Tungsten Oxide Nanopowders and Its Photocatalytic Activity under Visible Light Irradiation

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Abstract

The photocatalytic activity was monitored by studying degradation of the dye Methyl Orange (MO) in aqueous solution using modified Tungsten Oxide (WO₃) nanopowders as a photocatalyst under solar simulator irradiation. The Tungsten Oxide nanopowders were modified by loading metals on its surface. Wet impregnation and physical methods were applied for the incorporation of metal on these materials. In the wet impregnation process, the metals were reduced by two different methods, i.e. Chemical reduction method and Thermal reduction method. The Chemical reduction method showed the best results as compared to Thermal reduction and Physical methods. In the chemical reduction method, palladium (~1wt% on WO₃) demonstrated higher activity than the other metals (Ag and Pt) investigated.

The photocatalytic performance of the system upon applying a physical mixture of WO₃ with TiO₂ nanopowders was improved in comparison to a system with WO₃ only. The on-metal loading improved the activity of this mixture approximately 60 times. The degradation kinetics of all samples followed the pseudo-first order reaction kinetics.
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1. Introduction

Azo dye contains of aromatic compounds linked together with –N=N- structure. It is used in many industrial processes, namely, cosmetic, textile, dye, printing. Unfortunately, the azo dyes are highly harmful to human health, which show carcinogenic and toxic effects. Also, some materials including azo dye residue cause contaminations, which damage the environment. As a measure to remove these contaminations, some processes are applied such as membrane filtration, ion exchange, adsorption, microorganisms and heterogeneous photocatalysis.

Photocatalysis is a process, which is carried out by photocatalyst under light irradiation. In other words, initiation of the chemical reactions was accomplished by absorption of photons by the electrons on the surface of photocatalyst. The semiconductor, which is substrate of the photocatalysis, is called a photocatalyst.

On the basis of semiconductor photocatalytic reactions, the electrons are excited from the valence band (VB) to the conduction band (CB) with the absorption of photons (Figure 1) and they create electron-hole pairs on the surface of semiconductor. The absolute energy is referred as band gap between VB and CB. The energy of photons is equal to or more than the band-gap of the photocatalyst. The electron absorbs the photons and gets excited electron-hole pair. The electron-hole pair thus found can either recombine in the volume (2) or move to the surface and recombine (1). The electron-hole pair can also undergo some redox reactions on the surface of the semiconductor, i.e., reduction (3) and oxidation (4).

Heterogeneous photocatalysis is a widely developing research area since 1981, which encourages the removal of the environmental pollutants. This process is achieved by illumination with photons using semiconductor.

Several semiconductors are shown in Table 1 with their Band gap energy values.

\[ \text{Figure 1. Photoexcitation of semiconductor solid particle} \]
**Table 1. Semiconductors and their Band Gap energy values.**

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Band-gap energy, electron volt (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.1</td>
</tr>
<tr>
<td>WSe₂</td>
<td>1.2</td>
</tr>
<tr>
<td>CdS</td>
<td>2.4</td>
</tr>
<tr>
<td>WO₃</td>
<td>2.4–2.8</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>2.7</td>
</tr>
<tr>
<td>SiC</td>
<td>3.0</td>
</tr>
<tr>
<td>TiO₂ Rutil</td>
<td>3.02</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.1</td>
</tr>
<tr>
<td>TiO₂ anatase</td>
<td>3.2</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>3.2</td>
</tr>
<tr>
<td>SnO₂</td>
<td>3.5</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.6</td>
</tr>
</tbody>
</table>

**Figure 2. Semiconductors and their Band Gap energy diagram.**

TiO₂ is most widely explored photocatalyst but it is more efficient under ultra violet (UV) light. Recently, WO₃ is gaining a lot of importance and several researchers are exploring WO₃ as an effective visible light harvesting photocatalyst.

In this present work, pure non-toxic Tungsten Oxide (WO₃), which has a small variable band gap value between 2.4 and 2.8 eV, was applied as one of the photocatalyst. It is reported that, WO₃ is used as a photocatalyst, solar energy device and field-emission device. Its valence band (+3.1V) includes the holes that carry out the oxidation of water. Although the pure WO₃ has high oxidation power of VB; the conduction band shows +0.4V energy versus NHE at pH 0.

