CHAPTER - V
PHOTOCATALYTIC STUDIES

TiO$_2$ nanoparticles found application in photocatalysis, especially in the degradation of organic dyes. The degradation of methyl orange solution using pure and metal ions doped TiO$_2$ nanoparticles is studied experimentally and discussed in this chapter.

5.1 Definition of Photocatalysis

Catalysis is a chemical reaction that results from the action of a catalyst. Simply defined, a catalyst is a substance that increases the rate of reaction without being consumed during the reaction. Specialized catalytic process is photocatalysis. The early definition of photocatalysis, which is defined by IUPAC Commissions is “a catalytic reaction involving light absorption by a catalyst or a substrate”. Another definition for photocatalysis, which is described as a complimentary definition, is a “catalytic reaction involving the production of a catalyst by absorption of light”. This is usually referred to as photo-assisted catalysis.

Nowadays catalysis is defined by Serpone and Emeline as “a process in which a substance (the catalyst) accelerates, through intimate interaction(s) with the reactant(s) and concomitantly providing a lower energy pathway, or otherwise thermodynamically favored but kinetically slow reaction with the catalyst fully regenerated quantitatively at the conclusion of the catalytic cycle” [1].
5.2 Mechanism of Photocatalysis

The following mechanism takes place during photocatalysis. In a chemical reaction some compound A is converted to some compound(s) B:

\[ A \leftrightarrow B \]

In a catalytic process the catalyst changes the rate of the reaction, but the catalyst itself, by definition, must be preserved in both quantity and state, and is fully separable from the other reactants at the end of the catalytic cycle.

\[ A + \text{Cat} \leftrightarrow B + \text{Cat} \]

However, in the catalytic process the catalyst in its original state is also one of the final products. Regarding the actual rate of reaction of these two processes, the reaction rate will be increased using a catalyst only if the total activation energy is lower than that of the reactants alone.

In photocatalysis, the chemical reaction is induced by absorption of photons by the catalyst and the process is given by,

\[ A + h\nu + \text{Catalyst} \rightarrow B + \text{Catalyst} \]

where, \( h\nu \) is the quantum energy of the incident photons [1].

5.3 Electronic Processes of Photocatalysis

In photocatalysis, light photon imposed on a catalytic surface is used to drive chemical reactions. In other words, it can be considered as a photon-assisted generation of catalytically active species [2].
In photocatalysis, light photons with energy greater than or equal to the band gap of the semiconductor, excites an electron from the valence band to the conduction band (Figure (5.1)). The band gap of anatase is 3.2 eV, therefore UV light (< 387 nm) is needed to initiate the photocatalytic process. Light (< 387 nm) excites an electron (e\textsubscript{CB}) to the conduction band generating a positive hole (h\textsuperscript{+}\textsubscript{VB}) in the valence band [3, 4]. Charge carriers can be trapped as Ti\textsuperscript{3+} and O\textsuperscript{-} defect sites in the TiO\textsubscript{2} lattice, or they can recombine, dissipating energy [3].

### 5.4 Dyes

Dyes can be classified on the basis of chromophore groups they have contained. Various categories of these dyes are acridine dyes, azo dyes, arylmethane dyes, anthroquinone dyes, nitro dyes, xanthenes dyes, quinine–amine dyes etc. Among these different types of dyes, azo dyes are the major group of synthetic colorants (60–70%) and are highly applied in industrial applications such as textiles, papers, leathers, gasoline, additives, foodstuffs, cosmetics, laser materials, xerography, laser printing, etc. Only up to 45–47% dyestuffs are biodegradable, and the residual color is mainly due to insoluble dyes which have very little biodegradability [5].
5.5 Methyl Orange

