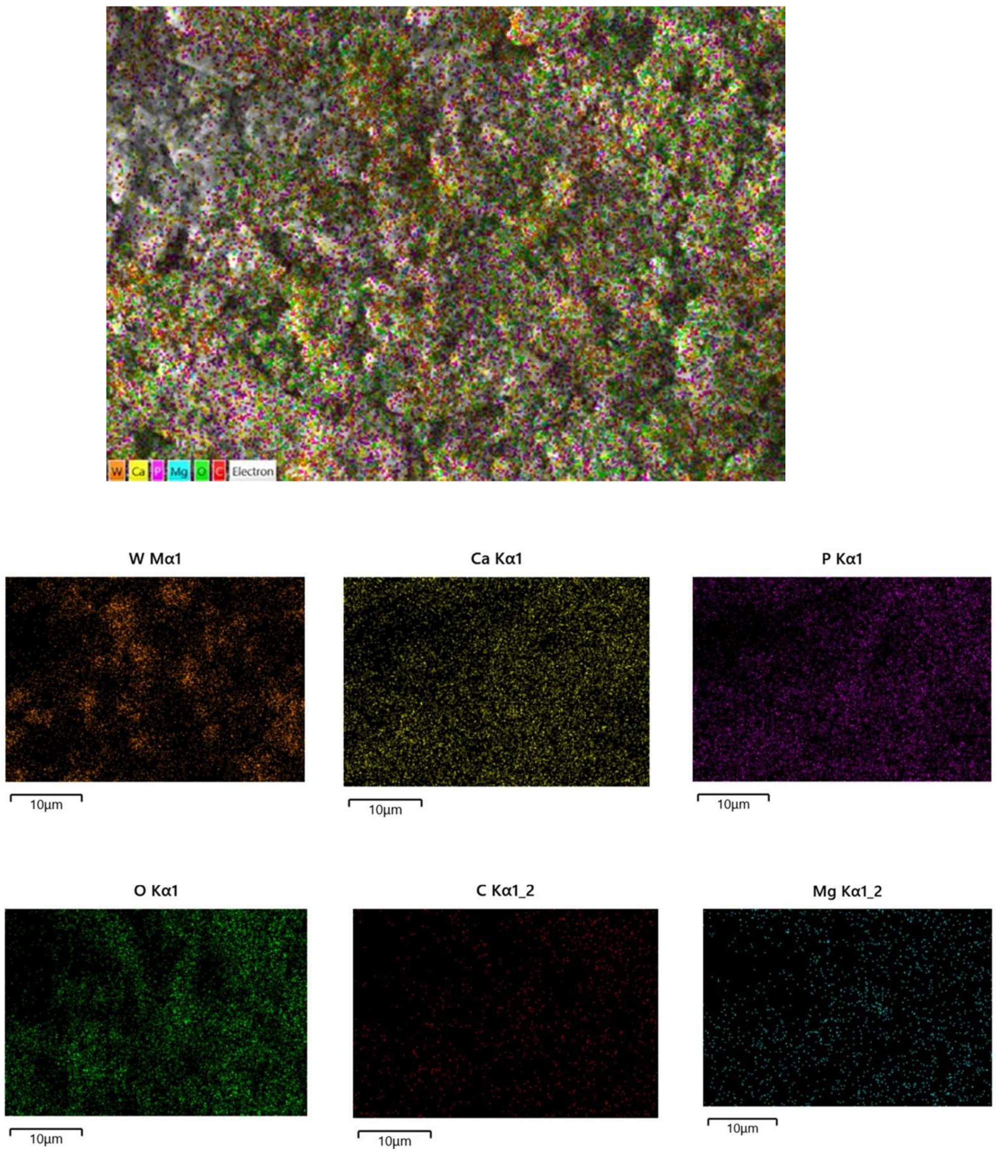


**Figure 3**. Elemental mapping of the $WO_3$/Hap composite showing the uniform distribution of tungsten, calcium, phosphate, oxygen, carbon and magnesium.

## Functional group analysis

The FTIR spectra performed in Figure 4 are to determine the chemical bonding of $WO_3$, HAp, and $WO_3$/HAp composite. Furthermore, it also strengthened the evidence of successful hybridization material. A wave number in a range of 400–4000 $cm^{-1}$ has been carried out to identify all chemical groups composed in the material. A vibration at 3568 $cm^{-1}$ in HAp and $WO_3$/HAp material has been attributed to a hydroxyl group (OH) presence. In $WO_3$/HAp spectra, the carboxyl (CO) and phosphate (PO) functional groups derived from HAp were also performed. These results are supported by other literature synthesizing and characterizing hydroxyapatite, which also obtained hydroxyl, carboxyl, and phosphate groups (Chandrasekar et al., 2013). At 850 and 779 $cm^{-1}$, the presence of W–O–W and W=O is performed respectively in $WO_3$ and $WO_3$/HAp material (Pu et al., 2019) (Jothivenkatachalam et al., 2014). The expected results prove that the $WO_3$ and HAp materials are well chemically bonded to form $WO_3$/HAp hybrid material. Moreover, all detected functional groups in all materials are tabulated in Table 2.

