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Characterization of (ZnO-TiO_2) nanoparticles prepared by impregnation method and study of their effect on the photodegradation of ampicillin

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Abstract

In this research, the photodegradation of the ampicillin antibiotic (AMP) in an aqueous solution was studied by using $ZnO–TiO_2$ nanoparticles prepared via the wet incipient impregnation method with TiO_2 and $Zn(NO_3)_2{\cdot}6H_2O$ as precursor materials using three different ratios of both oxides (1:1, 0.5:1, 1:0.5). The effects of different molar ratios of the prepared nanoparticles and ultraviolet radiation from sun rays and a UV lamp were studied. We utilized SEM, XRD, and EDX characterization techniques to study the structural features and morphology of the nanoprepared oxide. The removal of the antibiotic ampicillin was studied using an ultraviolet device at a wavelength of 254 nm in the presence of oxide nanoparticles and two radiation sources. The removal rate was 98% when using a composite oxide (ZnO-TiO_2) in a proportion of 0.5:1 and applying solar radiation.
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Keywords: (ZnO-TiO_2) nanoparticles, XRD, SEM, Ampicillin, Photodegradation

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INTRODUCTION

The discharge of wastewater from the pharmaceutical industry into the environment has caused soil, surface, and groundwater contamination. Numerous regenerated compounds, such as antibiotics, have been distinguished when examining the composition of wastewater. Ampicillin is one of the most broadly utilized antibiotics and is ingested in small amounts by the human body, while the rest are excreted from it. Inappropriate use of this medicates for treating irreversible illnesses in people and creatures has led to antibiotic resistance. (Bena Y., et, al. 2019)

Ampicillin is a penicillin β-lactam antimicrobial agent used to treat susceptible bacterial infections and is usually widely used for the treatment of human and veterinary diseases worldwide. It is a semisynthetic penicillin, and its antimicrobial properties result from the β-lactam ring of its structure. (Cuerda-Correa E., et, al. 2020)

Several strategies, specifically, adsorption, filtration, organic form, prostate oxidation, and photocatalytic

investigation, have been utilized to eliminate ampicillin from soil and water sources. The creation of secondary pollution, economic inefficiency, limited performance in industrial dimensions, and low efficiency are the main problems associated with these methods. Numerous research groups are investigating advanced approaches to efficiently eliminate antibiotics, with particular attention directed toward advanced oxidation processes (AOPs), which can potentially remove substantial amounts of antibiotics from pharmaceutical wastewater. (Akbari M. Z., et, al. 2021)

AOPs utilize the intermediate hydroxyl radicals (OH•) that are produced during the catalytic process, and these OH• radicals are highly reactive in comparison to alternative oxidants such as chlorine (Cl_2) and molecular ozone (O_3). (Samsuri S.A.M., et, al. 2017) These highly reactive radicals, such as OH•, are formed using oxidizing agents, including O3 and hydrogen peroxide (H_2O_2)، often in the presence of catalysts such as semiconductor materials or ultraviolet (UV) radiation. (Elnazer W., et, al. 2024) . These processes aim to oxidize initial organic compounds such as antibiotic molecules in wastewater, generating intermediary substances with reduced toxicity and enhanced biodegradability or even complete conversion into water (H_2O) and carbon dioxide (CO_2).

The application of nanomaterials in evacuating natural toxins has received increasing attention due to their electronic, optical, mechanical and expansive particular surface zones. Recently, metal oxides such as titanium, zinc, and copper have been used in treating environmental issues and decomposing a wide range of organic compounds, such as dyes, toxins, and medicinal compounds. (Gahrouei A. E., et, al. 2024)
Its high effectiveness, environmental compatibility, and reusability are highlights that have made the use of the photocatalytic deterioration strategy predominant over other strategies. In any case, stability and photocatalytic activity are fundamental in determining the optimal photocatalyst. (Baneshi M. M., et, al. 2018)

ZnO and TiO_2 have long been utilized in different fields due to their surprising properties, such as nontoxicity, strong photocatalytic action under bright radiation, and chemical stability. ZnO is one of the most broadly utilized semiconductors in numerous fields, such as piezoelectric converters, sun-oriented cells, and picture finders. With properties such as tall surface vitality, tall electron portability, and a large number of vitality crevices, ZnO has been utilized in numerous fields to break down a wide range of poisons. However, TiO_2 is a nontoxic semiconductor with tall chemical soundness. It has been considered due to its promising characteristics, such as optical material science, hardware, oil, warm exchange, and therapeutic applications. Additionally, TiO_2 has been utilized in natural applications to remove different contaminants from sea-going environments due to its antimicrobial properties. Compared to TiO_2, ZnO nanoparticles have greater electron portability, whereas in terms of chemical solidness, TiO_2 nanoparticles have greater solidness, particularly under acidic conditions. The expansive holes in TiO_2 and ZnO (3.2 and 3.1 electron volts, respectively) constrain their photocatalytic action to bright light. ZnO–TiO_2 nanoparticles could be efficient photocatalysts for the degradation of pollutants. . (Tola J. M., et, al. 2024) (Raheb I.and Manlla M. S.2021) (Adegoke A., et, al. 2019)