Methyl Orange (MO, C_{14}H_{14}N_{3}SO_{3}Na) belongs to a category of azo-dye common industrial dye favored for its stability and categorized and used as a model pollutant [6]. It is estimated that between 10-15% of the dye used in textile processing is lost and released as effluent [7]. The release of this effluent is considered “non-aesthetic pollution” as amounts smaller than 1 ppm is visible in water sources. Also the dye waste water can produce dangerous by-products during various chemical reactions such as oxidation and hydrolysis. Biological treatments may only decolourize the dye effluents as opposed to degrading the effluent. A similar decolouration phenomenon is discovered during the study for thermo chemically ammonia treated Degussa P-25 TiO_{2}, and is discussed in detail below. Physicochemical treatments are effective in discoloration, non-destructive and could transfer the organic compounds from the water to another phase [8]. Due to the difficulty in degrading pollutants such as MO, an advanced oxidation process is proposed as an alternative to water purification which differs from the traditional oxidation by holes, with oxidation by a very reactive species such as hydroxyl radicals (•OH). These reactive species can non-selectively oxidize a broad range of pollutants. It has been determined that heterogeneous photocatalysts, such as TiO_{2}, are the most destructive with regard to azo-compounds [9]. This destruction can be promoted by both artificial solar sources and sources employing solar technologies. The noted advantage of this method is that it is destructive and can occur under ambient conditions and may lead to the complete mineralization of organic carbon into CO_{2} [8].
5.6 Chemical Composition of Methyl Orange

The chemical formula for methyl orange, depicted in figure (5.2) is C_{14}H_{14}N_{3}SO_{3}Na. It is the presence of the benzene rings which keep this pollutant from decomposing easily by chemical or biological methods [10].

![Chemical Composition of Methyl Orange](image)

**Figure 5.2: Chemical Composition of Methyl Orange**

5.7 Optical absorption spectrum of Methyl orange

The experiment is conducted to determine the optical absorption spectra of Methyl orange using de-ionized water as the solvent, to determine the optical absorption spectra of methyl orange. Figure (5.3) shows the spectrum for a 10 ppm solution of methyl orange. This spectrum shows two absorption peak maxima, one at approximately 276 nm and the second with a higher absorption magnitude of 468 nm. Second maxima peak at 468 nm is used to calculate the concentration changes as a function of time for methyl orange [8, 10]. These peaks and corresponding spectra are in line with published works depicting absorption peaks at 270 nm and 458 nm [8].
Figure 5.3: UV-Vis absorption spectrum of Methyl Orange

In this study, phocatalytic experiment is conducted in an artificially assembled UV chamber. The photograph of the chamber is shown in figure (5.4).

Figure 5.4: Photograph of self assembled UV chamber
5.8 Photocatalytic Studies and Analysis

The photocatalytic application studies of pure and metal ions doped TiO$_2$ nanoparticles are observed by Systronics 2201 UV-Visible double beam spectrophotometer in the wavelength range 200-800 nm. The photocatalytic activities of pure and metal ions doped TiO$_2$ nanoparticles are evaluated by examining the degradation of model pollutant methyl orange under UV light irradiation. In this process, 18 W, UV-AB fluorescent lamp is used for UV irradiation.

For this typical study, 50 ml of 10 ppm aqueous methyl orange solution is taken in a 100 ml beaker. 100 mg of TiO$_2$ nanoparticles in the form of powder is added and stirred well for 10 min using magnetic stirrer. Then the methyl orange solution which contains dispersed TiO$_2$ nanoparticles is placed in a dark condition for half an hour to achieve adsorption-desorption equilibrium. Then the solution is irradiated with UV light up to 210 min. The degradation of methyl orange solution is observed by UV-Vis absorption spectra of methyl orange solution. For every half an hour, 5 ml of methyl orange solution was taken out and is centrifuged immediately to remove the catalyst. The catalyst removed methyl orange solution is characterized by UV-Vis absorption spectrum. Similar procedure is followed for observing the degradation efficiency of metal ions doped TiO$_2$ nanoparticles.