Full-spectrum light is a part of the electromagnetic spectrum; or the wavelengths between infrared and ultraviolet spectrum with time during a day that are utilized by plant or animal life. Despite of the modification of solar spectral distribution, sunlight is thought as full spectrum. The sunlight reaching the earth is at most 1004 watts per square meter (W/m²),
which comprises of 527 W/m$^2$ (53%) of infrared radiation, 445 W/m$^2$ (44%) of visible light, and 32 W/m$^2$ (3%) of ultraviolet radiation.

The light absorption features, reduction and oxidation rates on the surface and the electron-hole recombination rate control of the semiconductor photocatalytic reaction rate.

The smaller granule size of photocatalyst usually increases the specific surface area. Although the larger surface area supplies the higher photocatalytic activity, it facilitates the recombination rate of electron and hole. The fast or immediate electron-hole recombination, which decreases the photocatalytic efficiency, can be hindered by modification of the surface of the semiconductor.

Another approach to enhance the photocatalytic activity is decoration with reduced metal, ion or non-metal doping in photocatalyst, dye sensitization and composite or coupled semiconductor particles are indicated as the modification methods of the surface.$^5, 9, 13, 17$

In this present work, we have demonstrated the use of WO$_3$ as an effective photocatalyst in visible range.

2. Experimental

2.1. Instrumentation

2.1.1. Furnace

High temperature, horizontal tubular furnace (Carbolite Furnaces) with a heating range from room temperature (RT) up to 1000°C and filled with a quartz glass tube was applied. The furnace was equipped with Eurotherm digital temperature controller and controlled gas atmosphere with Bronkhorst mass flow controllers.

2.1.2. Solar Simulator

A simulated sunlight in the other words ‘Solar simulator’ was utilized as the light source. The experiments were carried out using a Newport solar simulator as the source of light. The lamp used gave the solar simulator an intensity equivalent to 1 sun. The output beam measured 4 x 4 inch. The working height was 4 inch from the source.
2.1.3. UV/Vis Spectrophotometer

Ultraviolet and visible (UV/VIS) spectroscopy is an instrument, which is used for measurement of the absorbance value of the sample at the UV-Visible wavelength range.

The absorbance is defined as the logarithmic ratio of the incident light to the transmitted light. That gives the Beer-Lambert law, which is proportional to concentration of the solution and absorbance. Equation is shown below:

\[
T = I/I_0
\]

\[
A = -\log_{10}\left(\frac{I}{I_0}\right) = -\log_{10}T
\]

\[
A = \varepsilon \times b \times c
\]

Where T is the transmittance,
I₀ is the incident light,
I is the transmitted light,
ε is the wavelength dependent molar absorptivity coefficient with units of M⁻¹cm⁻¹,
b is the path length (cm),
c is the analyte concentration (M)
A is the absorbance value.

The absorbance of any sample is dependent on its absorption maximum (λ_max) i.e. the wavelength of light at which it absorbs to the maximum extent. As shown in Figure 5, the energy value between excited and ground state depicts specific wavelength. The UV-Vis Spectrophotometer equipment contains a light source, monochromator, dispersion device (filter, grating or prism) and detector. Two types of spectrophotometer (single and double beam) are used as qualitative and quantitative analysis. Double beam, is preferred typically, includes reference cell in all spectral read (Figure 6), which decreases calculation errors.
In this study, all absorbance measurements were performed on the UV/VIS spectrophotometer, which has double beam system, manufactured by Shimadzu System Controllers.

2.2. Materials

Tungsten Oxide nanopowders (WO₃, <100nm NPs), titanium dioxide (TiO₂ <25nm anatase 99.7%), palladium (II) acetylacetonate (Pd(C₅H₇O₂)₂, 99%), platinum (II) acetylacetonate (Pt (C₅H₇O₂)₂, 99.99%), silver nitrate (AgNO₃, 99.9999%), silver per-chloride (AgClO₄, 97%), aluminium oxide (Al₂O₃, 100 mesh 99%) and sodium borohydride (NaBH₄, Sigma Aldrich, AF granules, 10-40 mesh, 98%) were received from Sigma-Aldrich as used as such. Methyl orange (MO, J.T. Baker) was used as received. Ethanol (≥99.5%, Solveco Ltd.), acetone (Fischer Chemical), 2-propanol (Merck) were received as used as such.

