Optimized Photocatalytic Degradation of Ciprofloxacin Using Nano SnO_2 Thin Films: Kinetic Studies and Operational Parameters

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Abstract :Pharmaceuticals constitute the largest group of organic pollutants discharged into wastewater by manufacturers and healthcare institutions. Therefore, the development of effective methods for degrading these pollutants is crucial for environmental protection. The pharmaceutical medication waste ciprofloxacin, which has several uses, was degraded using a thin film of a SnO_2 photocatalyst supported on the polymer. Among the tested semiconductors, SnO_2 thin film, which was found to be the best photocatalyst for ciprofloxacin degradation. Operational parameters were explored to optimize the conditions for the complete removal of pharmaceutical pollutants from aqueous solutions including various factors affect the ciprofloxacin degradation kinetics. In this study, kinetic studies of the photocatalytic degradation of ciprofloxacin were performed. This study demonstrated that SnO_2 was the most efficient photocatalyst for ciprofloxacin degradation among the tested materials, reaching an optimum degradation rate of 89 %. The SnO_2 photocatalyst was utilized in five consecutive batches, yielding consistent and acceptable results and demonstrating its reusability over four cycles. The percentage degradation of this antibiotic increased with increasing irradiation time. This clearly indicated that the efficiency decreased with increasing initial drug concentration. Among the studied pH ranges, pH 3 was found to be the optimal solution for ciprofloxacin degradation. The inclusion of 0.01M concentration of H_2O_2 in the Ciprofloxacin solution exhibited the most significant degradation efficacy. Here, we introduce SnO2-Polymer as a good catalyst for removal Ciprofloxacin from wastewater.

Keywords: Ciprofloxacin, Photodegradation, Pharmaceutical pollutants, SnO_2 thin films, Photocatalysts, Semiconductors.

1. Introduction

Since the late 20th century, there has been growing concern regarding the occurrence and environmental impact of pharmaceuticals in aquatic environments. Owing to their persistence, these compounds pose a serious threat to ecosystems and human health [1, 2].

The probable harm caused by pharmaceuticals in a given setting is that they are designed to influence biological objects. They are lipophilic, allowing them to pass through biomembranes, and their stability prevents them from being inactivated before a therapeutic effect is achieved [3]. Thus, drugs possess all the properties necessary for their accumulation in organisms, leading to changes in water and soil ecosystems. Sewage sludge containing drug residues is used as a fertilizer in the field [4]. Drugs finally reach the soil in this manner, which may alter microorganisms and accumulate in plants.

Synthetic and semi-synthetic antibacterial compounds have been extensively used. They are disconnected from nature and are resistant to degradation. Fluoroquinolones are part of the medication categories that have a prolonged presence in the environment [5].

Ciprofloxacin is used for the treatment of osteoarticular infections, intra-abdominal infections, select cases of infectious diarrhea, respiratory tract infections, dermal infections, typhoid fever, and urinary tract infections. This study selected ciprofloxacin as a model drug because it is a broad-spectrum antibiotic, considering its wide application and persistence in the environment. Therefore, a high degree of usage and environmental persistence poses several potential risks to aquatic life and human health [6, 7].

Common allergic reactions to this medication include skin rashes, itching, and breathing difficulties. Other possible side effects include confusion; nightmares or hallucinations; dizziness or fainting; irregular heartbeats; pain or swelling of joints, muscles, or tendons; and pain or difficulty in urinating. The symptoms include persistent headaches with or without impaired eyesight; inflammation; formation of blisters; shedding or loosening of the skin, particularly within the mouth; convulsions; and abnormal sensations of pain, numbness, tingling, or paralysis [8]. However, it should be noted that this medication has the potential to result in breathing difficulties, severe breathing difficulties, and even death [9]. The use of semiconductors and UV light to break down pharmaceutical wastewater pollutants, such as ciprofloxacin, can produce less harmful byproducts. This indicates that semiconductors and UV light can be used to treat wastewater. In recent years, semiconductor photocatalysis has attracted interest because of its potential contribution to environmental problems.

Various drugs can be successfully eliminated by processes such as adsorption by activated carbon, ultrafiltration, reverse osmosis, restricted coagulation using chemical agents, or

ion exchange using synthetic adsorbent resins [10]. They cause no damage because substances only transfer organic compounds from water into a phase other than water and, in doing so, cause secondary pollution. Advanced oxidation techniques have gained popularity over the past decade owing to their ability to effectively address the issue of drug degradation in water-based systems [11]. These extremely reactive molecules, experimental studies on processes such as hydroxyl radicals, Currently, many advanced oxidation processes (AOPs) such as Fenton and photo-Fenton catalytic reactions, H_2O_2/UV processes, and semiconductor-mediated photocatalysis are being used to remove water contaminants [12].

The experimental conditions of this research, that is, scenarios, were optimized with respect to irradiation time, initial drug concentration, solution pH, H_2O_2, concentration of radiation energy, and interference of inorganic salts such as NaCl, Na_2SO_4, $NaHCO_3$, and $NaNO_3$ [13] to achieve enhanced pollutant removal efficiency and complete decolorization [14].

The objective of this study is to investigate the ability of metal oxide semiconducting nanomaterials supported onto a polymeric substrate like PVC as a photocatalyst of the degradation of pharmaceutical waste Ciprofloxacin. The elimination of ciprofloxacin from wastewater effluents is crucial owing to its indispensable and prevalent practical application.

2. Materials and Methods

2.1. Chemicals and Solutions

$SnCl_4 \cdot 5H_2O$ (Fisher Scientific, UK), 99.0 % ammonia, HCl, Na_2SO_4, NaOH, $NaHCO_3$, $NaNO_3$, and ciprofloxacin (Merck, Germany) 37, these chemicals were used directly without further purifications.