During the photocatalytic process, the absorption of a photon by TiO$_2$ leads to the excitation of an electron from the valence band to the conduction band thus producing an electron-hole pair. The electron in the conduction band is removed by reaction with oxygen dissolved in water and the hole in the valence band reacts with OH$^-$ or H$_2$O species which are adsorbed on the surface of TiO$_2$ to give the hydroxyl radical, the source for various oxidation reactions. The mechanism of chemical reactions during photocatalysis is summarized below [11].
\[
\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow e^- + h^+_{\text{VB}} \\
\text{h}^+_{\text{VB}} & \rightarrow \text{h}^+_{\text{TR}} \\
\text{O}_2 + e^- & \rightarrow \text{O}_2^{*-} \\
\text{O}_2^{*-} + \text{O}_2^{*-} + 2 \text{H}^+ & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{O}_2^{*-} + \text{h}^+_{\text{VB}} & \rightarrow \text{O}_2 \\
\text{O}_2^{*-} + \text{h}^+_{\text{TR}} & \rightarrow \text{O}_2 \\
\text{OH}^- + \text{h}^+_{\text{VB}} & \rightarrow \text{OH}^+ \\
\text{OH}^+ + \text{OH}^+ & \rightarrow \text{H}_2\text{O}_2 \\
\text{e}^- + \text{h}^+_{\text{TR}} & \rightarrow \text{Recombination}
\end{align*}
\]

Since the reaction ability of OH\(^+\) is high enough to attack hazardous chemical compound of methyl orange, it has been assigned as a key species in the mineralization mechanism.

Figures (5.5-5.21) show the UV-Vis absorption spectra of methyl orange at different intervals under UV light irradiation with pure and metal ions doped TiO\(_2\) nanoparticles. The degradation efficiency of pure and metal ions doped TiO\(_2\) nanoparticles are calculated using the equation \([11, 12]\),

\[
D = \frac{C_0 - C_t}{C_0} \times 100\%
\]

where D is the degradation efficiency, \(C_0\) is the initial solution concentration of the methyl orange dye and \(C_t\) is the solution concentration of the methyl orange dye at definite interval of time. Figure (5.22) shows the degradation efficiency of prepared and calcinated pure TiO\(_2\) nanoparticles. The calcinated pure TiO\(_2\) nanoparticles show more photocatalytic efficiency than the prepared pure TiO\(_2\) nanoparticles. This is due
to improved crystallization and there is no significant variation found in the bandgap value of TiO<sub>2</sub> nanoparticles when they are subjected to calcination [13].

Figure (5.23) shows the degradation efficiency of pure and Fe<sup>2+</sup> doped TiO<sub>2</sub> nanoparticles. Photocatalytic oxidation of organic pollutants is initiated by electron-hole pairs. Recombination of photogenerated electron-hole pairs can decline the photocatalytic efficiency of TiO<sub>2</sub>. The high recombination rate of the electron-hole pairs can be limited by insertion charge traps for electrons and/or holes, thus delaying the recombination time. The high photocatalytic effect of the Fe<sup>2+</sup> can be described by considering the efficient separation of photogenerated electrons and holes. Fe<sup>2+</sup> can act as trap for photogenerated carriers. In this present study, it has been observed that the Fe<sup>2+</sup> doped TiO<sub>2</sub> nanoparticles show lower photocatalytic efficiency than pure TiO<sub>2</sub> nanoparticles. This is because that the Fe<sup>2+</sup> ions became recombination centers for the electrons and holes pairs due to higher concentration Fe<sup>2+</sup> ions. As a result, photocatalytic activity is reduced [14].

Figure (5.24) shows the degradation efficiency of pure and Zn<sup>2+</sup> doped TiO<sub>2</sub> nanoparticles. It is accepted that adsorbed oxygen is employed as electron charge acceptor, generating a superoxide radical, which evolves to form hydrogen peroxide and subsequently a hydroxyl radical. On the other hand, adsorbed water molecules or hydroxyl anions are electronic charge donors, which directly generate hydroxyl radicals [15]. Both species are responsible for the photocatalytic activity in the degradation of pollutants with titanium-based materials.