2.3. Methods for Preparation

2.3.1. Wet Impregnation Method

Wet impregnation method is commonly applied upon preparation of metal or non-metal loaded photocatalyst and is described below. In this study, for reduction of metals either the so-called ‘thermal reduction’ or chemical reduction methods were employed.
2.3.1.1. Catalyst Preparation using the ‘Thermal Reduction Method’

Loading of metal ions on WO$_3$ particles was carried out using wet impregnation method. Typically, 20.4 mg of Pt (II) Acetylacetonate, 28.7 mg of Pd (II) Acetylacetonate or 15.7 mg of AgNO$_3$ were dissolved in 100 mL of acetone and mixed with 1.0 g of WO$_3$ particles. The mixture was ultrasonically agitated for 30 min and then stirred overnight at room temperature (RT). The solvent was evaporated at ~80 °C under N$_2$ atmosphere. The dry samples were further calcined in air at 300 °C for 2 h, and then reduced in H$_2$ flow at 350°C for 4 h to obtain the product, i.e., 1%Pt$_{\text{WO}_3\_T}$, 1%Pd$_{\text{WO}_3\_T}$ and 1%Ag$_{\text{WO}_3\_T}$, respectively, with ~1 wt% metal loading on each catalyst. The symbol ‘T’ was used to denote the thermal reduction method. Furthermore, following the procedure above, TiO$_2$ was treated with ~1 wt% Pd and was denoted as 1%Pd$_{\text{TiO}_2}$.

2.3.1.2. Catalyst Preparation using the ‘Chemical Reduction Method’

Loading of metal ions on WO$_3$ particles was carried out using wet impregnation method. Typically, 20.4 mg of Pt (II) Acetylacetonate, 28.7 mg of Pd (II) Acetylacetonate or 19.2 mg of AgClO$_4$ was dissolved in the mixture of 15 mL of ethanol and 15 mL of Milli-Q water, and mixed with 1.0 g of WO$_3$ particles. The mixture was stirred overnight at RT. The solution was purged with N$_2$ to obtain an inert atmosphere. The reaction vessel was kept in an ice bath. 10 mM NaBH$_4$ solution was added to mixture drop by drop under nitrogen flowing. The mixture was allowed to stir under nitrogen flowing overnight. The solvent was evaporated at ~35°C under vacuum using of BUCHI rotary evaporator. The dry samples were further treated under nitrogen flow at 100°C for 2.5 h, to achieve the product, i.e., 1%Pt$_{\text{WO}_3\_C}$, 1%Pd$_{\text{WO}_3\_C}$ and 1%Ag$_{\text{WO}_3\_C}$, respectively, with ~1 wt% metal loading on each catalyst. Without metal doping, an equal procedure was applied for pure WO$_3$ and used as the reference solution. The reference product was indicated as WO$_3\_C$. In short, 28.7 mg of palladium (II) acetylacetonate was dissolved in a mixture of 15 mL of deionized (Milli-Q) water, 15 mL of ethanol, and physically mixing 1.0 g of TiO$_2$ NPs and WO$_3$ in the ratio of (1:1) (TiO$_2$ NPs: WO$_3$ 1:1). By following the general procedure of chemical reduction, (TiO$_2$ NPs: WO$_3$) (1:1) with ~1 wt% Pd was produced. The sample was denoted as 1%Pd$_{\text{(TiO}_2\text{NPs: WO}_3\text{)}\_1\_C}$. The symbol ‘C’ is used to denote chemical reduction method.

2.3.2. Catalyst Preparation Using the ‘Physical Method’

Physical method depicts mechanically mixing materials in a specific ratio to prepare the final catalyst mixture. In a typical experiment, 125 mg of 1%Pd$_{\text{TiO}_2}$ and 375 mg of WO$_3$ were mixed for ~20 minutes to obtain the product, i.e., 1%Pd$_{\text{TiO}_2}$: WO$_3$ (1:3) P. Similarly, Al$_2$O$_3$: WO$_3$ (1:3) P, 1%Pd$_{\text{TiO}_2}$: WO$_3$ (1:1) P, TiO$_2$ NPs: WO$_3$ P were prepared separately. The samples were mixed thoroughly. The symbol ‘P’ is used to denote the ‘Physical method’.

