Proceedings of Science and Mathematics
Faculty of Science, Universiti Teknologi Malaysia

https://science.utm.my/procscimath/
Vol. 20 (2023)

Chitosan Modified Titanium Dioxide Photocatalysts for Dye Degradation

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Abstract

This study aimed to explore the potential effectiveness of chitosan-modified titanium dioxide (CS-TiO_2) in degrading an azo dye, methyl orange which has high toxicity. Various chitosan concentrations (2%, 4%, and 6%) were doped into TiO_2 through wet impregnation method. FTIR analysis revealed the successful loading of chitosan in the prepared samples. The band gap energy of the chitosan doped TiO_2 (2.98 eV) was lower than that of TiO_2 as evidenced by the Tauc plots. Consequently, the composite photocatalysts exhibited enhanced catalytic activity under visible light irradiation for 4 hours at room temperature. The current findings indicated that the highest methyl orange removal (68.2%) was achieved when 6.0 wt% chitosan doped TiO_2 photocatalyst was used.

Keywords: titanium dioxide, chitosan, dye degradation, photocatalyst, wet impregnation

1. Introduction

The use of synthetic dyes in various industries, particularly in textiles, has greatly enhanced the aesthetic appeal of products. However, the discharge of non-biodegradable textile dyes into natural water bodies has led to significant environmental concerns (Elbadawy et al., 2023; Iwuozor et al., 2021). These concerns revolve around the persistent pollution caused by these dyes, posing serious threats to aquatic life and human health (Peramune et al., 2022; Sadiq et al., 2021; Selvaraj et al., 2021).

Consequently, the urgent need to address this environmental challenge has prompted researchers to explore innovative and sustainable solutions for removing these pollutants from wastewater. In response to this critical issue, researchers have turned their attention to chitosan (CS). CS, derived from the abundant natural biopolymer chitin, has shown potential in adsorbing pollutants, including dyes, due to its high solubility in acidic conditions and unique chemical properties (Anaya et al., 2020; Janani et al., 2022; Phan et al., 2019).

Additionally, its ability to effectively adsorb dyes from wastewater presents an attractive avenue for mitigating the harmful environmental impact caused by these synthetic substances (Islam et al., 2018; Samueal et al., 2020). Moreover, CS's cationic behaviour, large surface area, and biodegradability further enhance its appeal as an ideal candidate for environmental applications (Sadrjavadi et al., 2018; Zhang et al., 2019).

In parallel, titanium dioxide (TiO_2), a widely used semiconductor known for its photocatalytic activity, has captured the interest of researchers. Despite its stability, affordability, and non-toxic nature, TiO_2's photocatalytic efficiency remains limited to ultraviolet (UV) light region and high charge recombination rates (Ali et al., 2018; Wang et al., 2023). This limitation has sparked interest in modifying the surface of TiO_2 through metal and non-metal modifiers, aiming to enhance its photocatalytic performance under visible light (Basavarajappa et al., 2020).

Researchers have focused on strategies such as metal ion doping, which introduces localized energy levels or Schottky junctions within the band gap, extending the lifetime of electron-hole pairs (Prakruthi et al., 2022). Noble metals like platinum have shown promise in enhancing the photocatalytic activity of TiO_2, but concerns related to cost and photocorrosion have prompted the exploration of other modifiers (Katal et al., 2020; Sakar et al., 2019).

To maximize the potential of TiO_2 and overcome its limitations, researchers have investigated composite materials of TiO_2 and CS. This approach aims to synergistically enhance the photocatalytic performance of TiO_2 under visible light, resulting in a composite photocatalyst with improved efficiency. By combining the unique properties of both materials, this composite photocatalyst offers a promising solution for effective dye degradation, contributing to the development of an advanced wastewater treatment process.

In the context of environmental sustainability, this study focuses on the synthesis and characterization of CS-TiO_2 using the wet impregnation technique. The successful synthesis and characterization of its properties using spectroscopic and X-ray diffraction analyses of this composite photocatalyst are crucial steps in this study, enabling the evaluation of its photocatalytic activities under visible light. Moreover, assessing its photodegradation effect on dyes provides valuable insights into its potential applications in wastewater treatment and other fields.

This research aimed to contribute significantly to the advancement of photocatalytic material science, addressing the growing need for sustainable solutions to environmental challenges. By developing a composite photocatalyst with improved performance, this study supports broader environmental sustainability goals while contributing to the scientific understanding of photocatalytic materials.

2. Materials and methods

The chemicals used in this study involved titanium dioxide (TiO_2), chitosan (CS), acetic acid (CH_3COOH), distilled water and methyl orange.