K. Mori et al. [16] proposed that the tetrahedrally coordinated isolated Ti-oxide species, excited by UV irradiation, transport an electron from oxygen (O<sup>2−</sup>) to
Ti$^{4+}$ ions resulting in the formation of pairs of trapped hole centers ($O^-$) and electron centers ($Ti^{3+}$). In the present investigation, the Mori mechanism is extended by proposing that Ti$^{3+}$ can transfer the accepted electron to a Ti on the surface, which is linked to adsorbed O$_2$. This adsorbed O$_2$ receives the electronic charge generating a superoxide radical and then the electronic state in Ti ions (Ti$^{4+}$) is recovered. To recover the electronic state in $O^-$ hole centers, irradiated $OH^-$ adsorbed on the surface and linked to Ti$^{4+}$ transfers one electron towards the Ti$^{4+}$, generating a hydroxyl radical and photoreduced Ti$^{3+}$. The electron captured by Ti can be transferred through the network towards the $O^-$ hole center recovering its ground state. This mechanism is repeated several times and the adsorbed species are continuously replaced.

In the present study, the Zn$^{2+}$ doped TiO$_2$ nanoparticles show higher photocatalytic performances than that of pure and Fe$^{2+}$ doped TiO$_2$ nanoparticles. The increased photocatalytic activity in Zn$^{2+}$ doped TiO$_2$ nanoparticles is attributed to two factors; 1) the generation of surface oxygen vacancies in Zn$^{2+}$ doped nanoparticles promoting a decrease in the electron-hole charge recombination and increased concentration of surface OH and chemisorbed oxygen; 2) the formation of tetracoordinated Ti on nanometric particles [17].

Figure (5.25) shows the degradation efficiency of pure and Ag$^+$ doped TiO$_2$ nanoparticles. It has been observed that 1wt% Ag$^+$ doped TiO$_2$ nanoparticles show higher photocatalytic performance similar to pure and Zn$^{2+}$ doped TiO$_2$ nanoparticles. When UV light falls on dispersed solution of methyl orange and Ag$^+$ doped TiO$_2$ nanoparticles, a slight colour change to black is observed which reduces the silver ion thereby increasing the photocatalytic activity producing metallic silver on TiO$_2$.
surface. This effect is observed in our experiments too as similar to Sahoo et al. [18] and Rao et al. [19]. However, 3wt% and 5wt% Ag\(^+\) doped TiO\(_2\) nanoparticles show very much lower degradation efficiency than 1wt% Ag\(^+\) doped TiO\(_2\) nanoparticles.

When the doping content of silver clusters is low, the photogenerated electrons efficiently transfer to the silver cluster and better separation of electron-hole pairs will be achieved with increase of silver loading up to the optimum content. These electrons can react with adsorbed molecular oxygen or surface Ti\(^{4+}\) to form reactive species \(O_2^-\) and reactive centre surface Ti\(^{3+}\), respectively. This suggests that the recombination is slow and the generation of \(O_2^-\) and surface Ti\(^{3+}\) is accelerated. The yield of h\(^+\) would also be increased [20-22]. Hence, the photocatalytic efficiency increases for 1wt% Ag\(^+\) doped TiO\(_2\) nanoparticles. On the other hand, the content of silver doping is increased the number and size of silver cluster gradually becomes larger and the silver sites become recombination centres for photogenerated electrons and holes [20-22]. Thus, the photocatalytic efficiency decreases for 3wt% and 5 wt% Ag\(^+\) doped TiO\(_2\) nanoparticles.

The degradation efficiency of pure and Ni\(^{2+}\) doped TiO\(_2\) nanoparticles are shown in figure (5.26). It can be noted that 1 wt% Ni\(^{2+}\) doped TiO\(_2\) nanoparticles show higher photocatalytic activity as compared to that of 3 wt% and 5 wt% Ni\(^{2+}\) doped TiO\(_2\) nanoparticles. But, all these Ni\(^{2+}\) doped TiO\(_2\) nanoparticles show lower photocatalytic efficiency than pure TiO\(_2\) nanoparticles. The photocatalytic activity strongly depends on the amount of Ni\(^{2+}\) concentration. When the concentration of Ni\(^{2+}\) is low, Ni\(^{2+}\) ions can capture the electrons and improve charge separation [23]. For this reason, 1 wt% Ni\(^{2+}\) doped TiO\(_2\) nanoparticles show better degradation efficiency.
However, Ni\(^{2+}\) ions with high concentration may become recombination center of photogenerated carriers and decreases the photocatalytic activity [23]. Hence, the photocatalytic response of 3 wt\% and 5 wt\% Ni\(^{2+}\) doped TiO\(_2\) nanoparticles is lower than 1 wt\% Ni\(^{2+}\) doped TiO\(_2\) nanoparticles.