It has been reported in a number of studies that ZnO–TiO_2 binary composites exhibit excellent photocatalytic activity for the degradation of pollutants compared to ZnO and TiO_2 alone. The increase in the photocatalytic activity of the binary composite is due to the photostability of the composite, increase in the lifetime of the hole-electron pairs formed by irradiation of the composite and interfacial charge transfer to the adsorbed substrates. In this study, we report the improvement in the photocatalytic activity of commercial-grade TiO_2 by decorating it with ZnO via an impregnation method. (Loh K., et, al. 2018) (Ayanda O. S., et, al. 2023)

MATERIALS AND METHODS:

Chemicals

The following chemicals and pharmaceuticals were used:

- Aqueous zinc nitrate (Zn(NO3)2.6H2O, high purity 99%) was obtained from Loba Chemie.
- Titanium oxide produced by Fine Chem LLP
- Ampicillin is a pure pharmaceutical substance.

Instruments

- An electric drying oven (300 °C) produced by the R-LABINCO company was used for heating.
- The calcination muffle heat treatment (1200 °C) was performed by Carbolite.
- UV lamp (10 W).
- A sensitive electronic scale (JA-Series) was manufactured by FITHFUL with high accuracy.
- The slides were heated with a magnetic mixer.
- An electric drying oven (300 °C) produced by the R-LABINCO company was used for heating.
- The calcination muffle heat treatment (1200 °C) was performed by Carbolite.
- A 150 W spectrophotometer (T70) produced by PG Instruments Limited Company was used to determine the concentration of the AMP solution at a wavelength of 254 nm.
- SEM (scanning electron microscope)
- XRD (X-ray diffraction).

ZnO-TiO_2 photocatalyst synthesis

An impregnation method was used for the synthesis of ZnO–TiO_2 in a 1:1 ratio using TiO_2 and $Zn(NO_3)_2{\cdot}6H_2O$ as precursor materials. Typically, a homogeneous solution was prepared by dissolving

3.62 g of $Zn(NO_3)_2 \cdot 6H_2O$ in 500 mL of distilled water. Then, 1.00 g of TiO_2 was suspended in the prepared solution. The resulting mixture was stirred for 18 h at 25 °C and then dried for 1 h at 110 °C until evaporation of the solvent. The solid residue obtained was calcined at 550 °C to obtain the ZnO–TiO_2 composite .(., et, al. 20). The same procedure was followed for the synthesis of ZnO and TiO_2 at a 0.5:1, 1:0.5 ratio with different weights.

ZnO/TiO_2 characterization

X-ray diffraction patterns of ZnO–TiO_2 were obtained by a Philips PW-1840 instrument. The elemental composition of ZnO–TiO_2 was determined by energy dispersive X-ray spectroscopy with an EDX PV77-60770 ME. The morphologies of the prepared composite oxides were studied by a Quanta 200 scanning electron microscope manufactured by FEI.

Photocatalytic activity

The aqueous phase photodegradation of ampicillin was studied for comparison of the photocatalytic performance of ZnO–TiO_2 at different ratios and from different sources of UV rays. We added 0.1 g of the prepared oxide (1:1) to the prepared ampicillin solution at three different concentrations (20, 40, and 80 mg/L). The solutions were placed under the rays of a UV lamp, and the reaction mixture was stirred under irradiation for 3 h. Subsequently, the photocatalyst was separated by filtration from the reaction samples, and the absorbance of each sample was determined at 254 nm using a UV–visible spectrophotometer. The same steps were repeated, but the solutions were placed under sunlight for 24 hours, after which the absorbance was measured. The observed absorbance values were subsequently used to calculate the catalytic efficiency. (Als Duarate A., et, al. 2017) .(Yasmine K., et, al. 2022). The same steps were repeated but using the oxides prepared with other molar ratios.