2.2. Solutions preparation

- A ciprofloxacin aqueous solution was prepared at different concentrations by diluting a stock solution of (5×10^{-3}M)
- The pH of the ciprofloxacin solution was adjusted to various values. Furthermore, the addition of H_2O_2 at different concentrations and the addition of different salts was achieved.
- Ciprofloxacin solutions with different pH values (3, 5, 9, and 11) were prepared.
- Ciprofloxacin solutions with different H_2O_2 concentrations (0M, 0.05M, 0.1M, 0.2M and 0.5M) were prepared.
- The ciprofloxacin solution with a concentration of 250 parts per million (ppm) of salts, including NaCl, $NaNO_3$, Na_2SO4, and $NaHCO_3$ was prepared.

2.2.1. Preparation of ciprofloxacin stock solution

A stock solution of $1x10^{-3}$ M was prepared by dissolving 0.038 g of ciprofloxacin powder in distilled water. Different concentrations of 1×10^{-5}M, 5×10^{-5}M, 10×10^{-5} M, and 12×10^{-5} M were generated by diluting the stock solution.

2.2.2. Ciprofloxacin solutions of different pH values

Ciprofloxacin solutions were prepared by combining specific amounts of 0.1M NaOH solution and HCl (0.1M HCl solution to obtain pH values of 3, 5, 6.5, 9, and 11. During the experiments, a pH meter was used to measure and record the acidity levels in the fluid.

2.2.3 Preparation of ciprofloxacin-salts solution

Separately, 0.019 g of each salt (NaCl, $NaNO_3$, Na_2SO_4, and $NaHCO_3$) was added to a 100 ml solution of ciprofloxacin.

2.3. Catalyst preparation

2.3.1. SnO_2 Nanoparticle preparation

Nanopowders of SnO_2, Zn, Fe_2O_3, and Co_3O_4 have been used as active photocatalysts for the purification of water contaminated with ciprofloxacin.

2.3.2. Preparation of photocatalyst thin films

A nano-SnO_2, Zn, Fe_2O_3, and Co_3O_4 photocatalysts supported in a polymer thin film were used in this work.

As illustrated in Fig. 1, the metal oxide nanoparticles used in this study were supported and immobilized on a suitable substrate polymer as follows:

Two separate 10 ml volumes of tetrahydrofuran (THF) were used to dissolve 300 mg of PVC. Proportional amounts of metal oxide powder were suspended in the dissolved polymer. The mixture was evenly distributed in a Pyrex glass petri dish and allowed to dry for 24 h at room temperature prior to processing.

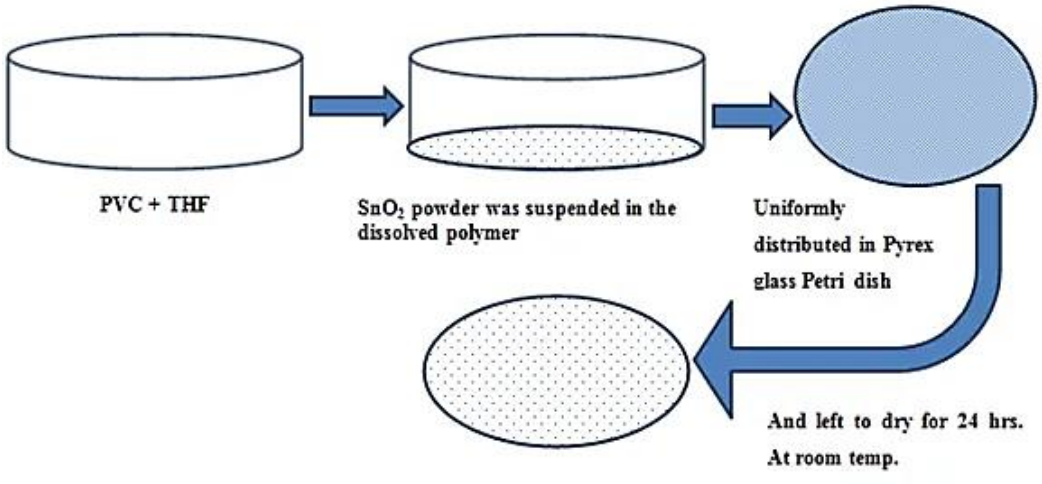

Fig. 1: The process of producing a thin coating of a metal oxide (MO) photocatalyst.

2.4.1. Characterization techniques and equipment

2.4.1.1. UV-Vis spectrophotometer

The absorbance of acridine orange was measured using a UV-VIS 3101-PC spectrophotometer (Shimadzu, UV-2450) to capture the entire degradation process.

2.4.1.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is extensively employed in material research to examine and collect information on the surface structures of materials. High-resolution scanning electron microscopy (FR-SEM) was used to visualize the surface morphologies of the coatings. Imaging was performed using a JSM6400F apparatus (JEOL). Imaging was performed by exciting the secondary electron signal using a primary beam with an energy of 10 keV.

2.4.1.3. X-ray diffraction (XRD)

The main use of an X-ray diffractometer is for phase identification and determination of the crystallite size of the powders.

2.4.2 Light source

Multiple light sources, including a UV lamp (VL-4-LC, 4 W-365 nm, 4 W-254 nm, power: 8 W, France) and direct sun radiation were employed to eliminate contaminants.

2.4.3 pH Meter

The pH of the dye solutions was adjusted to the required values using a pH meter (HM-40V).

