Volume 15, Issue 1, 152503 (1-7)

Iranian Journal of Catalysis (IJC)

https://doi.org/10.57647/j.ijc.2025.1501.03

Visible-light-assisted photocatalytic removal of cefixime and cloxacillin sodium using cobalt oxide nanosheets

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Original Research

Received:
27 April 2024
Revised:
29 June 2024
Accepted:
16 November 2024
Published online:
25 November 2024

Abstract:

The rise of consumerism and the pharmaceutical industries has led to an increase in waste drugs being dumped into water resources, causing severe environmental and health consequences. The Cobalt Oxide (Co_3O_4) nanosheets were prepared using the precipitation method under mild conditions. The formed Co_3O_4 was characterized using various spectroscopic techniques, including FTIR, X-ray diffraction, SEM, and UV-Vis analysis. The Co_3O_4 photocatalytic process has shown significant potential as an affordable, sustainable, and eco-friendly method of treating pharmaceutical drugs from wastewater. The highest photocatalytic degradation was obtained at an initial concentration of 10 ppm with an irradiation time of 180 minutes for cefixime and cloxacillin sodium. This study provides new insight and potential for practical application to overcome the pollution of emerging pollutants.

Keywords: Cefixime; Cobalt oxide; Cloxacillin Sodium; Nanosheets; Photodegradation; Pharmaceuticals

1. Introduction

Photocatalysis has gained popularity in recent years due to its promise for renewable energy and environmental cleanup. As a result, there are numerous reviews on the subject, each focused on a distinct type of photocatalyst and its applications. The word photo (which refers to a photon) and catalyst (which refers to a substance that, when present, changes the rate of a reaction) combine to form the phrase photocatalyst. Materials known as photocatalysts alter the rate of a chemical reaction when exposed to sunlight or other light [1]. This process is known as photocatalysis [2]. A substrate that absorbs light and serves as a catalyst for chemical reactions is known as a photocatalyst. Semiconductors are the main component of all photocatalysts [3]. Photocatalysis takes place when a semiconducting material is exposed to light, creating an electron-hole pair as a result [4].

Photocatalysis is the reaction that occurs when a light source comes into contact with the surface of a substance (often semiconductor materials). During this action, an oxidation process using photo-generated holes and a reduction reaction using photo-generated electrons must occur simultaneously. Since the photocatalyst species shouldn't change at all during the process, the two processes mentioned above need to occur at the same time [5]. In 1972, Fujjishima and Honda were credited with the first electrochemical photocatalysis [6] of water at a semiconductor electrode [7]. Later, it was discovered that TiO_2 (titanium dioxide, also recognized as titania) helps break down cyanide in the water [8], which eventually led to a growing interest in the material's environmental applications [9].
In the field of semiconductor photocatalysis [10], doped or undoped Nano-structural materials are typically utilized to develop, characterize, and execute future photo-catalytical applications [11]. Particle sizes and shapes are heavily taken

into account in such procedures [12]. Porous metallic oxides, porous carbons, metallic nanoparticles [13], and their synthetic mixtures are limited examples of nanoparticles that are heavily explored for their possible use in gas storage, energy conversion devices, and photocatalysis. The phenomenon known as photocatalysis is one in which photon impact catalyzes an event. A conductive nanocrystal that directly captures incident light to increase its energy state and then transfers that energy to a reacting substance, causing a chemical reaction to occur, is usually thought to be an efficient photocatalyst [14]. For more than twenty-five years, research into photocatalysis techniques stopped due to a lack of interest in the topic and a lack of relevant applications.

In 1972, Akira Fujjishima and Kenichi Honda discovered electrical and chemical photolysis of water between coupled TiO_2 and platinum (Pt) electrodes, which was a groundbreaking discovery in the field of photocatalysis [6]. Ultraviolet light was absorbed by the TiO_2 electrode during this process [15]. The use of titanium dioxide (TiO_2) [16] and zinc oxide (ZnO) [17] as photocatalysts for different dyes is extensively researched. However, because of their larger bandgap (3.0–3.2 eV), these materials only work effectively in UV light and perform poorly in solar and visible light. Many efforts are currently being made to create an effective photocatalyst using visible sources. In addition, metal oxides with narrow band gaps (2.6–3.0 eV), such as CuO, V_2O_5, WO_3, Fe_2O_3, and so on, can absorb the most solar light, which causes e−/h+ pairs to recombine quickly. This lowers charge kinetics and ultimately defeats the photocatalytic activity of semiconducting metal oxides. To get over these limitations, it is therefore essential to design and employ efficient metal oxide photocatalytic materials with superior qualities [18].