RESULTS AND DISCUSSION:

X-ray diffraction analysis

The XRD pattern of synthesized ZnO-TiO_2 is shown in Fig. 1. According's the XRD pattern, the peaks located at 2θ = 32.1°, 34.5°, 36.6°, 56.7°, 62.8°, and 68.0° are related to the ZnO NPs according to JCPDS NO 36-1451. Additionally, the peaks related to TiO_2 NPs are located at 25.4°, 37.8°, 48.0°, 53.9°, 55.0°, 69.1°, 70.2°, and 75.1° according to JCPDS NO 21-1272. The XRD peaks indicate the formation of a high-crystallinity phase of ZnO-TiO_2, which is similar to what was previously reported .(Heris, Z. S., et, al. 2023) No diffraction peaks corresponding to any other phase were present in the prepared samples, which is a sign of the phase purity of the prepared samples.

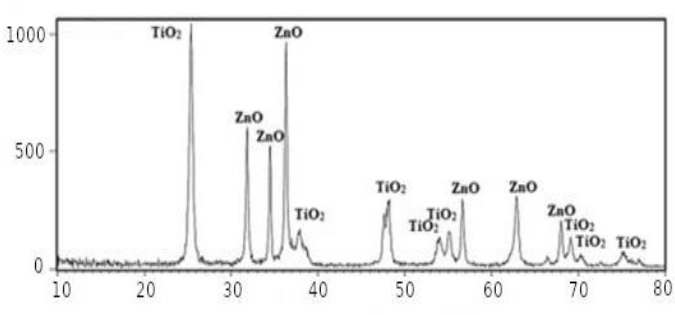


Fig. 1. XRD pattern of the synthesized ZnO-TiO_2 nanoparticles.

Morphological analysis (SEM)

Scanning electron microscopy was used. Fig. 2 shows the morphology of the ZnO-TiO_2 nanoparticles with a width of 10.5 nm, a narrow particle size distribution and little agglomeration. The average crystallite size of the nanoparticles calculated from the XRD patterns using Scherrer's equation was approximately 19.4 nm, which is in agreement with the result obtained from the SEM image.

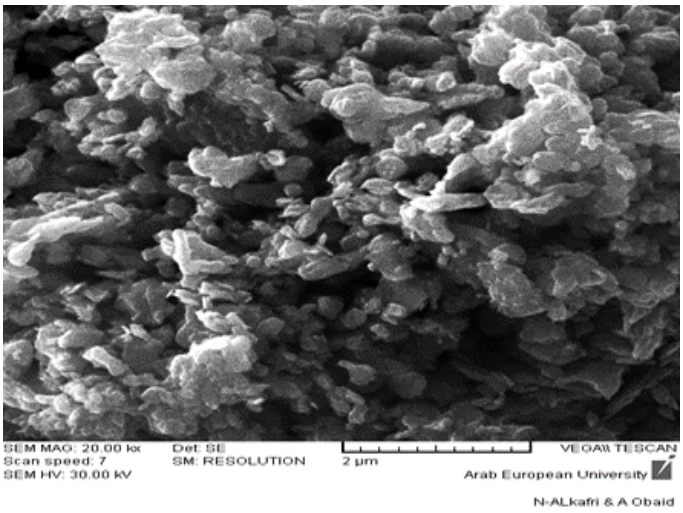


Fig. 2. SEM image of synthesized ZnO-TiO_2 NPs.

Elemental composition and chemical structure

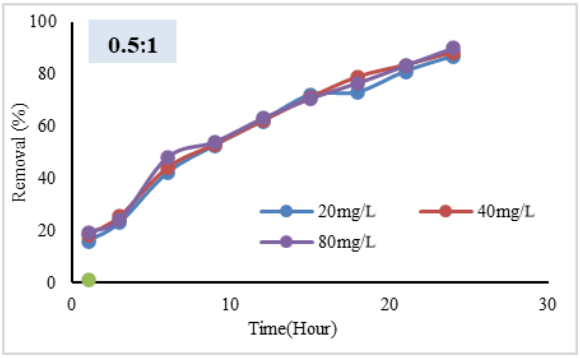
EDX is an X-ray characterization technique that allows extremely rapid elemental concentration data to be gathered. Elemental concentrations can be collected from points, along lines, or as maps. visualization of the distribution of the constituent elements in the specimen by two-dimensionally displaying the characteristic X-ray intensities or the concentrations of the elements .(Liu S., et, al. 2019)
EDX analysis revealed that the elemental composition of the composite sample was the same as expected without any impurities for the prepared ZnO-TiO_2 sample, as shown in Table 1.

