Synthesis of TiO_2 nanotubes for photocatalytic degradation of drugs

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Highlights

- Copper-doped TiO_2 nanotubes were synthesized.
- Cu/TiO_2 nanotubes show a higher activity than pristine titanium oxide.

1. Introduction

A significant portion of ingested drugs leave our bodies through urine and fesses, entering wastewater streams continuously. Unfortunately, these pharmaceutical contaminants often escape detection and treatment by conventional wastewater treatment plants (WWTPs). Their presence in various water bodies, including rivers, lakes, and seas, poses a serious threat to human health and the environment [1]. Heterogeneous photocatalytic degradation offers a promising solution to address this potential toxicity. This process utilizes sunlight to convert contaminants into harmless compounds. Titanium dioxide (TiO_2), a semiconductor with a bandgap of 3.2 eV, serves as the most common photocatalyst. Upon exposure to sunlight, electrons in TiO_2 absorb the photon energy and become excited, jumping to the conduction band. These energized electrons then react with contaminants, oxidizing and transforming them into harmless substances like CO_2, water, and inorganic salts.

Recent research has shown that transition metal-doped TiO_2 nanotubes possess a lower bandgap, making them more efficient photocatalysts. This lower bandgap allows electrons to be excited to higher energy levels, enabling them to react with a wider range of contaminants.

Leveraging this advantage, we synthesized TiO_2 nanotubes using the hydrothermal method and subsequently doped them with copper (Cu). This approach aimed to demonstrate the photocatalyst's effectiveness in degrading common drugs like ibuprofen, naproxen, and ciprofloxacin.

As a crucial next step, we are developing a comprehensive and effective kinetic model to describe the photocatalytic degradation of drugs. This model will provide valuable insights into the reaction mechanisms and optimize the process for maximum efficiency, paving the way for a more sustainable and environmentally friendly solution to pharmaceutical contamination.

2. Methods

For the synthesis of the nanotubes, the hydrothermal method was used at 110°C for 72 hours, inside a stainless-steel autoclave and Teflon coating, using 2.5 g of spherical titanium dioxide nanoparticles in the anatase phase (Sigma Aldrich, 99.7% purity) in 25 ml of 10 M NaOH solution. The product was washed with a solution of 1 M hydrochloric acid and distilled water. The products were dried in an oven at 75°C for 24 hours. Finally, they were calcined in a muffle at 400 °C with a slow heating ramp.

The nanotubes were dry-impregnated with the selected transition metals, using precursor salts, such as copper acetylacetonate in powder form for the Cu/ TiO_2 nanotubes.

Evaluations of the photocatalytic performance of the synthesized catalysts were carried out in a mini reactor using a magnetic stirrer and using a cylinder-shaped UV light lamp at a wavelength of 365 nm. The various solutions with different amounts of photocatalyst were kept under magnetic stirring at 500 rpm for a period of 4 hours to perform UV-Vis spectroscopy analysis. The above was done with each drug (ibuprofen, naproxen, and ciprofloxacin).

A calibration curve was constructed for each drug from solutions with dilution factors of 1/10, 1/100, 1/1000, and 1/10000 based on their concentration (2.4, 1, and 5 ppm) for ibuprofen, naproxen, and ciprofloxacin respectively; that corresponds to the range of typical concentrations in wastewater.

Finally, the percentage of drug degradation was estimated, through the following equation, and compared with the results obtained with the proposed kinetic model.

$$\%Degradation = \frac{C_0 - C_f}{C_0} \times 100 \qquad 1)$$

Where, C0 is the initial concentration and Cf the final concentration.

3. Results and discussion

TiO2 nanotubes were successfully synthesized by a hydrothermal method using 10 M NaOH solution. The micrograph in Figure 1 confirms the formation of the nanotubes. Subsequently, they were doped with copper, reducing the bandwidth of the semiconductor from 3.25 eV to 2.8 eV, Figure 3, as evidenced by the Kubelka-Munk equation. The photocatalytic capacity of the synthesized materials was evaluated in the degradation of ibuprofen, Figure 2. The results demonstrated that Cu-doped TiO2 nanotubes (Cu/NT-TiO2) exhibited higher photocatalytic reaction efficiency compared to undoped TiO2 particles and TiO2 nanotubes.

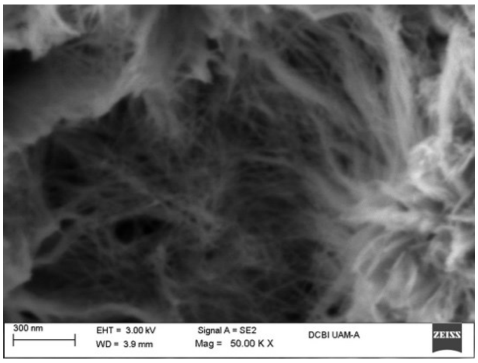

Figure 1. Photographs of the Cu/TiO₂ nanotubes obtained in SEM.

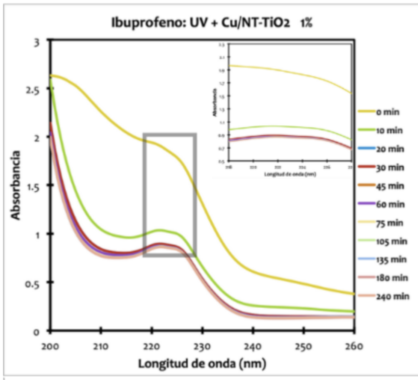

Figure 2. Photodegradation tests at different reaction times under UV irradiation (365nm) with Cu/NT- TiO_2 1%Cu catalyst for ibuprofen.

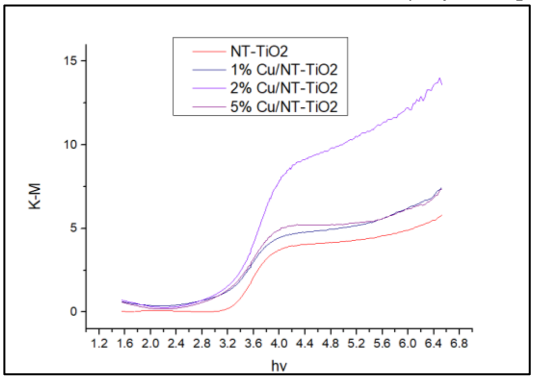

Figure 3.Plot of Kubelka-Munk transformed reflectance vs. energy (hv) for the band gaps of NT- TiO_2 and Cu/NT-TiO_2.

4. Conclusions

Copper-impregnated titanium dioxide nanotubes (Cu/NT-TiO_2) are a promising photocatalytic material for the degradation of emerging contaminants in wastewater. This material has greater photocatalytic activity than the anatase phase TiO_2 and titanium dioxide nanotubes without the impregnation of any metal. The higher photocatalytic activity of Cu/NT-TiO_2 is attributed to the presence of copper in the material structure. Copper is a transition metal that has a lower bandgap than TiO_2.

References

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Keywords

Nanotubes, wastewater, emerging contaminants, catalysts.