2.3.3. Preparation of Methyl Orange Solution

10 mg Methyl Orange (MO) dye was dissolved in 100 mL of deionized (Milli-Q) water to obtain 100 ppm Methyl Orange stock solution. Standard solutions at different concentrations (i.e., 2, 4, 6, 8, 10 and 12 ppm) were prepared using the Stock solution to obtain a standard curve. Moreover, the optimized concentration of 5 ppm Methyl Orange Solution was used for degradation experiments.
2.4. Degradation of Methyl Orange Solution under Solar Simulator

The photocatalytic degradation experiments were carried out using Newport 94043A Solar Simulator. The intensity of solar simulator was calibrated to ~80mW/cm$^2$ using Thor Labs PM100USB power and energy meter. The working distance between the solar simulator light source and the solution was measured. The photocatalytic degradation experiments were carried out by addition of 30mL of MO dye solution (5ppm) and 30mg of catalyst. In order to homogenize the distribution of catalyst in the methyl orange solution, the solution was continuously stirred. The temperature was maintained at 20°C by means of a water bath. After certain intervals in time, samples were drawn from the reaction mixture. The sample was centrifuged and the absorbance of supernatant solution was measured using UV-3101PC SHIMADZU UV-Vis-NIR Scanning Spectrophotometer. All samples in the Eppendorf tubes were centrifuged at 13000rpm using HERMLE Z160M Centrifuge until the particles settled down. The true, actual concentrations of all samples were calculated with using the slope and intercept values of calibration curve of Methyl Orange solution, according to absorbance values at 464nm.

3. Results and Discussion

![Figure 7. The structure of Methyl Orange](image)

In principal, azo dyes can be arranged according to their pKa efficiency, such as acid orange 8, chrome violet, ethyl orange, methyl red and methyl orange. The structure of methyl orange (Figure 7), which absorbs blue-green color light, is known as 4-[4-(Dimethylamino)phenylazo]benzenesulfonic acid sodium salt. Approximate color change of methyl orange is observed in the pH range 3.1 to 4.4 from red to yellow respectively. Decolorization of MO is carried out the presence of •OH radical group, which attacks an Azo compound on the methyl orange structure in the reaction conditions.

3.1. Photocatalytic Degradation of Methyl Orange

A photocatalytic reaction in an aqueous medium involves a series of events following the photogenerated electrons upon irradiation (scheme 1).

$$\text{WO}_3 + h^\nu \rightarrow \text{WO}_3(\text{e}_{\text{CB}}^- + \text{h}_{\text{VB}}^+)$$

$$\text{h}^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+$$

$$\text{O}_2 + 2\text{e}_{\text{CB}}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2$$

$$\text{H}_2\text{O}_2 \rightarrow 2\cdot\text{OH}$$

MO Dye + •OH $\rightarrow$ Degradation products

Scheme 1

Aqueous solution of methyl orange was used as a target organic dye in the present
During irradiation the dye concentration decreased with the increase in time due to the hydroxyl radicals formed in the system.\(^{17}\)

In case of all the catalysts used, the degradation of MO solutions followed pseudo first-order kinetics in line with the classical Langmuir-Hinshelwood model steps.\(^7\) The photocatalytic rates were calculated from the equation

\[
\ln \left( \frac{C_0}{C_t} \right) = kt
\]

which was derived with equation shown below.\(^7\)

\[
\int_{C_0}^{C_t} \frac{dc}{c} = -k \int_0^t dt
\]

Where \(C_0\) is the concentration of the first solution (ppm).

\(C_t\) is the actual concentration (ppm) of each solution at time ‘t’.

\(t\) is indicated as the irradiation time (min).

\(k\) is the degradation rate constant of methyl orange dye solution.

Actual concentration \((C_t)\) of the all measurements was calculated from a previous calibrated standard curve.

Even though \(\text{WO}_3\) degraded MO dye in the aqueous solution, its photo-efficiency was really low. Having a short band gap (2.4 -2.8 eV) recombination of the holes and excited electrons is a fast phenomenon. Hence it is important to find methods to modify \(\text{WO}_3\) in order to improve its photoactivity. In the present study three methods are used to modify the surface Physical method, Chemical reduction method and Thermal reduction method. The activity of each catalyst prepared via various methods was checked by following the kinetics of degradation of methyl orange dye solution.