2.5. Photocatalytic degradation experiments

The photocatalyst (0.38gm weight) was introduced into a reactor cell, and then 100 ml of the drug solution, which had known initial concentrations of 1×10^{-5} M, 5×10^{-5} M, 10×10^{-5} M and 12×10^{-5} M, was added. The solution was pressurized using UV irradiation at a specific wavelength of either 254 nm or 365 nm with an intensity of 8 W at room temperature. Alternatively, the solution was placed in an area with direct solar radiation from 11 am to 3 pm on June days, and the temperature around this part of the day was approximately 25-30 °C. The reaction solution (5 mL) was withdrawn at various time intervals for analysis. To study the degradation process, the drug samples were examined using a UV-Vis spectrophotometer. They used the% remaining (% A_t/A_o) or % degradation (% A_o-A_t/A_o) to express the extent to which the photocatalytic degradation reaction was completed. The rate at an instant, C_o-C_t/t, at various time intervals of the reaction, A_o, is the initial absorbance at time t. This was observed in the maximum absorption band of ciprofloxacin at λ= 254 nm.

3. Results and Discussion

3.1. Photocatalytic activity in ciprofloxacin degradation using different metal oxides

In this study, the activities of ZnO, Fe_2O_3, Co_3O_4, and SnO_2 as photocatalysts for ciprofloxacin degradation under UV irradiation were compared. Table 1 presents the percentage degradation of antibiotics in aqueous solutions after different irradiation periods using various photocatalysts. The data indicated that the SnO_2 photocatalyst achieved the highest degradation efficiency of 89 %, significantly outperforming Co_3O_4 (75 %) and ZnO (74 %). The superior performance of SnO_2 can be attributed to its higher surface area and better light absorption properties. Among the tested photocatalysts, Fe_2O_3 exhibited the lowest degradation.

Table 1: %Degradation of Ciprofloxacin after 185 minutes with various catalysts.

Catalyst	%Degradation after 185min
SnO_2	89
Co_3O_4	75
ZnO	74
Fe_2O_3	47

The most powerful electrostatic contact occurs between ciprofloxacin molecules and SnO_2 particles when the pH is neutral. This is because the pKa of ciprofloxacin falls between 6.09 and 8.62, whereas the pzc of SnO_2 is 4.8. Under neutral pH conditions, ciprofloxacin exhibited a positive charge, whereas the surface of SnO_2 had a negative charge. Thus, SnO_2 exhibited superior photocatalytic properties for the breakdown of ciprofloxacin. Co_3O_4 showed high efficacy in the photodegradation of ciprofloxacin. The observed outcome can be explained by the significant adsorption of dye molecules onto the Co_3O_4 surface. ZnO and Fe_2O_3 exhibited lower photocatalytic activity for ciprofloxacin degradation compared to SnO_2 and Co_3O_4 due to their limited adsorption capacity between drug molecules and catalyst particles, resulting in less catalytic activity.

3.2. Characterization of SnO_2 nanoparticles

3.2.1. X Ray Diffraction (XRD)

The crystal structures of the nano powder constituted of tin oxide (SnO_2) were analyzed using the X-ray diffraction (XRD) method. Fig. 2 shows the resultant pattern. The detected peaks were solely attributed to the formation of SnO_2 nanocrystals with a pristine cassiterite configuration. Each peak may be precisely correlated with the pure phase pattern No. 41-1445. There is no impurity phases present. The average size of the crystal particles in the nano powder, determined by measuring the broadening of the diffraction peaks using Scherrer's formula, was 28 nm. The nanoscale architecture of SnO_2 offers a substantial surface area that facilitates drug adsorption.

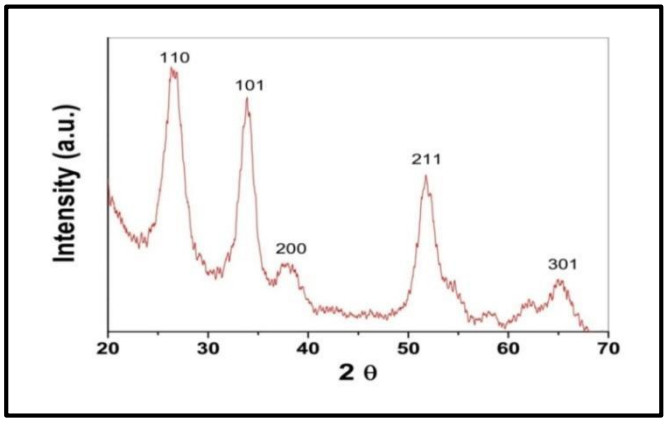

Fig. 2: XRD Pattern of SnO_2 Nano powder, reproduced with permission of Munahi and Ahel [15].

3.2.2. Scanning electron microscopy (SEM)

The SEM image reveals the morphology of the tin oxide layer, with small particles clustered together in a practically microscopic arrangement. Their individual sizes ranged from 20 to 30 nm. In Fig. 3 a mesoporous nanostructure was observed, which helps liquid go inside pores more easily, increasing surface area and making it possible for interaction at particle's surface.

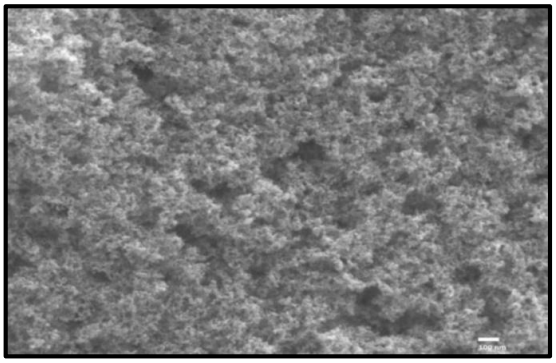

Fig.3: SEM Micrograph of SnO_2 nanoparticles.

3.2.3 Absorption spectrum

The characteristics of the SnO_2 powder photocatalyst were analyzed using a UV-visible spectrophotometer.