Table 1. EDX percentage of synthesized ZnO-TiO_2 NPs.

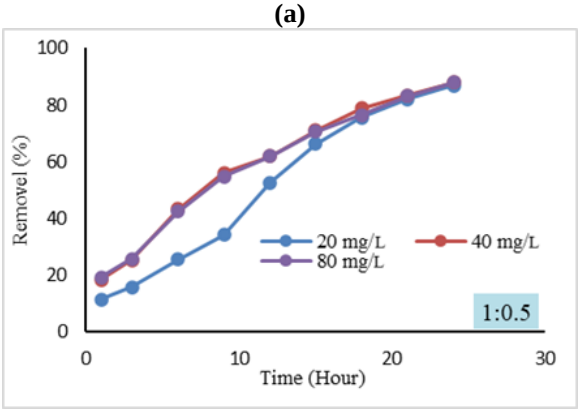
Element	Weight%
Zn	40.89
Ti	31.6
O	28.51
Total	100.00

Determination of Removal Ampicillin Removal Photo -catalytic activity

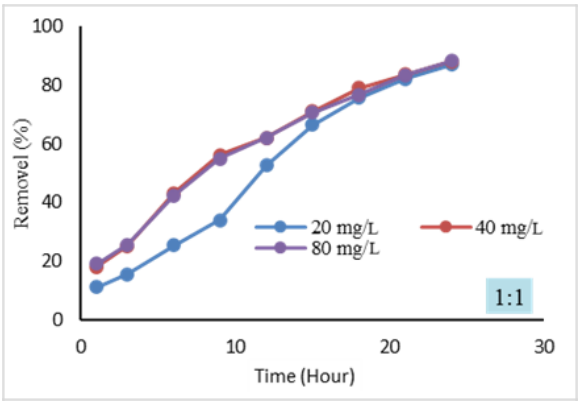
The photocatalytic activities of the ZnO–TiO_2 nanoparticles were compared by performing degradation experiments on the AMP antibiotic.



(a)



(b)

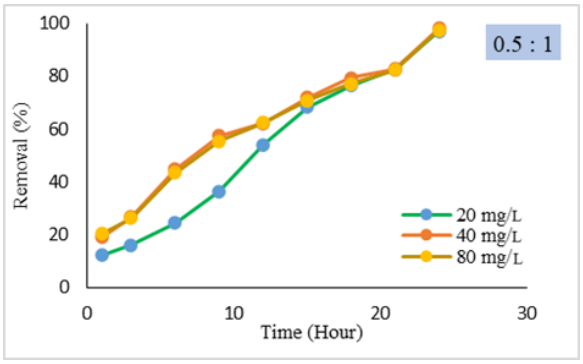


(c)

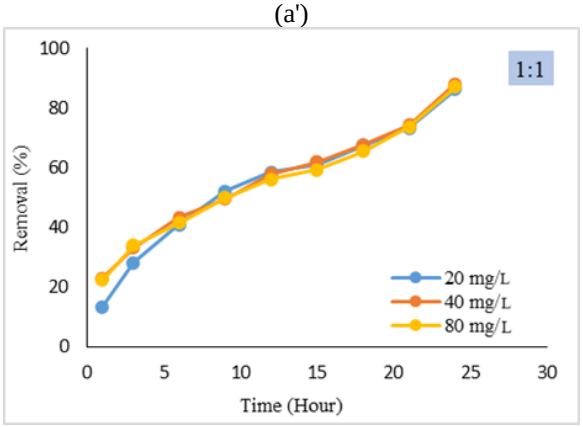
Fig. 3. (a, b, c) Dissociation curves for AMP after the addition of ZnO-Tio2 at different molar ratios for the concentrations studied in the presence of a UV lamp.

The catalytic effectiveness of the prepared oxides in degrading ampicillin was tested in the presence of two sources of UV radiation, the first a 10-watt UV lamp and the second sunlight.

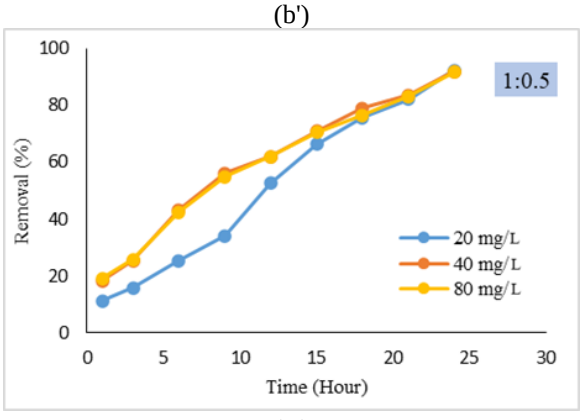
Ampicillin solution (100 ml) of the antibiotic ampicillin (AMP) was prepared at a concentration of 100 mg/L, and three solutions were prepared from it at concentrations ranging from 20-40-80 mg/L. Then, 25 ml of each solution was taken, and 0.1 g of the composite oxide (1:1) was added to each sample. The solutions were exposed to UV lamp rays for 3 hours at room temperature.