To cover all the problems mentioned above, new materials must be prepared which are more effective. So, Cobalt-based oxides have drawn a lot of interest from researchers and technologists in a variety of fields Because of their potential uses. Due to their abundance on Earth, afford ability, and favorable environmental properties, cobalt oxides have attracted attention in various research fields. Cobalt oxides come in four common varieties: cobalt(II) oxide (CoO), cobalt(III) oxide (Co_2O_3), cobalt(IV) oxide (CoO_2), and cobalt(II,III) oxide (Co_3O_4). Cobalt oxides are most commonly found in Co_3O_4 and CoO due to their remarkable physical and chemical properties, as well as their excellent thermal stability. [19]

Accordingly, this study aims to develop gram-scale cobalt oxide (Co_3O_4) nanosheets using a simple precipitation method. The nanosheets have more surface area, which is very beneficial for photocatalytic activity. The optical band gap of cobalt oxide was 1.5 eV. It demonstrates that the energy required to transfer electrons from the valance band to the conduction band can be obtained from visible light. The formed Co_3O_4 was used for the photocatalytic degradation of two pharmaceuticals under an aqueous environment. Moreover, figure 1 shows the formation route for the cobalt oxide.

2. Material and method

2.1 Materials

All the reagents and chemicals were of analytical grade and used in the research without further purification. The Cobalt Nitrate hexahydrate (97%), Sodium Hydroxide (98%), Acetic acid (99%), Hydrochloric acid (937%), and Methanol (99%) were purchased from Sigma Aldrich. Distilled water was used in all experiments.

2.2 Synthesis of Cobalt oxide (Co_3O_4) nanosheets

For sample-A preparation (0.2 M NaOH and 0.1 M Cobalt nitrate Hexahydrate), 0.1 M Cobalt Nitrate Hexahydrate solution was prepared in a 200 mL beaker and transferred to a 500 mL beaker. A 0.2 M NaOH solution was prepared in a 200 mL beaker and taken in a burette. Then, 0.1 M Cobalt Nitrate Hexahydrate solution was placed under the burette. The stopper of the burette was opened, and drops

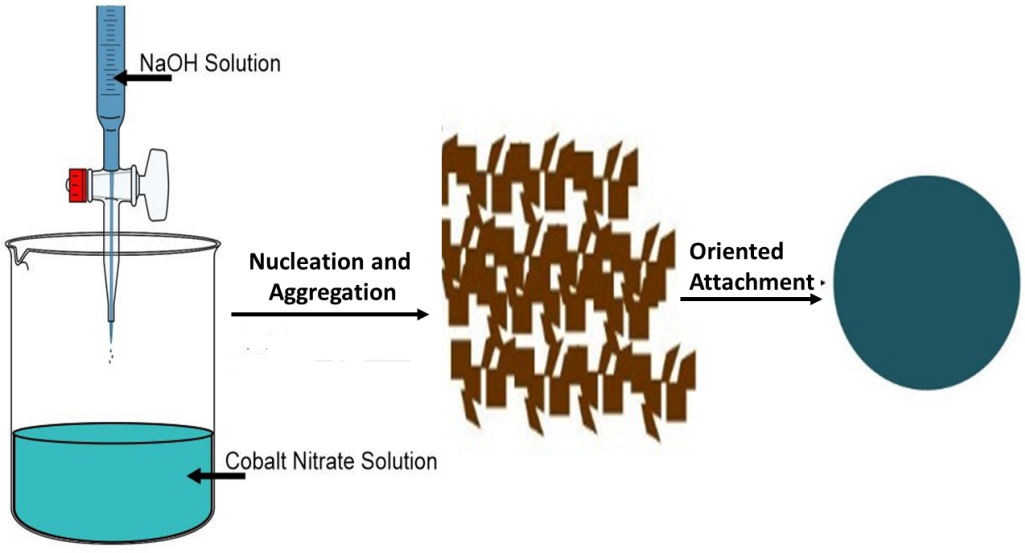

Figure 1. Formation of cobalt oxide nanosheets using precipitation for the degradation of pharmaceuticals.