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![Figure 8. Semiconductor-metal interaction](image)

Chemical and Thermal reduction method reduce the noble metal, which plays a major role as an electron-trapping center, to zero-valent state. There are reports that have investigated the improved photocatalytic efficiency due to loading metals such as Palladium, Platinum, Silver, and Copper on the surface of semiconductor (Figure 8).\(^{12, 13, 14, 22}\) The photocatalytic efficiency is enhanced with electron trapping center by preventing the recombination of electron and hole.\(^{23, 24}\)
In this study, palladium, platinum and silver were utilized as an electron trapping center on pure WO$_3$ to improve its photocatalytic impact. Alternatively, the metal efficiency on the semiconductor was examined by using physical method.

### 3.2. Physical Method

Yonggang Liu et al. claimed that the efficiency of mechanically mixing of semiconductor (WO$_3$) and metal (Pd) depicted positive results on their investigation. In this study, physical method was employed by mixing two different semiconductors such as WO$_3$ and either TiO$_2$ NPs (3.2eV) or 1%Pd_TiO$_2$ to check whether any specific effect could be observed.

![Figure 9](image.png)

_Figure 9. The comparison of kinetic plots of MO degradation using 1%Pd-TiO$_2$: WO$_3$ (1:3) and 1%Pd-TiO$_2$: WO$_3$(1:1)_

First, the photocatalytic efficiency of 1%Pd_TiO$_2$: WO$_3$ (1:3) P was examined under irradiation solar simulator. To check the individual activity of WO$_3$, 1%Pd_TiO$_2$ was replaced by Al$_2$O$_3$, which has negligible activity under solar simulator. The activity of pure WO$_3$ and Al$_2$O$_3$ were also measured as considered as reference sample for this study. Table 2 depicts the rate constant for the degradation of MO dye using different catalyst prepared by physical mixing method.

When ratio of mixing was modified from 1:3 to 1:1, the activity increased proportionally as shown in Figure 9. Moreover, when 1%Pd_TiO$_2$ was replace with Al$_2$O$_3$ in Al$_2$O$_3$: WO$_3$ (1:3) P, the activity observed coincided with that of pure WO$_3$. Thus, it is clear when studying the rates that the high activity is purely due to 1%Pd_TiO$_2$ in the catalyst and there no improvement on the activity of WO$_3$ could be observed (Table 2).
Table 2. The rate constant of MO decomposition by catalysts prepared using the Physical method.

<table>
<thead>
<tr>
<th>Product</th>
<th>Rate (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Pd-TiO₂:WO₃ (1:1) P</td>
<td>0.0166</td>
</tr>
<tr>
<td>TiO₂ NPs: WO₃ (1:1)</td>
<td>0.0123</td>
</tr>
<tr>
<td>1%Pd-TiO₂:WO₃ (1:3) P</td>
<td>0.0099</td>
</tr>
<tr>
<td>Al₂O₃:WO₃ (1:3) P</td>
<td>0.0005</td>
</tr>
<tr>
<td>WO₃</td>
<td>0.0004</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
</tr>
</tbody>
</table>

3.3. Chemical Reduction Method

Table 3 depicts the rate constants for degradation of methyl orange dye solution when applying the catalysts prepared by Chemical Reduction method. Amongst all (Pd, Ag and Pt) 1%Pd-WO₃ displayed better photocatalytic effect than the other 1wt.% metal loaded on tungsten oxide composites.

Table 3. The rate constant of MO decomposition by catalysts prepared using the Chemical reduction method.

<table>
<thead>
<tr>
<th>Product</th>
<th>Rate (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Pd-WO₃ C</td>
<td>0.0071</td>
</tr>
<tr>
<td>1%Ag-WO₃ C</td>
<td>0.0052</td>
</tr>
<tr>
<td>WO₃</td>
<td>0.0004</td>
</tr>
<tr>
<td>WO₃ C</td>
<td>0.0002</td>
</tr>
<tr>
<td>1%Pt-WO₃ C</td>
<td>-</td>
</tr>
</tbody>
</table>

The activity upon loading with Pd and Ag increased almost 17 and 13 times, respectively, as compared to pure WO₃. However, Pt did not show any improvement at all. The reason could be that Pt did not get be properly reduced using this procedure.