(a')



(b')



(c')

Fig. 4. (a',b',c') Dissociation curves for AMP after the addition of ZnO-Tio_2 at different molar ratios for the concentrations studied in the presence of sun rays.

The resulting solution was filtered, and the remaining concentration of ampicillin was determined spectrographically at a wavelength of 254 nm.

The removal ratio was calculated using the following equation:

$$\text{Removal } \% = \frac{A0 - Ae}{A0} \times 100$$

A0: initial concentration of AMP (mg/l).
Ae: residual concentration of AMP (mg/l) (Abdul Jabbar M., 2020)

Prior to irradiation, adsorption-desorption equilibrium was established by stirring the reaction mixture for 30 min in the dark. Stirring of the reaction mixture in the dark did not cause any decrease in the concentration of AMP. The photocatalytic degradation experiments were carried out for 180 min and were measured by a UV–visible spectrophotometer. The same steps were repeated, but each time, a molar percentage of the studied co-oxide was used.

The data given in Fig. 3 show that the composite of ZnO–TiO_2 with a 0.5:1 ratio has higher photocatalytic activity than does the other composite when we used a UV lamp, and the removal rate reached 95%.

The steps applied in the presence of a UV lamp were repeated on other samples at the same concentrations but by applying solar radiation for 24 hours. The removal ratio for AMP was subsequently calculated, and the data given in Fig. 4 show that the composite, ZnO–TiO_2, which has a 0.5:1 ratio, has higher photocatalytic activity than does the other ratio when sun rays were used; moreover, the removal rate reached 98%.

The photocatalytic efficiency of both ZnO and TiO_2 toward the degradation of AMP was enhanced by the composite material. The increase in the photocatalytic activity of the composite, ZnO–TiO_2, is due to the synergistic effect between TiO_2 and ZnO. This increase in catalytic activity might be due to the formation of heterojunctions as a result of interfacial contact between ZnO and TiO_2. Irradiation of the photocatalyst leads to the formation of a pair of positive holes and electrons in the valence band and conduction band of the catalyst, respectively. The photogenerated positive holes shift from the VB of TiO_2 to the VB of ZnO, while the photoexcited electrons shift from the CB of ZnO to the CB of TiO_2. This results in the separation of positive holes and photoexcited electrons, ultimately increasing the lifetime of the charge carriers (Noman M. T. et, al, 2021). (Shangye C. et, al,2024). (Kancherla R. et, al,2024)

The positive holes oxidize H_2O molecules and yield OH radicals, while photoexcited electrons reduce the dissolved oxygen molecules, yielding superoxide anions and OH radicals. These OH radicals degrade dye molecules to inorganic products. As a result of the separation of positive holes and photoexcited electrons, more OH radicals were produced, improving the photocatalytic activity (Das A. et, al, 2019, Wattanwikkam C., et, al,2017)

CONCLUSION

In this research, co-oxide was prepared by impregnation. The scanning electron microscopy results showed that the grains were nanoscopic, with dimensions ranging from 13.58 nm and a fleece shape. The EDX results revealed a good match between the experimental and elemental analysis rates.

The results of the composite oxide study showed that the oxidation of the parent antibiotic is highly efficient when the reaction occurs in the presence of rays from a UV lamp and in the presence of solar rays.

The prepared samples showed the best catalytic activity when ZnO-TiO_2 was used at a ratio of 0.5:1, and the effectiveness was greatest when solar rays were used. The percentages of photodegradation of the AMP solution (50 mL, 100 mg/L) at 25 °C were 98, 87 and 92% after 24 h of reaction over ZnO–TiO_2 .(1:0.5، 1:1 ،0.5:1)

Hence, we recommend improving the structure of the prepared nanocomposite oxide by adding elements or compounds that lead to an increase in catalytic effectiveness and thus an increase in the rate of destruction of pharmaceutical and organic wastes; using solar radiation as a source of ultraviolet light instead of using a UV lamp; preparing common oxides using other methods, such as hydrothermal methods and the sol-gel method; and studying their effectiveness in destroying pollutants.

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