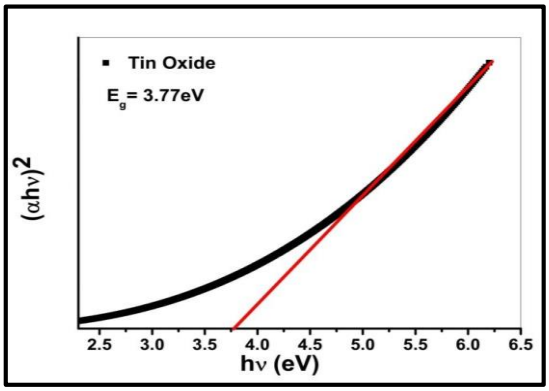

Fig. 4: UV-Vis absorption spectrum of SnO_2**,** reproduced with permission of Munahi and Ahel [15].

A baseline was established by measuring the suspended solution composed exclusively of ethanol. The UV-visible absorption spectra of the photocatalyst nanoparticles in ethanol were recorded. The absorption spectra of the SnO_2 nanoparticles are shown in Fig. 4, indicating that the peak absorption occurs at a wavelength of 315 nm.

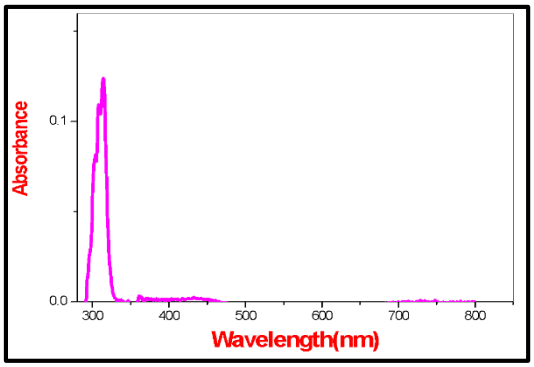

Fig. 5: (αhν)2 vs hν plot for SnO_2 photocatalyst**,** reproduced with permission of Munahi and Ahel [15] .

The energy gap (*Eg*) of SnO_2 was determined to be 3.77 eV, as shown in Fig. 5. The energy gap was derived by extending the linear segment of the plot of (αhν)2 versus the photon energy (hν), specifically for pure SnO_2 nanoparticles.

3.3 SnO_2 Nanocatalyst with UV solar light effect

Control studies were conducted because of the susceptibility of certain chemicals to degradation by direct UV solar irradiation. Fig. 6 shows the absorbance of ciprofloxacin treated using the different methods. Treatment with ciprofloxacin under UV illumination using a SnO_2 film as the photocatalyst represents the optimum treatment. No noticeable degradation was apparent in the absence of UV light or SnO_2 thin films; however, a marginal decrease was observed. Less degradation occurred when direct UV treatment was used in the absence of the SnO_2 photocatalyst. This confirms that both the SnO_2 photocatalyst and UV irradiation are crucial for the removal of ciprofloxacin from water.

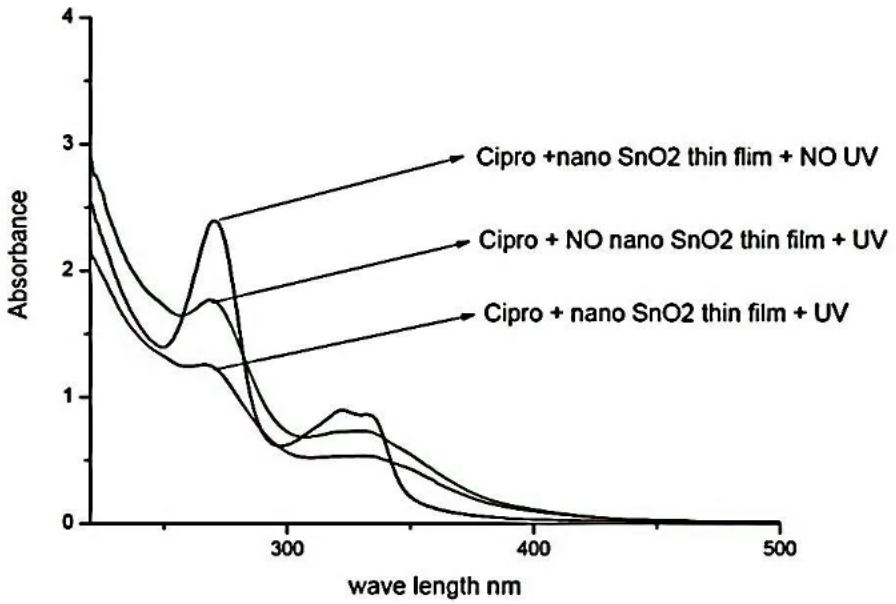

Fig.6: UV-Vis absorption spectra after 90 min showing how UV light and the SnO_2 photocatalyst eliminated color in ciprofloxacin degradation at 1×10-5 M concentration.

Fig. 7 illustrates the percentage of ciprofloxacin remaining over time under illumination. At wavelengths of 254 and 365 nm, the deterioration was more efficient at shorter wavelengths. In the absence of UV irradiation, ciprofloxacin degradation was not observed. However, treatment with a shorter wavelength (λ= 254 nm) resulted in greater degradation of ciprofloxacin than treatment with a longer wavelength (λ= 365 nm).