of 0.2 M NaOH solution were added to the beaker. The process continued until the solution's pH reached 12. The solution was stirred for half an hour, and the precipitates were placed near a window for several hours. The precipitates were filtered out through a filtration apparatus, and the pure product (precipitates of cobalt oxide) was obtained by washing with warm water until the filtrate's pH approached 5. The obtained solid material was dried in an oven at 90 ^{O}C for one hour. Similarly, sample-B (0.2 M NaOH and 0.2 M Cobalt nitrate Hexahydrate) and sample-C (0.2 M NaOH and 0.3 M Cobalt nitrate Hexahydrate) were used following the same procedure mentioned above for sample A.

2.3 Characterization of cobalt oxide NPs

The FTIR (Fourier transform infrared) spectra were obtained using a Thermos-Scientific infrared spectrometer with ZnSe ATR in the range of 4000 cm^{-1} to 400 cm^{-1}. UV-VIS spectrophotometer (UV-8000) was utilized in the range of 200 nm to 800 nm for photocatalytic activities. X-ray diffraction analysis of the synthesized catalyst was performed using Bruker D2 phaser and the crystallinity of CoO nanoparticles. The surface morphology of synthesized cobalt oxide nanoparticles was observed using scanning electron microscopic (SEM) analysis.

2.4 Photocatalytic degradation of pharmaceutical drugs

A closed wooden container (36 cm × 20 cm) was taken as a reactor to carry photodegradation. So, photocatalytic degradation of the drugs Cefixime and Cloxacillin sodium was observed with respect to time, concentration, pH, etc. For ultraviolet light, a UV lamp (T8GL LEO SUPER, 18 W) was employed as a source. A closed wooden box of 36 cm × 20 cm was taken, and a UV lamp was placed in it to illuminate the sample of drugs for a suitable time. The experiment was performed in a beaker inside a wooden box. The visible lamp containing the solution was 5 cm above the beaker. Each experiment dispersed an aqueous solution of pharmaceutical drugs (Cloxacillin Sodium and Cefixime) with a specified concentration into the photoreactor. Subsequently, a certain amount of cobalt oxide nanoparticles were introduced into the beaker, which provided constant stirring.

Many organic compounds absorb electromagnetic radiation in the UV and VIS ranges. Beer-Lambert law is used to calculate absorbance. According to this law, the amount of light absorbance at a given temperature and wavelength varies proportionally with solution concentration and path length. Absorbance is displayed at a wavelength of 205 nm, depending on the nature of a particular substance. From the values of absorbance, concentration was calculated, and degradation efficiency was calculated using Equation 1. Where,ap C sub 0 is the Initial concentration and cap C sub t is the final concentration.

$$\text{Degradation efficiency}(\%) = \left(\frac{c_0 - c_t}{c_0}\right) \times 100 \qquad (1)$$

2.5 Mechanism of degradation

Photocatalysis is a light-driven degradation mechanism that occurs when a photon gets excited enough to cross the band gap of cobalt oxide. Electrons (e−) are stimulated from the valence band (VB) to the conduction band (CB). This ejection creates a void (vacancy of e−), known as a hole (h+), and certain electron-hole pairs are recombined at a