The synthesis of the photocatalyst involved the preparation of a CS solution in an acidic medium. CS compounds were slowly added to an acetic acid solution, ensuring complete dissolution. The CS solution was then mixed with TiO_2 and stirred to achieve a homogeneous suspension. After sonication and centrifugation, the sample was washed, filtered, and dried to obtain CS- TiO_2 catalyst powder.

The synthesized photocatalyst was characterized using various techniques. Fourier-transform infrared spectroscopy (FTIR) was used to analyze the chemical structure of the photocatalyst. UV-vis spectroscopy was employed to determine the optical properties and of the synthesized material. UV-vis spectra were recorded over a range spanning from 400 to 800 nm. In order to calculate the band gap of the samples, the absorption spectra were subsequently transformed into a Tauc plot X-ray diffraction (XRD) was used to observe the crystallographic structure and phase of the photocatalyst.

The photocatalytic activity of the synthesized CS- TiO_2 photocatalyst was tested using a methyl orange (MO) dye. A stock solution of MO was prepared, and standard solutions of varying concentrations were derived from it. The photodegradation test was conducted by stirring the photocatalyst with the MO solution in a closed box under dark and visible light conditions. Samples were withdrawn at different time intervals, and the concentration of the degraded dye solution was measured using UV-vis analysis. The percentage of dye removal was calculated based on the initial and final dye concentrations.

$$\text{Degradation (\%)} = \frac{C_0 - C}{C_0} \times 100\%$$

where C_o is the initial concentration of dye solution and C is the concentration of dye solution after photocatalytic reaction.

3. Results and discussion

3.1 Fourier Transform Infrared (FTIR)

Figure 1 shows the FTIR spectra of pure TiO_2 and synthesized CS-TiO_2 samples. A broad band can be observed at 3404 cm^{-1} at all of the samples indicating the presence of chitosan functional groups which are $-NH_2$ and $-OH$ groups stretching vibrations. There was also band at wavenumber of 1624 cm^{-1} which was described as primary amine present in CS and bending vibrations of Ti−OH.

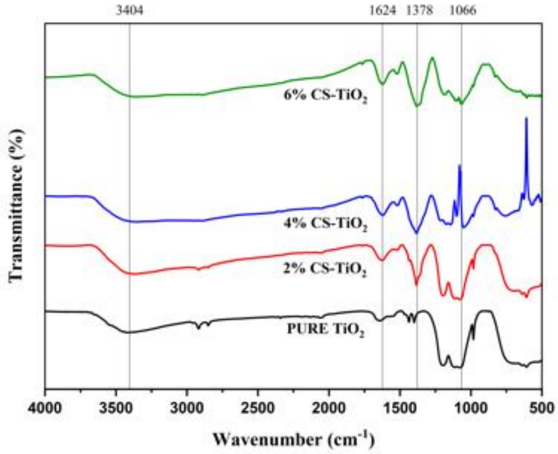

Figure 1 FTIR spectra of pure TiO_2 and synthesized CS-TiO_2 samples

3,2 UV-vis Spectroscopy

As depicted in Figure 2, a prominent absorption spectrum is evident at 338 nm, and the absorption edge emission occurs at approximately 410 nm. Among the various samples tested, 6% CS-TiO_2 exhibited the most substantial absorbance. With an increase in the amount of chitosan, the absorption edge becomes less pronounced, suggesting that the addition of chitosan has led to a narrowing of the size distribution of the suspended particles (Binsabt et al., 2022).

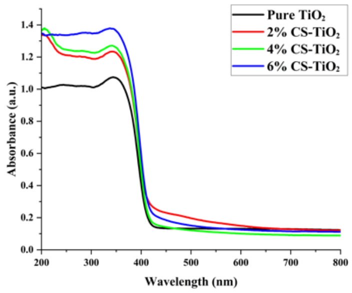

Figure 2 UV-vis spectra of pure TiO_2 and synthesized CS-TiO_2 samples

Table 1: Band gap energy of TiO_2 and synthesized CS-TiO_2 samples

Sample	Band gap energy (eV)
Pure TiO_2	3.08
2% CS-TiO_2	3.04
4% CS-TiO_2	3.03
6% CS-TiO_2	2.98

Table 1 shows the band gap energy of TiO_2 and synthesized CS-TiO_2 samples. Band gap energy was determined by plotting Tauc plot where the the band gap of the pure TiO_2 sample was found to be 3.08 eV and decrease gradually to 2.98 eV (6% CS-TiO_2) as the CS concentration increase.

