

# **P-N HETEROJUNCTION PHOTOCATALYST FOR DEGRADATION OF CIPROFLOXACIN DRUG POLLUTANT**

Submitted in partial fulfillment of the requirements for the award of  
Bachelor of Technology degree in  
Chemical Engineering

By

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**DEPARTMENT OF CHEMICAL ENGINEERING**

**SCHOOL OF BIO AND CHEMICAL ENGINEERING**

## **SATHYABAMA**

**INSTITUTE OF SCIENCE AND TECHNOLOGY  
(DEEMED TO BE UNIVERSITY)**

**Accredited with Grade "A" by NAAC**

**JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI – 600 119**

**MAY 2022**





# SATHYABAMA

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## DEPARTMENT OF CHEMICAL ENGINEERING

### BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **ARAVIND ANILKUMAR MUTTATHIL (Reg.No.38190002)** and **GANNI BILVIK SRI SAI CHANDU (Reg.No.38190003)** who have done the project as a team, who carried out the project entitled "**CoO-ZnO@rGO TERNARY NANOCOMPOSITE WITH P-N HETEROJUNCTION PHOTOCATALYST FOR DEGRADATION OF CIPROFLOXACIN DRUG POLLUTANT**" under my supervision from November 2021 to April 2022

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## DECLARATION

I **ARAVIND ANILKUMAR MUTTATHIL (Reg.No.38190002)** hereby declare that the Project Report entitled “**CoO-ZnO@rGO TERNARY NANOCOMPOSITE WITH P-N HETEROJUNCTION PHOTOCATALYST FOR DEGRADATION OF CIPROFLOXACIN DRUG POLLUTANT** ” done by me under the guidance of **Dr. D. PRABU M.S(By Research), Ph.D.**, at Sathyabama Institute of Science and Technology, Chennai is submitted in partial fulfillment of the requirements for award of Bachelor of Technology degree in Chemical Engineering.

**DATE:**

**PLACE:**

**SIGNATURE OF THE CANDIDATE**

## DECLARATION

I **GANNI BILVIK SRI SAI CHANDU (Reg.No.38190002)** hereby declare that the Project Report entitled “**CoO-ZnO@rGO TERNARY NANOCOMPOSITE WITH P-N HETEROJUNCTION PHOTOCATALYST FOR DEGRADATION OF CIPROFLOXACIN DRUG POLLUTANT** ” done by me under the guidance of **Dr. D. PRABU M.S(By Research), Ph.D.**, at Sathyabama Institute of Science and Technology, Chennai is submitted in partial fulfillment of the requirements for award of Bachelor of Technology degree in Chemical Engineering.

**DATE:**

**PLACE:**

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## ABSTRACT

A series of CoO-ZnO@rGO composite photocatalysts was established by depositing ZnO and CoO nano-crystal on the surface of rGO via hydrothermal method. It has recently been discovered that antibiotics have been present in the aquatic environment, which has sparked widespread worry. It is required to produce visible light semiconductor photocatalysts with high catalytic activity in order to use sunlight for antibiotic breakdown. The nanocomposites were made using a one-pot hydrothermal process, which was very efficient. We studied the photocatalytic degradation of the antibiotics Ciprofloxacin in nanocomposites of CoO-ZnO@rGO and found that they performed significantly better. The photocatalytic activity of CoO-ZnO@rGO is attributed to the electron transfer between the g- CoO-ZnO and CoO-ZnO@rGO which enables the production of photogenerated  $e/h^+$  pairs by facilitating the movement of electrons between the two nanosheets. When it comes to photocatalytic activity for antibiotic degradation, the CoO-ZnO@rGO nanocomposites beat raw materials and other composites in the lab. Upon five cycles of treatment, Ciprofloxacin had a degradation rate of more than 95 percent. Through the use of trapping assays, it was discovered that the principal active species during the degradation process were superoxide anion radicals and hydroxyl radicals. Ciprofloxacin mineralization values for CoO-ZnO@rGO nanocomposites were 94.6 percent, respectively, after 105 minutes of exposure. The intermediates were identified by LC-MS analysis, and a feasible mechanism for Ciprofloxacin photodegradation was proposed based on the findings. It has been discovered that the CoO-ZnO@rGO system has a mechanism and pathways for antibiotic degradation that have not before been discovered.