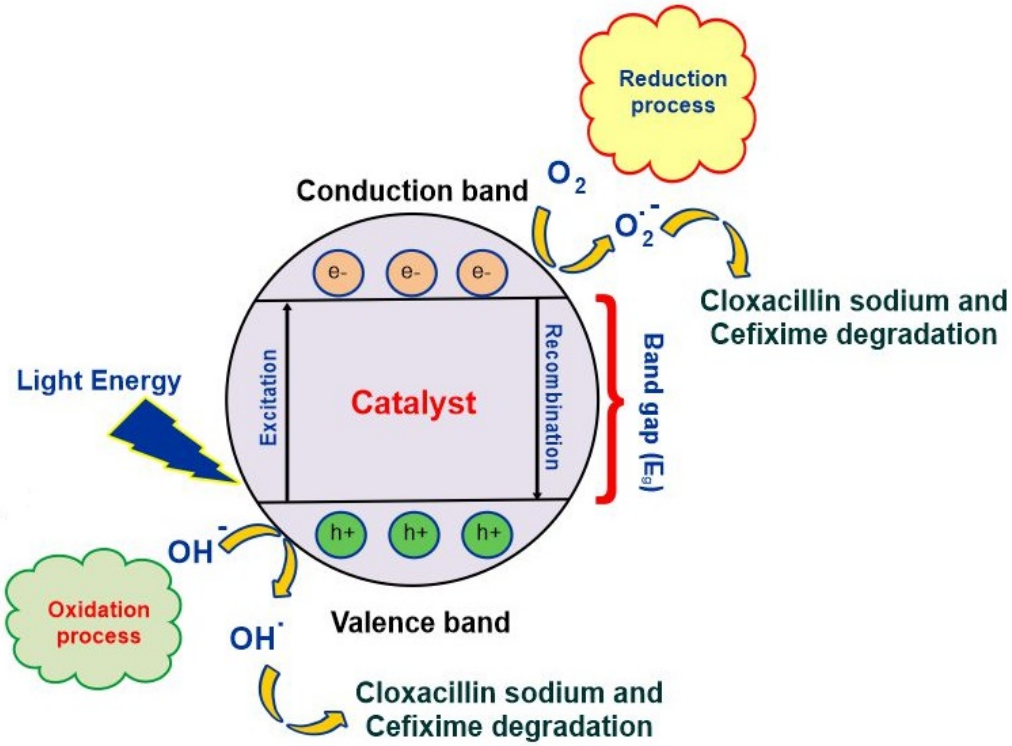

Figure 2. Mechanism of photocatalytic degradation of pharmaceuticals.

rapid rate. Figure 2 depicts the excitation and recombination mechanism in cobalt oxide photocatalysts with a pollutant degradation stage. Photocatalytic degradation of aqueous impurities typically occurs in the presence of air, resulting in the generation of superoxide ions ($O_2-\bullet$) at CB through free electron interactions with O_2 and hydroxyl radical ($HO\bullet$) at VB due to the presence of H_2O. The degradation of pollutants occurs at the reactive sites of cobalt oxide nanoparticles, resulting in CO_2, H_2O, and various intermediate products.

3. Results and discussion

3.1 Fourier transform infrared spectroscopic analysis

A Nicolet IS5 Thermo Scientific FT-IR spectrophotometer was used for the analysis. The sample was dried and then ground into powder. The obtained spectrum is represented in the figures below. The measurement range for the spectrum was set to 500-4000 cm^{-1}. Figure 3 shows the FT-IR spectrum of all three samples before calcination. The spectrum agrees with the FTIR spectrum of cobalt oxide−based precursors in the literature [20], with all characteristic bands. The peaks obtained at 3629 cm^{-1} are the characteristic peaks of the hydroxyl group of the moisture content.

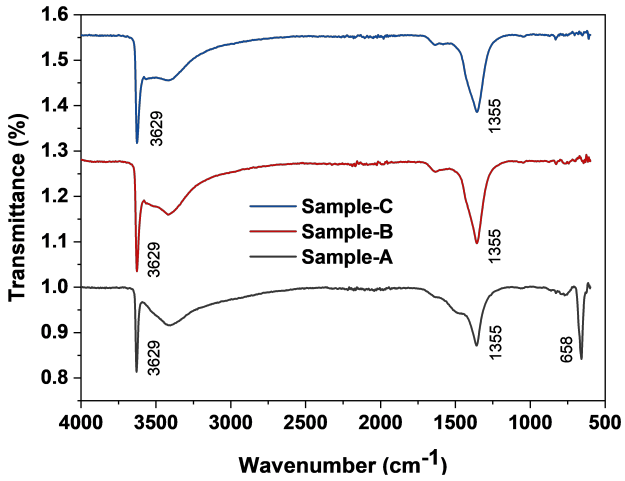

Figure 3. FTIR graph of all three samples before calcination.

Figure 4 displays the FT-IR spectrum of Cobalt oxide nanoparticles after calcination. The high−frequency band at 654 cm^{-1} indicates the cubic structure of Cobalt oxide nanoparticles. The change is that the moisture content has been removed after calcination.