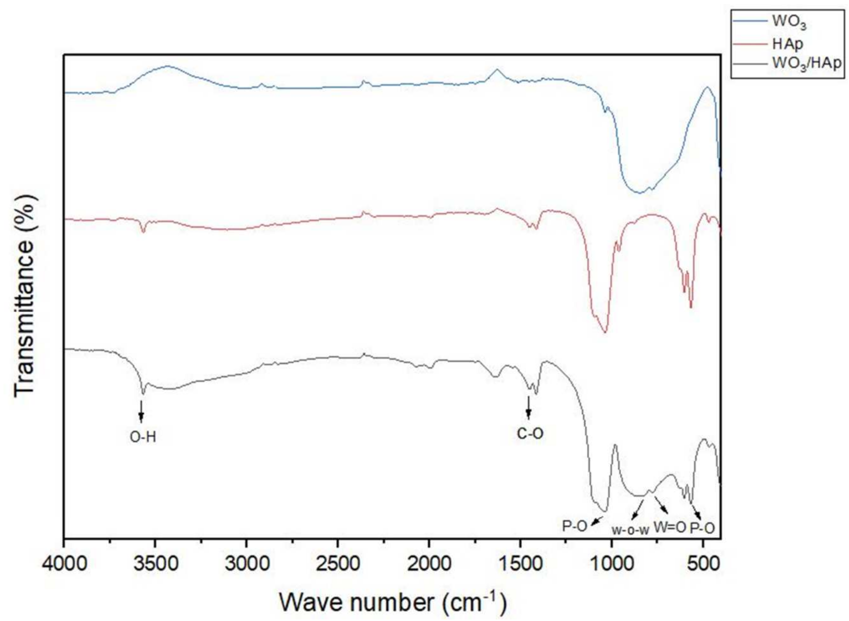


**Table 2.** Functional group of tungsten trioxide/hydroxyapatite nanocomposites

| Wave number ($cm^{-1}$) | Functional groups |
|---|---|
| 3568 | OH |
| 1450 | CO |
| 1033 | PO |
| 850 | WOW |
| 779 | W=O |
| 567 | PO |

## Photocatalytic degradation

The absorption spectrum of the MB dye solution with the $WO_3$ and $WO_3$/HAp under directly visible light irradiation at different time intervals is shown in Figure 5. The changes in the intensity of the absorption maximum could be correlated with the degradation of the dye molecules. It was found that the absorbance peak intensity decreases with the increase in irradiation time and indicating that the MB molecules are affected. The functional group of the dye is altered by degradation, and the absorption spectrum of the dye may be affected, leading to a decrease in the intensity of its color. MB degradation efficiency using the $WO_3$/HAp hybrid catalyst shows better performance results than the $WO_3$ catalyst. Combining the adsorption capabilities of HAp and the photocatalytic properties of $WO_3$ generate better characteristic to obtain an optimal waste degradation process. This adsorption mechanism is explained by pollutants diffusing into the pores of the solid surface via electrostatic interactions between adsorbate/adsorbent using hydrogen bonds and Van der Waals forces (Labrag *et al.*, 2021).

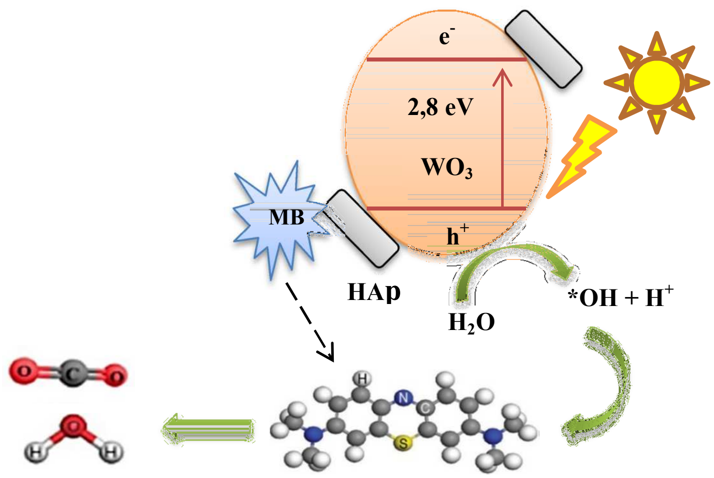


**Figure 5**. Mechanism of MB degradation by $WO_3$/HAp photocatalyst

The degradation mechanism begins with the adsorption of MB on the surface of the composite, followed by the photodegradation process. MB degradation process using $WO_3$/HAp photocatalyst with the help of visible light is illustrated in Figure 5. First, exposure to visible light triggers the transfer of electrons from VB to CB $WO_3$. This causes the formation of pairs of holes (h+) and electrons (e-). The holes that have been formed then change the water molecule ($H_2O$) to •OH, which is highly reactive. These radicals will attack the MB molecule and oxidize it into harmless compounds such as $CO_2$ and water (Türkaslan, et. all, 2022). The presence of HAp serves to attract MB dye molecules to make contact with the $WO_3$/HAp composites easier so that the degradation process can take place more efficiently.