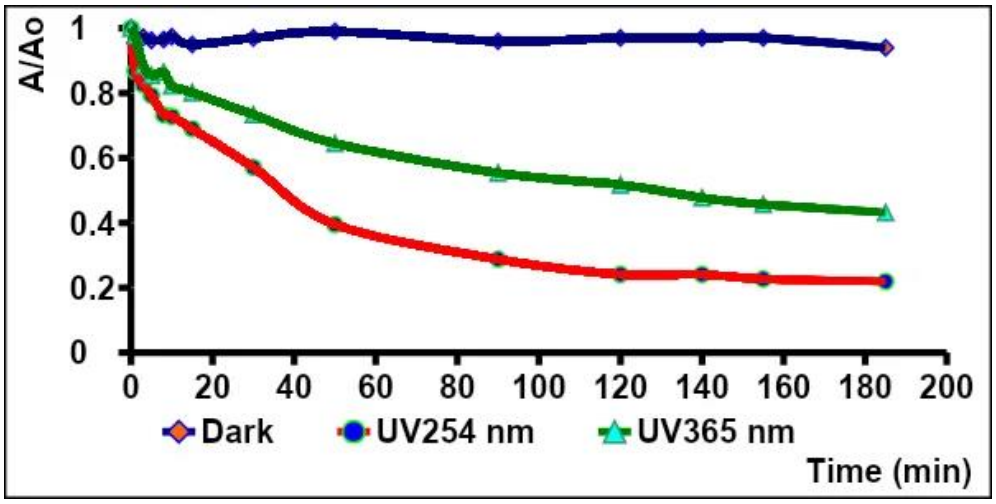

Fig. 7: Absorption spectra of ciprofloxacin at a concentration of 5×10^{-5} M measured for 185 min during the photocatalytic breakdown by SnO_2 under various wavelengths of illumination.

3.4 SnO_2 thin film photocatalyzed ciprofloxacin degradation.

CIP degradation was investigated using a thin layer of nanostructured SnO_2 photocatalyst. Multiple solutions were prepared with different concentrations: 1×10^{-5}M, 5×10-5M, and 10×10^{-5}M. Fig. 8 illustrates the calibration curve of ciprofloxacin in solutions with concentrations of 1×10^{-5} M, 5×10^{-5} M, and 10×10^{-5} M.

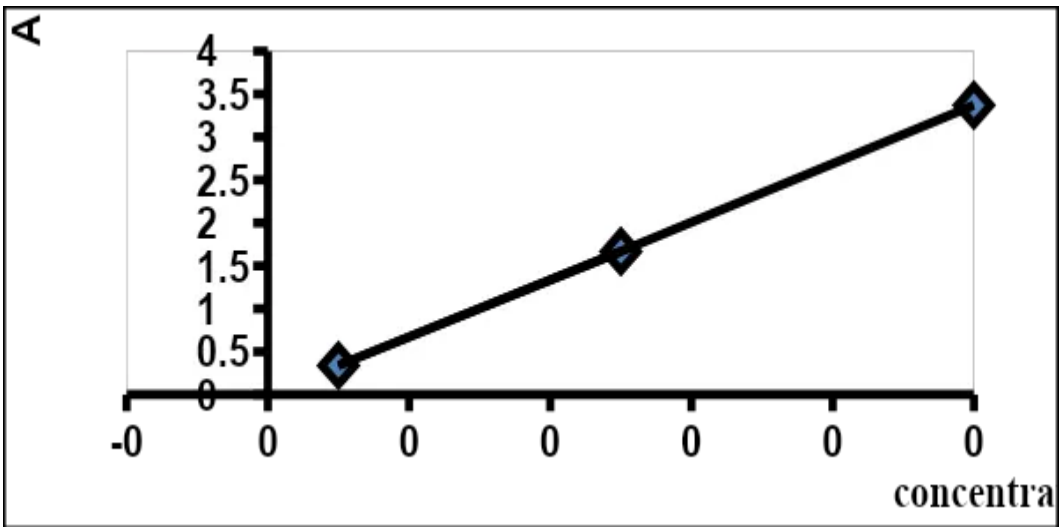

Fig. 8: Calibration curve of Ciprofloxacin.

3.4.1 Optimization and investigation of operational parameters

3.4.1.1 Irradiation time impacts

Figure 9 shows the UV-Vis spectra measured during ciprofloxacin photodegradation. This study investigated the degradation of ciprofloxacin by measuring its absorbance at different treatment durations using a UV-Vis spectrophotometer. A wavelength range of 200–400 nm was used to observe the changes in color during this process. The absorption strength in this wavelength range decreased steadily over time. This demonstrated that ciprofloxacin degraded gradually, and that oxidation-reduction reactions, which broke down the dye molecules into smaller pieces, removed the color. The breakdown of dye molecules over time is caused by the combined influence of UV light and the SnO_2 photocatalyst. The results indicated that ciprofloxacin underwent total degradation after 210 min in the reaction sequence.

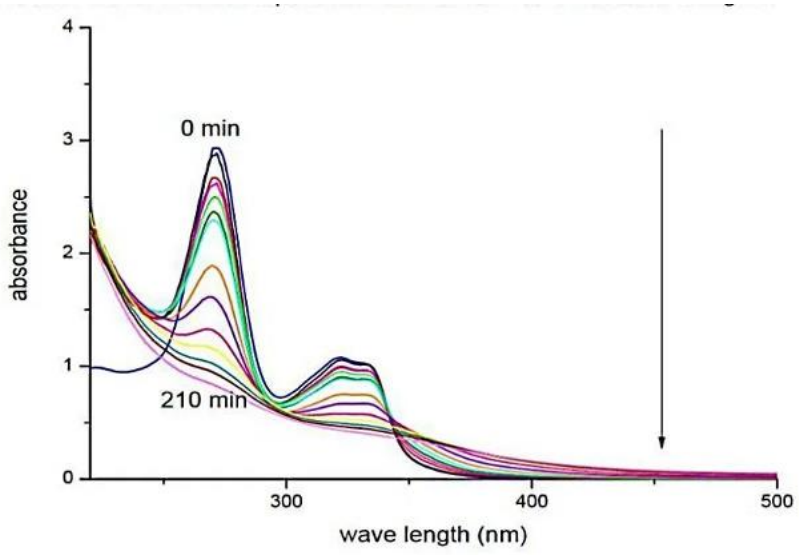

Fig. 9: UV-Vis absorption spectrum of 0.00012 M Ciprofloxacin on Nano SnO_2 thin film using UV irradiation.