3.2 X-ray diffraction Analysis

The X-ray diffraction draft of different samples of cobalt oxide is shown in figure 5. The spectrum measurement range was set at 10 to 70. The XRD pattern for three cobalt oxide samples confirmed the crystalline nature of prepared cobalt oxide nanoparticles (figure 5). The diffraction peaks appearing at $2\theta = 37.01^{O}$, 36.98^{O}, 38.86^{O}, 59.38^{O}, 65.41^{O}, and 67.13^{O} for samples A, B and C (cubic close pack structure). Based on X-ray diffraction data, the Debye-Scherrer equation was used to calculate the crystallite size of cobalt oxide nanoparticles based on Equation 2.

$$D = \frac{\kappa\lambda}{\beta \cos\theta} \tag{2}$$

where D represents the average crystallite size of nanoparticles, κ is a dimensionless shape factor with a value close to unity, λ denotes X-ray wavelength, β represents the line widening at half the maximum intensity (FWHM) after subtracting the instrumental line broadening in radians, and θ denotes Bragg angle respectively. The Scherrer equation is limited to nano-scale crystallites and does not apply to grains larger than 0.1 to 0.2 μm. The particle size of cobalt oxide nanoparticles was in the range of 10-15 nm. The crystallinity was found to be 83% based on the XRD data.

3.3 Scanning electron microscopy(SEM) analysis:

The SEM images of cobalt oxide nanoparticles at different magnifications exhibit a nanosheet-like morphology. They also indicate well-uniform particles with a narrow size of 25-35 nm (figure 6). The surface of synthesized nanoparticles is very smooth, which provides better contact with pharmaceutical drugs and hence increases their degradation power.

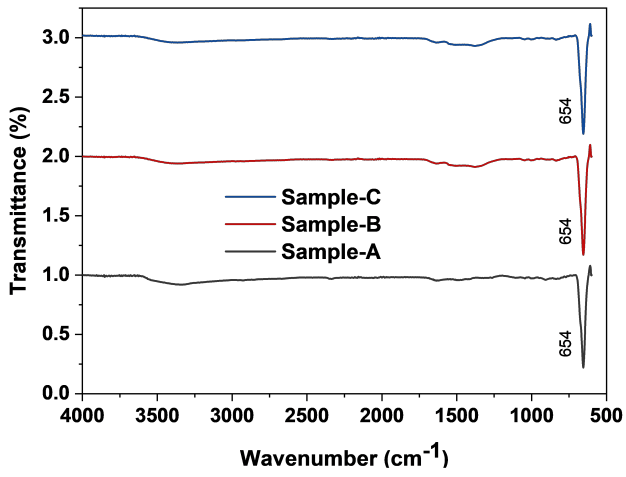

Figure 4. FTIR graph of all three samples after calcination.

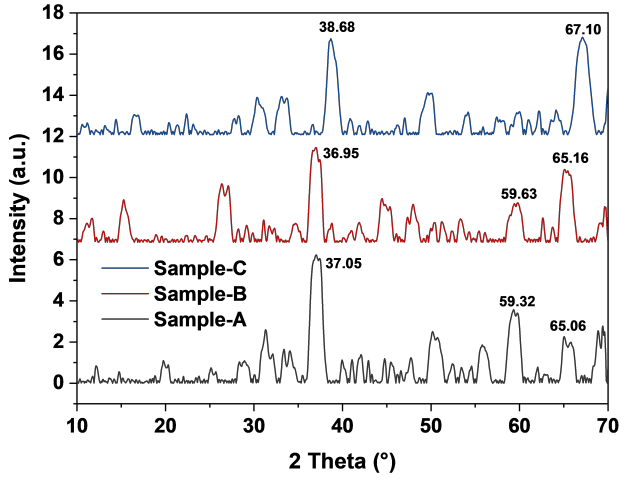

Figure 5. XRD graph of cobalt oxide for three samples after calcination.