3.2 X-Ray Diffraction (XRD)

XRD spectra (Figure 3) of the synthesized samples were found to have 11 resemblance peaks (Table 2) to the standard rutile phase. The obtained result agreed with standard pattern of monoclinic phase which is in accordance with the JCPDS card no. 7206075. There were no changes between pure TiO_2 and modified TiO_2 indicating that the modifying of CS retained the characteristic crystal structure of rutile TiO_2.These findings from the XRD analysis indicate that the CS was not fully incorporated into the

TiO_2 lattice as there were no substantial alterations to its crystal structure. The XRD patterns of the samples exhibited sharp and well-defined peaks, indicating the presence of large and well-ordered crystal domains (You et al., 2022). However, from the UV-Vis analysis above, it can be said that the surface was successfully modified by CS.

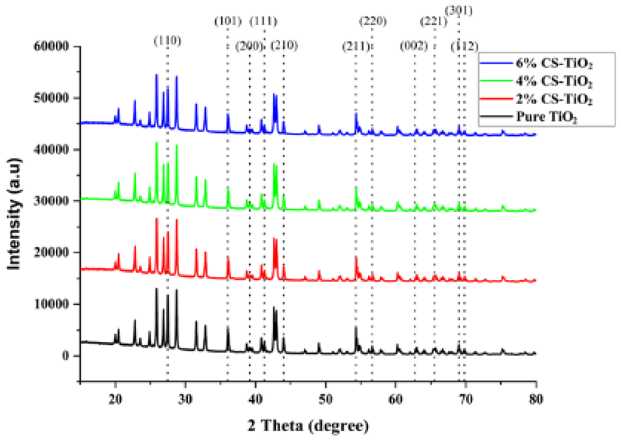

Figure 3 XRD patterns of pure TiO_2 and synthesized CS-TiO_2 samples

Table 2: Comparison of pure TiO_2 and synthesized CS-TiO_2 peaks with standard rutile peaks

Peak No.	Planes (hkl)	Sample (2θ)	Rutile (2θ)
1	(110)	27.5	27.4
2	(101)	36.1	36.1
3	(200)	39.2	39.2
4	(111)	41.3	41.2
5	(210)	44.0	44.0
6	(211)	54.3	54.3
7	(220)	56.6	56.6
8	(002)	62.8	62.8
9	(221)	65.5	65.5
10	(301)	69.0	69.0
11	(112)	69.8	69.8

3.3 *Photocatalytic Test*

The photocatalytic activity of different CS-TiO_2 samples was evaluated by measuring the photodegradation of MO dye. Following 4 hours of visible light exposure, it can be seen that 6% CS-TiO_2 achieved the highest dye removal percentage of 68.22% (Table 3). The results indicate that solar irradiation facilitated the degradation of MO dye, with higher chitosan concentrations leading to increased dye degradation. It can be confirmed that the 6% CS-TiO_2 sample exhibited the highest adsorption capacity compared to other modified samples and pure TiO_2. The successful modifying process enhanced the adsorption properties of TiO_2, overcoming the limitations associated with TiO_2's wider bandgap energy, limited surface area, and active sites.

Table 3: Dye removal percentage of all of the synthesized samples in dark and light condition.

Sample	Dye removal percentage (%)	
	Dark	Light
Pure TiO_2	26.29	35.96
2% CS-TiO_2	36.03	63.48
4% CS-TiO_2	43.76	61.74
6% CS-TiO_2	39.58	68.22

4. Conclusion

In conclusion, this study successfully prepared CS-TiO_2 samples using the wet impregnation method. The structural properties of the modified samples were characterized FTIR, confirming the presence of chitosan in the samples with the peaks at 3404 cm^{-1} and 1624 cm^{-1}. The UV-Vis spectra indicated that the 6% CS-TiO_2 sample had the highest absorbance, while the bandgap energy decreased with increasing CS concentration. XRD analysis revealed well-defined peaks resembling the standard rutile phase, indicating a tetragonal rutile crystal structure in the composite samples. Photocatalytic activity was evaluated through dye degradation test, with the 6% CS-TiO_2 sample exhibiting the highest percentage of dye removal (68.22%). These findings demonstrate that modifying TiO_2 with 6% CS significantly enhances its photocatalytic activity, with modifications in the bandgap energy and defect states.

Acknowledgement

The authors would like to express sincere gratitude to Universiti Teknologi Malaysia for the financial support through UTM Fundamental Research Grant (cost center no.: Q.J130000.3854.22H42).

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