3.4.1.2 Initial ciprofloxacin concentration effect

The study showed how the initial concentration of Ciprofloxacin affects its breaking down under UV radiation **λ**=254nm as a function of irradiation time. it was found that the initial drug concentration had a significant effect on the ciprofloxacin breakdown rate. The effectiveness of ciprofloxacin photodegradation decreased as the initial drug concentration increased. It is clear that the more drug there is

initially, the more drug molecules are absorbed onto the photocatalyst surface. Drugs occupy the active sites on the catalyst surface, which may cause a decrease in OH generation. When an increased amount of drug is adsorbed on the catalyst surface, it also results in lower catalytic activity within these photocatalysts. Additionally, as the concentrations and depths of drugs in solution increase, we cannot overlook the reduction in the light path length. Fig. 10 illustrates that increase in the remaining ratio occurred when the initial ciprofloxacin concentration increased over 185 min.

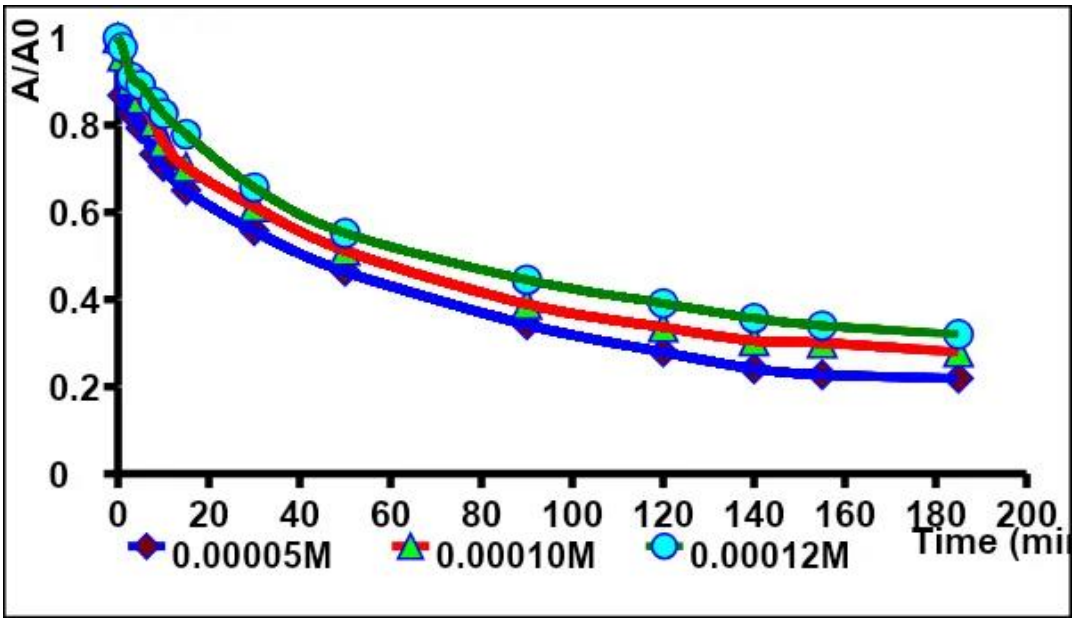

Fig. 10: Effect of initial concentration on the degradation of Ciprofloxacin using UV as a function of time.

3.3.1.3 Impact of pH:

Fig. 11 shows that the photodegradation was higher in acidic medium at a pH value of 3, with a degradation of 70 %, and it increased slightly from acidic to neutral pH in the range (5-7), The photodegradation was reduced to 60 %, whereas in basic medium pH (9-11), photodegradation decreased to 35 % after 50 min of UV irradiation. In an acidic medium (pH < 4.8), the SnO_2 surface is positively charged. An excess negative charge in the basic environment promotes the repulsion of the SnO_2 surface, thereby decreasing the catalytic activity of the semiconductor.

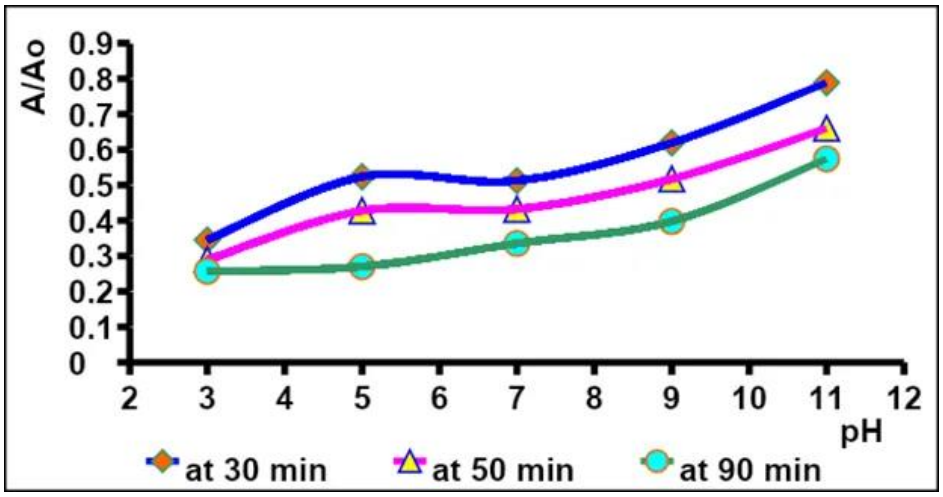

Fig. 11: Effect of Ph on photodegradation of Ciprofloxacin using SnO_2 after different times of exposure.