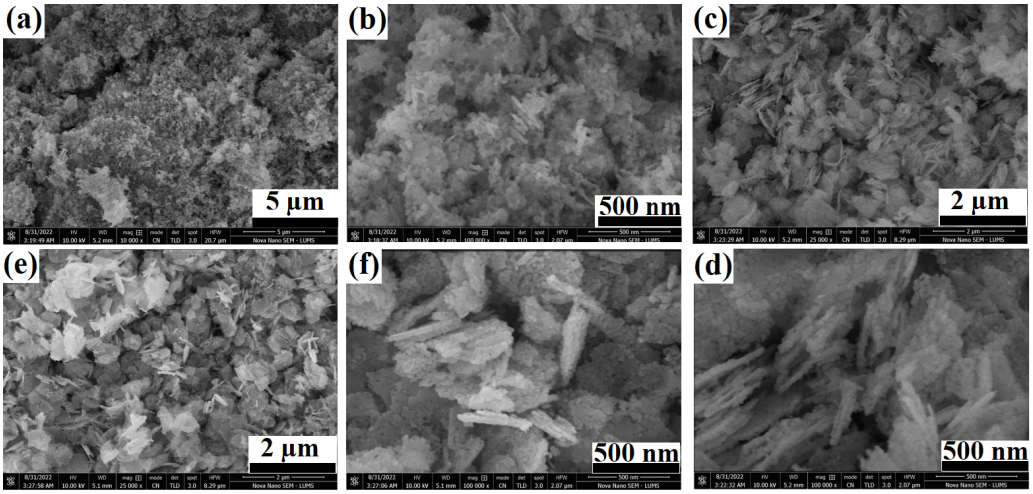

Figure 6. SEM results of all three samples after calcination, (a, b) sample-A, (c, d) sample-B, and (e, f) for sample-C.

3.4 Photocatalytic study of pharmaceuticals

1. Effect of Time

Figures 7 and 8 show the degradation efficiency of two pharmaceuticals. The results indicate that the degradation was more rapid during the first 25 to 30 minutes of exposure and that it then increased steadily for the Cefixime and Cloxacillin sodium. The reason behind the initial fast degradation of cefixime and cloxacillin sodium drugs could be the rapid oxidation of radicals. However, over time, the radicals produced were absorbed, and the degradation efficiency progressively improved as a result of the creation of intermediates.

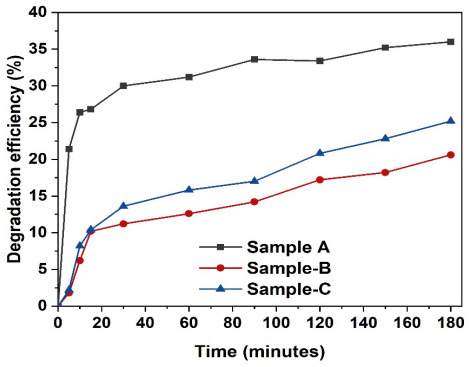

Figure 7. Degradation of Cefixime using three cobalt oxide samples.

2. Effect of catalyst dose

By adjusting the catalytic dose between 1 and 7 mg while maintaining a constant pharmaceutical concentration, the impact of the dose was assessed. When the catalytic dose was raised from 1 to 3 mg in the case of cefixime and 1 to 2 mg in the case of cloxacillin sodium, the degradation rate was higher. However, the degradation rate decreased with more catalyst dosage. An increase in the number of active sites accessible may be the cause of the degradation rate when the amount of catalyst was increased from 1 to 3 mg with cefixime and 1 to 2 mg with cloxacillin sodium. This could be because the contact with the low-level molecules may deactivate the activated complex, which in turn decreases the amount of degradation in the solution. Consequently, it was determined that the maximum degradation was achieved at 3 mg with cefixime and 2 mg with cloxacillin sodium (figures 9 and 10).

3. Effect of pharmaceutical concentration

Different concentrations of pharmaceuticals were tested separately under UV light to investigate the effect of drug

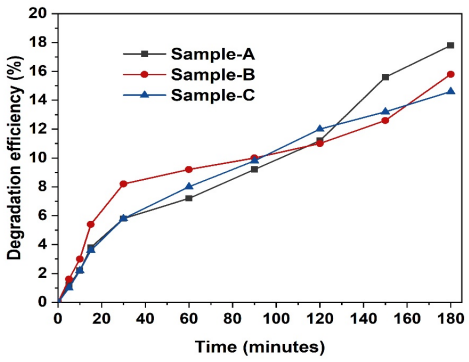

Figure 8. Degradation of cloxacillin sodium using three cobalt oxide samples.

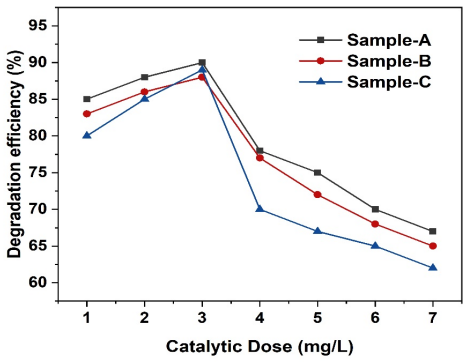

Figure 9. Percentage degradation of the cefixime drug as a function of catalytic doze.