The degradation efficiency of pure and Cu\(^{2+}\) doped TiO\(_2\) nanoparticles are shown in figure (5.27). It is seen that the Cu\(^{2+}\) doped TiO\(_2\) nanoparticles with Cu content of 1 wt\% shows improved photocatalytic performance than 3 and 5 wt\% Cu\(^{2+}\) doped TiO\(_2\) nanoparticles. The doped Cu\(^{2+}\) ion induces an impurity energy level playing an important role in the effective separation of photoinduced electron-hole pair. Since the valence of Cu\(^{2+}\) ion is less than that of Ti\(^{4+}\), doping of Cu\(^{2+}\) will induce oxygen vacancies, which act as the active sites for water dissociation on the surface of TiO\(_2\), and can also capture the holes to restrain the recombination of hole-electron pairs [23]. Thus, the photocatalytic performance of 1 wt\% Cu\(^{2+}\) doped TiO\(_2\) nanoparticles is enhanced.

However, when much more Cu\(^{3+}\) ions are doped, they can trap the photoinduced electrons to form Cu\(^{+}\) ions. The Cu\(^{+}\) ions formed can capture the photoinduced holes and generate Cu\(^{2+}\). Thus, a short-circuiting forms and both photoinduced electron and hole are consumed. Consequently, the photocatalytic activity is reduced [23]. Therefore, the photocatalytic performance of 3 and 5 wt\% Cu\(^{2+}\) doped TiO\(_2\) nanoparticles diminished. All these Cu\(^{2+}\) ions doped TiO\(_2\) nanoparticles show lower photocatalytic efficiency than pure TiO\(_2\) nanoparticles.

The degradation efficiency of pure and metal ions doped TiO\(_2\) nanoparticles are listed in table (5.1). It has been observed that 1wt\% Ag\(^{+}\), 1, 3 and 5wt\% Zn\(^{2+}\)
doped TiO$_2$ nanoparticles show higher photocatalytic activity than the prepared and calcinated pure TiO$_2$ nanoparticles.

According to this result, the metal ion dopants such as Ag$^+$ and Zn$^{2+}$ on the TiO$_2$ surface can accelerate the transport of photoexcited electrons to the outer system and inhibit electron-hole pair recombination. Therefore, it is concluded that the doped samples 1 wt% Ag$^+$, 1, 3 and 5wt% Zn$^{2+}$ TiO$_2$ nanoparticles have shown higher photocatalytic efficiency [24].

On the other hand, when the concentration of doping is high, the doped ions act as trapping sites, and they can influence the lifetime of charge carriers. Usually, they boost up the recombination of photogenerated electrons and holes, and therefore do not allow further reactions. Therefore, any remarkable effect under ultraviolet light irradiation could not be received [25]. Hence, 3 and 5wt% Ag$^+$, all Ni$^{2+}$ and all Cu$^{2+}$ doped TiO$_2$ nanoparticles show lower photocatalytic efficiency than pure, Zn$^{2+}$ and 1 wt% Ag$^+$ doped TiO$_2$ nanoparticles.

From the above result, it is suggested that the photonic efficiency increases with increase in the metal ions loading up to certain level (optimum metal loading) and then decreases. The excess loading of metal ions may cover active sites on the TiO$_2$ surface, thereby reducing the photodegradation efficiency [24].
Figure 5.5: UV-Vis Absorption spectra of methyl orange at different intervals under UV light irradiation with prepared pure TiO$_2$ nanoparticles

Figure 5.6: UV-Vis Absorption spectra of methyl orange at different intervals under UV light irradiation with calcinated pure TiO$_2$ nanoparticles
Figure 5.7: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 1wt% Fe$^{2+}$ doped TiO$_2$ nanoparticles