3.4.1.4 Concentration of H_2O_2.

H_2O_2, which is an electron acceptor, was introduced into the drug solution because of the significant involvement of $OH^{\bullet}$ radicals in photocatalytic degradation. Hydrogen peroxide has been demonstrated to improve the breakdown of specific substances by increasing the production of $OH^{\bullet}$ radicals and preventing the recombination of electron/hole pairs, thus enhancing the degradation efficiency.

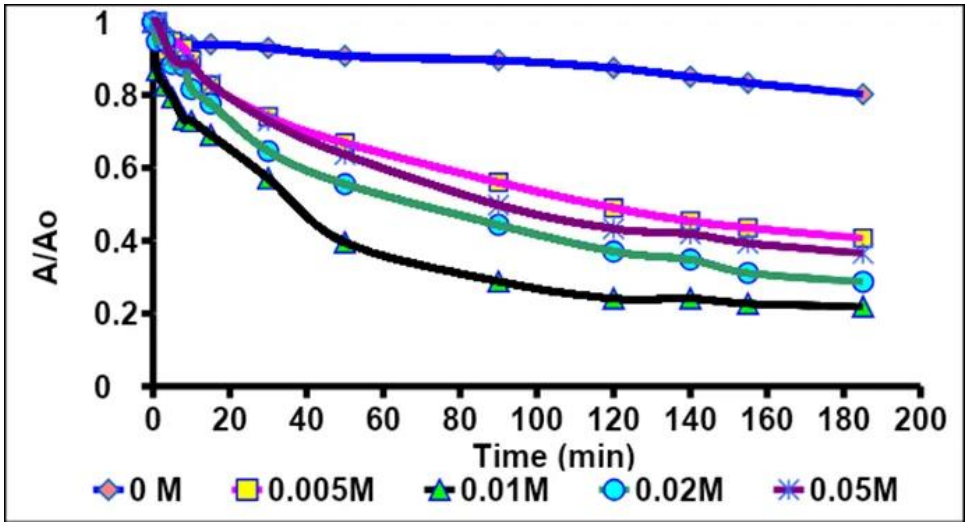

Fig. 12: Shows how the amount of H_2O_2 affects the breakdown of 0.00010 M of Ciprofloxacin by a thin film of SnO_2 under UV light.

The observations in Fig. 12 indicate that photodegradation was enhanced by adding H_2O_2 to the Ciprofloxacin drug solution. The maximum degradation was observed at 0.01 M of H_2O_2; however, with higher concentrations of H_2O_2, the degradation efficiency decreased. Electron-hole recombination poses a significant challenge for photocatalytic degradation in the presence of SnO_2. One effective strategy to inhibit electron–hole recombination is to add an electron acceptor to the reaction.

3.4.1.5 Effect of co-occurring ions

Additional categories of coexisting molecules, including sulfate, nitrate, carbonate, bicarbonate, and dissolved organic matter, can significantly impede the pace at which pollutants degrade. The current study investigated the role played by some ions, such as $NaNO_3$, $NaHCO_3$, Na_2SO_4, and NaCl, on the degradation efficiency of ciprofloxacin under conditions in which the SnO_2 thin film was irradiated by UV light. The photodegradation of ciprofloxacin at a concentration of 5×10^{-5} M was measured within a time span of 90 min. This reaction was supported by a thin layer of SnO_2 in the presence of 250 parts per million $NaNO_3$, $NaHCO_3$, Na_2SO_4, and NaCl. The obtained values are listed in Table 2. The % degradation values of the dye under test showed a small reduction in the presence of the specified salts. According to the observed data, inorganic anions hindered the photocatalytic degradation of ciprofloxacin.

Table 2: %Degradation of $5x10^{-5}$ M Ciprofloxacin with 250 ppm NaCl, $NaNO_3$, and $NaHCO_3$.

Co-occurring ion	%Degradation after 90 minutes
Pure Ciprofloxacin	67
Cl^-	63
NO_3^-	47
HCO_3^-	55
SO_4^{-2}	65

3.4.2. Ciprofloxacin degradation kinetics

Given the plot of log C_o/C_t versus time, the slope obtained through linear regression represents k_{app}. Using the Langmuir-Hinshelwood equation, a plot of the slopes, as shown in Fig. 13, we analyzed the relationship between the initial concentration of

ciprofloxacin and its degradation rate to calculate the apparent rate constant, kapp. The apparent rate constants are provided in Table 3 and displayed in Figure 13. Upon scrutinizing the results in Fig. 13 and Table 3, it is evident that the observed rate constant of photodegradation of ciprofloxacin decreased when the starting concentration of the medication was raised. With increased starting drug concentrations, a greater number of drug molecules were adsorbed onto the catalyst surface. As a result, the presence of drug molecules on the surface led to a decrease in the production of OH radicals owing to the occupancy of the active sites. Moreover, owing to its elevated drug concentration, it acts as a UV light absorber, leading to a decrease in the quantity of photons that reach the surface of the photocatalyst.