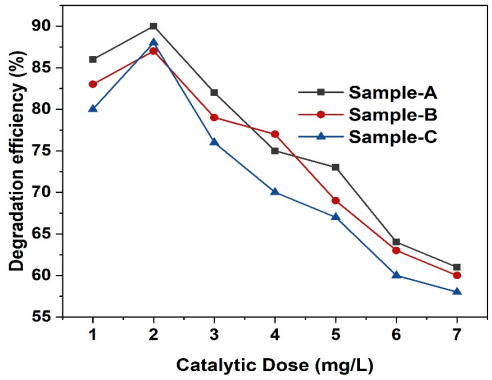

Figure 10. Percentage degradation of the cloxacillin sodium drug as a function of catalytic doze.

concentration on photodegradation. The catalytic doze was kept constant at 15 mg/L with pharmaceutical concentration in the range from 1-20 ppm. The obtained degradation efficiency is shown in figures 11 and 12.

At ten ppm pharmaceutical concentration, the maximum photodegradation percentage was achieved. The photodegradation ratio becomes small at higher concentrations. There are two explanations for this. First, by increasing the drug concentration while maintaining the catalytic doze constant, the active sites on the surface of the NPs become increasingly occupied with drug molecules and intermediates. This reduces the availability of active sites for water molecule attachment. As a result, the NPs produce fewer OH free radicals. Because free radicals are the agents that react with drug molecules and cause them to degrade, fewer of them degrade the molecules of both drugs. The second reason is the same as for catalytic doze. The greater the number of drug molecules in the solution, the greater the scattering of light photons. This prevents photons from penetrating the solution, resulting in the activation of fewer catalyst particles. As a result, the photocatalytic activity of cobalt oxide NPs decreases.

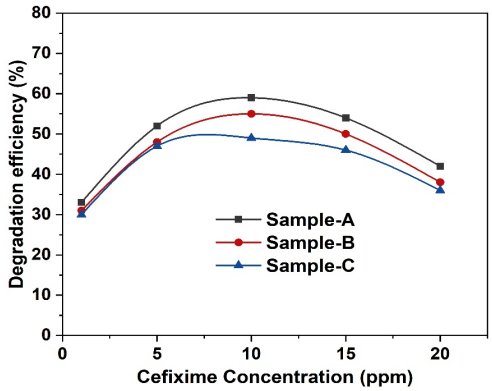

Figure 11. Percentage degradation of the Cefixime as a function of concentration.

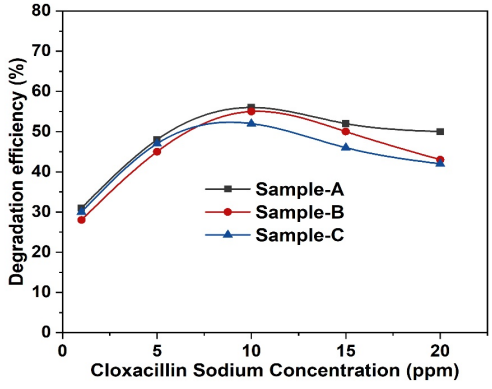

Figure 12. Percentage degradation of the cloxacillin sodium as a function of concentration.

4. Conclusion

A simple co-precipitation method was used to synthesize cobalt oxide nanoparticles for use as a photocatalyst. Cobalt oxide nanoparticles have been used as a photocatalyst against various drugs (in this case, Cloxacillin sodium and Cefixime) in various studies with promising results. These prescription drugs included oxytetracycline, anticancer therapeutics, diclofenac, and others. Various analytical techniques confirmed the synthesized material, including UV-visible, FT-IR, XRD, and SEM analysis. The cobalt oxide has a particle size of 10-15 nm. This implies that UV sources produce more effective photocatalytic activity. Drug degradation is investigated using various factors such as time, a dose of catalyst, and drug concentration. The study provides insight into the use of metal oxide for the reduction of emerging pollutants.

Authors contributions
Authors have contributed equally in preparing and writing the manuscript.

Availability of data and materials
The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Conflict of interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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