Figure 5.8: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 3wt% Fe$^{2+}$ doped TiO$_2$ nanoparticles
Figure 5.9: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 5wt% Fe$^{2+}$ doped TiO$_2$ nanoparticles

Figure 5.10: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 1wt% Zn$^{2+}$ doped TiO$_2$ nanoparticles
Figure 5.11: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 3 wt% Zn²⁺ doped TiO₂ nanoparticles

Figure 5.12: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 5 wt% Zn²⁺ doped TiO₂ nanoparticles
Figure 5.13: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 1 wt% Ag$^+$ doped TiO$_2$ nanoparticles

Figure 5.14: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 3 wt% Ag$^+$ doped TiO$_2$ nanoparticles
Figure 5.15: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 5 wt% Ag⁺ doped TiO₂ nanoparticles

Figure 5.16: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 1 wt% Ni²⁺ doped TiO₂ nanoparticles
Figure 5.17: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 3wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles

Figure 5.18: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 5 wt% Ni$^{2+}$ doped TiO$_2$ nanoparticles
Figure 5.19: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 1 wt% Cu$^{2+}$ doped TiO$_2$ nanoparticles

Figure 5.20: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 3 wt% Cu$^{2+}$ doped TiO$_2$ nanoparticles
Figure 5.21: UV-Vis Absorption spectrum of methyl orange at different intervals under UV light irradiation with 5 wt% Cu$^{2+}$ doped TiO$_2$ nanoparticles

Figure 5.22: Degradation efficiency of prepared and calcinated TiO$_2$ nanoparticles
Figure 5.23: Degradation efficiency of Fe$^{2+}$ doped TiO$_2$ nanoparticles

Figure 5.24: Degradation efficiency of Zn$^{2+}$ doped TiO$_2$ nanoparticles
Figure 5.25: Degradation efficiency of $\text{Ag}^{+}$ doped $\text{TiO}_2$ nanoparticles

Figure 5.26: Degradation efficiency of $\text{Ni}^{2+}$ doped $\text{TiO}_2$ nanoparticles
Figure 5.27: Degradation efficiency of Cu$^{2+}$ doped TiO$_2$ nanoparticles
Table 5.1: Degradation efficiency of pure and metal ions doped TiO$_2$ nanoparticles

<table>
<thead>
<tr>
<th>Name of the Sample</th>
<th>Degradation (%)</th>
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</thead>
<tbody>
<tr>
<td>Pure TiO$_2$ (prepared)</td>
<td>84</td>
</tr>
<tr>
<td>Pure TiO$_2$ (calcinated)</td>
<td>90</td>
</tr>
<tr>
<td>TiO$_2$: 1 wt % Fe$^{2+}$</td>
<td>32</td>
</tr>
<tr>
<td>TiO$_2$: 3 wt % Fe$^{2+}$</td>
<td>22</td>
</tr>
<tr>
<td>TiO$_2$: 5 wt % Fe$^{2+}$</td>
<td>23</td>
</tr>
<tr>
<td>TiO$_2$: 1 wt % Zn$^{2+}$</td>
<td>94</td>
</tr>
<tr>
<td>TiO$_2$: 3 wt % Zn$^{2+}$</td>
<td>94</td>
</tr>
<tr>
<td>TiO$_2$: 5 wt % Zn$^{2+}$</td>
<td>95</td>
</tr>
<tr>
<td>TiO$_2$: 1 wt % Ag$^+$</td>
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</tr>
<tr>
<td>TiO$_2$: 3 wt % Ag$^+$</td>
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</tr>
<tr>
<td>TiO$_2$: 5 wt % Ag$^+$</td>
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</tr>
<tr>
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</tr>
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<td>TiO$_2$: 5 wt % Ni$^{2+}$</td>
<td>58</td>
</tr>
<tr>
<td>TiO$_2$: 1 wt % Cu$^{2+}$</td>
<td>55</td>
</tr>
<tr>
<td>TiO$_2$: 3 wt % Cu$^{2+}$</td>
<td>26</td>
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<tr>
<td>TiO$_2$: 5 wt % Cu$^{2+}$</td>
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REFERENCES