WO₃ C was prepared and treated as reference sample and it showed negligible absorbance values during spectrophotometric measurement and is similar to pure WO₃. This proves that sodium borohydrate used for reduction of metals did not influence or modify the semiconductor catalyst WO₃.

3.4. Thermal Reduction Method

Table 4 indicates the degradation rate of MO dye solution using catalysts prepared via Thermal Reduction method. Amongst all (Pt, Pd and Ag) 1%Pt-WO₃ displayed better photocatalytic effect than the other 1wt.% metal loaded on tungsten oxide composites.

Table 4. The rate constant of MO decomposition by catalysts using the Thermal reduction method.

<table>
<thead>
<tr>
<th>Product - Thermal</th>
<th>Rate (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Pt-WO₃ T</td>
<td>0.0078</td>
</tr>
<tr>
<td>1%Pd-WO₃ T</td>
<td>0.0009</td>
</tr>
<tr>
<td>1%Ag-WO₃ T</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

In this method, reduction of the metal at high temperature using H₂ gas modified the structure of WO₃. The percentage of oxygen diminished from 20.7 to between 19.6 and 20.4.
The new structure of WO₃ was denoted as WOₙ (n=2.90-2.99). In this study, that could be thought, the metal loading efficiency on the surface shows diversity because of modified structure of WO₃.

3.5. Comparison of Chemical and Thermal Reduction Method

Figure 10 depicts a comparison between 1%Pd_WO₃ prepared by the Chemical and Thermal reduction methods.

Upon reaction results, the Chemical reduction method demonstrated higher degradation rate of MO dye than the Thermal reduction method (Figure 10, Table 5).

Table 5. The comparison of the rate constant of MO decomposition for 1%Pd_WO₃ prepared using the Chemical and Thermal reduction methods

<table>
<thead>
<tr>
<th>Product</th>
<th>Rate (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Pd_WO₃ C</td>
<td>0.0071</td>
</tr>
<tr>
<td>1%Pd_WO₃ T</td>
<td>0.0012</td>
</tr>
</tbody>
</table>

In brief the comparison of catalyst prepared by Chemical and Thermal reduction methods are summarized in Table 6.

Table 6. The validity of the Thermal or Chemical reduction methods for each metal loaded Tungsten Oxide.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Chemical Reduction Method</th>
<th>Thermal Reduction Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Pd_WO₃</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>1%Pt_WO₃</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>1%Ag_WO₃</td>
<td>+</td>
<td>-</td>
</tr>
</tbody>
</table>
As the results above indicate, the excited electrons were held much longer on the conduction band by loading Pd metal on WO₃ surface with the Chemical reduction method. (Figure 10, Table 3).

1%Pt_WO₃_T indicated better photocatalytic activity compared to 1%Pt_WO₃_C (Table 6). Nevertheless, Thermal reduction method needs further investigation because of its characteristic of modification on the structure of WO₃.

Since, amongst Ag, Pt and Pd loaded WO₃, Pd loading indicated the best results. Hence, the work was focused on reducing 1wt.% Pd using the Chemical reduction method.

3.6. Comparison of Tungsten Oxide and its Modified Products

According to results depicted in Table 3, the photocatalytic activity of pure tungsten oxide alone was not enough and could not be improved with chemical reduction methods. On the other hand, the physical method (mixing of two materials) was not adequate for the case of 1%Pd_TiO₂ and WO₃, because Pd, which was loaded on TiO₂ surface, could not interact with the WO₃ catalyst. For that reason, in a typical experiment, TiO₂ NPs was mixed with WO₃ using the physical method (Table 7). Then the chemical reduction method was applied for loading ~1wt.% of Pd on the surfaces of both WO₃ and TiO₂ for performing the impact of Pd metal on the both semiconductors.

The results shown in Figure 11 demonstrate that the impact of Pd loading on the both semiconductor surfaces increased the photocatalytic efficiency.