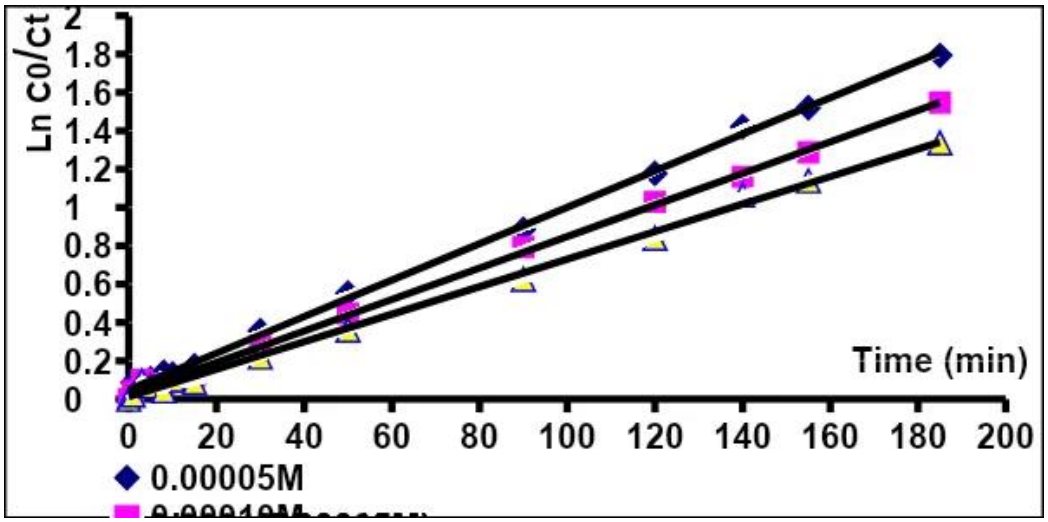

Fig. 13: Plot of photodegradation rate of Ciprofloxacin on SnO_2 *vs* irradiation time at different drug concentrations.

Table 3: k_{app} and T½ of ciprofloxacin photodegradation with SnO_2 at various drug concentrations.

Concentration(M)	k_{app}(mi n^{-1})	$T_{1/2}$(min)
5×10^{-5}	0.0095	50
10×10^{-5}	0.0082	70
12×10^{-5}	0.0072	90

3.4.3 Catalyst reusability

To obtain favorable outcomes using photocatalyst thin films, the photocatalysts themselves need to be long-term stable even after several cycles of use. While studying the use of photocatalysts, all other conditions were kept constant, that is, the irradiation period, ciprofloxacin concentration, medium pH, and H_2O_2 concentration. The recycling of SnO_2 was investigated by assessing the effectiveness of the photodegradation process over several cycles. The results indicated that the activity of the SnO_2 photocatalyst either remained relatively stable or significantly declined after four consecutive uses with the same duration of irradiation. When the retrieved catalyst was used for four further iterations, the results were obtained according to how well it degraded under continuous photo processing. As shown in Fig. 14, there were no changes in the activity of the SnO_2 photocatalyst, which slightly decreased after four consecutive uses with the same irradiation time.

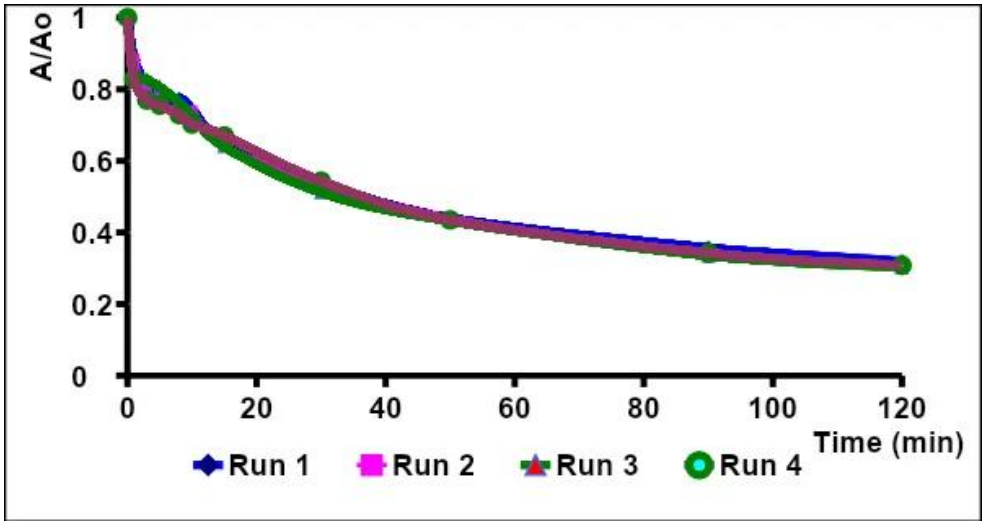

Fig. 14: Reuse of SnO_2 affects the photocatalytic degradation of 5×10^{-5} M Ciprofloxacin after 120 min.

4. Conclusion

The photocatalytic degradation of ciprofloxacin was successfully achieved. The most effective way to break down ciprofloxacin, compared to the other tested photocatalysts, was to use a SnO_2 thin film on a PVC substrate. Control experiments showed that efficient drug degradation requires both UV radiation and a semiconducting photocatalyst, along with a suitable concentration of an electron acceptor, such as H_2O_2. The reusability of the SnO_2 thin-film photocatalysts was demonstrated in four or

more consecutive batches, demonstrating their excellent capacity for reuse. For Ciprofloxacin, the most effective operating parameters for photocatalytic degradation employing a SnO_2 thin-film photocatalyst were as follows: the percentage of degradation increased as the irradiation period increased and the degradation rate increased as the starting concentration of the drug decreased. The optimal concentration of H_2O_2 was determined to be 0.01 M, while the optimal pH of the medium was found to be 3. In this instance, solar radiation yielded outcomes comparable to those of UV (λ254 nm) radiation, indicating that optimizing the operating conditions might eliminate the need for artificial radiation and instead utilize solar radiation. This approach would result in cost savings and more sustainable utilization of natural resources. The computed rate constant, k_{app}, for the degradation of 5×10^{-5} M ciprofloxacin by photocatalysis was 0.0095 min^{-1}.

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