The $WO_3$ particles show the maximum degradation of MB dye is 73.02% after irradiating for 4 hours, as shown in Figure 6. This result is slightly lower than the study by Jeevitha et al (2018), which tested the activity of pure $WO_3$ under visible light and obtained a degradation efficiency of 75% after 4 hours of irradiation. Furthermore, in another study conducted by (Wang et al., 2017) the degradation of MB synthetic waste was only 18% after 150 minutes of photodegradation using visible light with a commercial WO3 photocatalyst. The results indicate that the $WO_3$ semiconductor is less optimal to use as a photocatalyst.

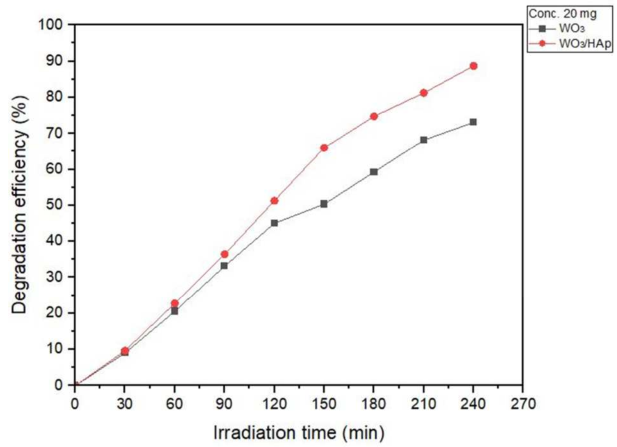


**Figure 6**. The degradation efficiency of methylene blue by $WO_3$ and $WO_3$/HAp with 20 mg catalyst concentration

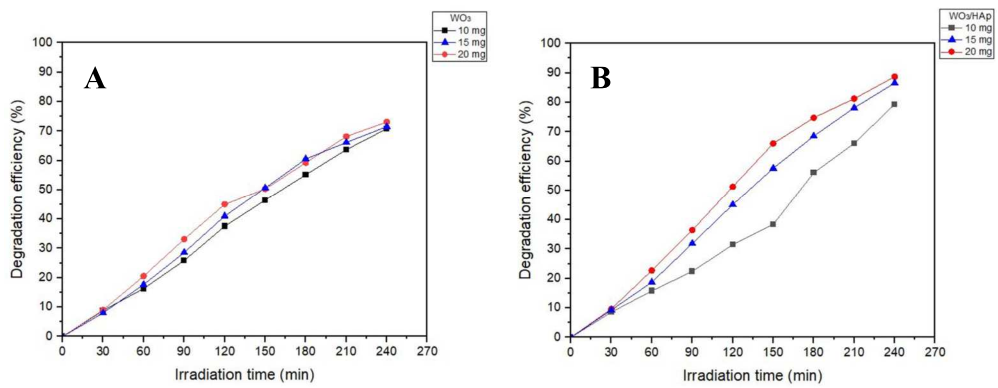


**Figure 7**. The degradation efficiency of methylene blue by (a) $WO_3$ and (b) $WO_3$/HAp with catalyst concentrations 10, 15, and 20 mg

A comparison of degradation efficiency using $WO_3$ and $WO_3$/HAp catalysts with different concentrations can be seen in Figure 7, where the linearity of the degradation products with the increased catalyst concentration is obtained. The highest efficiency was performed using 20 mg of the photocatalyst. The higher concentration of the catalyst improves the degradation rate of the MB pollutant due to increased contact with catalyst surfaces. The exhibition of 20 mg of $WO_3$ catalyst reaches a degradation efficiency of 73.02%, while the $WO_3$/HAp composites improve the degradation to 88.69%. This result shows that the hybridization of HAp into the $WO_3$ catalyst surface raises the photocatalytic effectiveness.

## Conclusions

Tungsten trioxide-hydroxyapatite ($WO_3$/HAp) particles have been successfully synthesized using the sol-gel method under sonication. The evidence of the chemical composition of the $WO_3$/HAp hybrid material was ensured by SEM-EDX and FTIR spectra. The degradation of methylene blue by $WO_3$/HAp composite showed higher results than pure $WO_3$ catalysts. The $WO_3$/HAp catalyst degraded MB pollutants by up to 88.69% after being exposed to visible light for 4 hours compared to the $WO_3$ catalyst, which only showed 73.02% efficiency.

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