![Figure 11. The kinetic plots of MO degradation using 1%Pd_(TiO₂ NPs: WO₃) 1:1_C and (TiO₂ NPs: WO₃) 1:1](image)

Briefly, just to compare the effect of preparation methods on the photocatalytic activity was studied. Even though Pd loaded on WO₃ with ~1 wt% equally using individual method, such as chemical and thermal reduction or physical methods, their photocatalytic activities demonstrated different levels. Since the structure of WO₃ changes due to high temperature upon thermal reduction method (also resulting in lower photocatalytic activity), this
preparation method is not desirable. According to Table 7 merely chemical reduction method (1%Pd_WO3_C) did not depict promising result. To study the influence of having two semiconductors in the system, we physically mixed them. When Pd was loaded on TiO2 with ~1 wt% and mixed with WO3, Pd did not enhance the photocatalytic activity of WO3. In fact, it influenced the TiO2 activity only.

Table 7. The comparison of the rate constant of MO decomposition by Pd loaded photocatalysts

<table>
<thead>
<tr>
<th>Product</th>
<th>Rate (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Pd_(TiO2 NPs: WO3) (1:1)_C</td>
<td>0.0244</td>
</tr>
<tr>
<td>(TiO2 NPs: WO3) (1:1)</td>
<td>0.0123</td>
</tr>
<tr>
<td>1%Pd_WO3_C</td>
<td>0.0071</td>
</tr>
<tr>
<td>WO3</td>
<td>0.0004</td>
</tr>
</tbody>
</table>

The following procedure was then applied: mixture of TiO2 NPs: WO3 in the ratio (1:1) as a reference product. The activity increased with comparison to the activity without Pd loading. The activity of blank product was enhanced with Pd loading on its surface by using the chemical reduction method (Figure 12, Table 7). This approach facilitated distribution of Pd on both TiO2 and WO3. Hence, the activity of WO3 was improved almost 60 times upon use of 1%Pd_(TiO2 NPs: WO3) (1:1)_C.

Figure 12. The comparison of kinetic plots of MO degradation using Pd loaded photocatalysts

In a photocatalyst containing WO3 and TiO2 NPs, the hypothetical connection between the two semiconductors is demonstrated in Figure 13. The electrons of TiO2, which are on the higher VB energy level, jump down to VB of WO3 under the photon excitation. In other words, the VB of WO3 plays a role as electron trapping center under irradiation of solar simulator. That could cause an increase in the photocatalytic impact.23, 27 Nevertheless, it is possible that the effect is merely a ‘mirror’ one so that the photons can bounce from surfaces and are, consequently, more efficiently utilized.
In the perspective of future, this present study could be developed further by means of loading noble metals with chemical method on WO₃ and TiO₂ structures produced chemically as a composite material, in line with the approach reported by Seung Yong Chai research group.²³

4. Conclusions

In this study, degradation of MO was investigated over WO₃ and its modifications under irradiation of solar simulator. All the degraded MO dye samples followed the Langmuir-Hinshelwood pseudo first-order kinetics. The state, composition and structure of catalysts depended on the preparation techniques.

Although WO₃ exhibited weak photocatalytic efficiency under solar simulator, its enhanced versions synthesized by using physical, chemical reduction and thermal reduction method. The 1wt.% noble metals (palladium, platinum or silver) were successfully loaded on tungsten oxide by using Chemical or Thermal reduction methods separately. Chemical reduction method was the most effective for Pd & Ag metals. However 1%Pt_WO₃, which was produced using Thermal reduction method, depicted better photocatalytic activity as compared to 1%Pt_WO₃ produced by using Chemical reduction method. Unfortunately, Thermal reduction method changes the chemical composition of WO₃ to WO₃₋ₙ(n=0.01-0.10).²⁵ This work needs further investigation.

The chemical reduction method demonstrated that palladium was the best loaded metal we studied and gave rise to an increase in the photocatalytic degradation reaction of MO dye solutions.

1%Pd_TiO₂: WO₃ in the ratio 1:3 and 1:1 were produced using the so called ‘physical method’. This study indicated that Pd did not enhance the photocatalytic activity of WO₃ in these mixtures. Thus, that could be thought ‘Physical method’ is not effective technology in this project.

A 1 wt.% Pd loaded by chemical reduction method on the mixture of WO₃ and TiO₂
(1:1) was synthesized which supplied distribution of Pd on both TiO$_2$ and WO$_3$ surface. This approach demonstrated the best photocatalytic activity in this investigation.

In summary, the present study illustrated most promising result to prevent the environmental pollutions upon use of 1\%Pd\_TiO$_2$ NPs: WO$_3$ 1:1\_C under solar light irradiation.

5. References


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