Keywords: Photocatalytic degradation, zinc oxide, ciprofloxacin, nanocomposite, photocatalytic studies, cobalt oxide, reduced graphene oxide

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## **ABBREVIATIONS**

|     |                         |
|-----|-------------------------|
| CIP | Ciprofloxacin           |
| ZnO | Zinc Oxide              |
| CoO | Cobalt Oxide            |
| rGO | Reduced graphene oxide  |
| NC  | Nanocomposite           |
| ROS | Reactive Oxygen Species |

## CHAPTER 1

### INTRODUCTION

Antibiotics are one of the most commonly utilized pharmaceuticals. As population increases the demand for antibiotics for sustainability of humans, animals and plants also increases. The unchecked availability, excessive use and improper metabolic activity of antibiotics will eventually lead to accumulation of antibiotics in water bodies. With the constant exposure to antibiotics in the environment over time the resistance of microbes to antibiotics increases which will be followed by the unbridled microbial growth and it will lead to hazardous conditions to human, animal and plant health and environmental instability.

To remove such pollutants various water treatment methods can be implemented such as Membrane filtration like reverse osmosis and nanofiltration, carbon adsorption, advanced oxidation processes (heterogeneous photocatalyst) which utilize electro -oxidation and ultraviolet radiation, physical adsorption, microbial degradation .

However due to factors such as energy conservation and efficiency such traditional methods are not satisfactory. One of the most promising approaches of degrading antibiotics is the use of photo catalysis. Photocatalytic technology(advanced oxidation processes) can be effectively utilized in the degradation of organic compounds of antibiotics to non toxic compounds and under the right conditions it doesn't produce secondary pollutants. It is an eco-friendly method as the photocatalyst absorbs light energy exceeding its bandwidth it produces an abundance of reactive oxygen species(ROS) for example  $H_2O_2$ , hydroxyl radicals, singlet oxygen, superoxide radicals etc. The ROS breaks down the organic compounds to simpler nontoxic compounds.

Various studies have shown  $TiO_2$  is a well known effective semiconductor for photo catalytic reaction but due to economic factors and availability it is not suitable. Moreover, Zinc Oxide is another semiconductor which shows great potential as a photocatalyst as it is non toxic, cost efficient and has excellent

photocatalytic performance. Zinc Oxide have a wide band gap which is crucial for photocatalytic activity. Because photo-induced carriers in photocatalysts quickly recombine, the efficiency of this approach is severely harmed. Increased photocatalytic efficiency and reduced recombination may be achieved by creating heterojunctions by putting semiconductors into the gap between two electrodes, element doping and metal ion loading. Many studies have been done on doping and coupling ZnO with other semiconductors like  $V_2O_5$ , CuO,  $CeO_2$ ,  $Mb_2O_5$  and CoO. Even Though a heterojunction can improve activity of photocatalyst agglomeration of heterojunction is an undeniable problem .Therefore, to inhibit the agglomeration a suitable carrier is required. It is also found out that various composite in materials having high electrical conductivity such as CNT, rGO, CNP, CNF, and so on can be used as a carrier which can be combined with metal oxides with higher redox reactions resulted from the formation of a Z-scheme heterojunction and it shows great potential in increasing the photo catalytic activity. Due to the excellent properties, inexpensiveness and abundance of material we are synthesizing CoO-ZnO nanocomposite and using reduced graphene oxide (rGO) as the carrier for photocatalyst

In addition to the sol gel approach, there are several ways for making nanocomposites, Microwave-assisted method, Inter matrix synthesis, In situ polymerization, Slurypolymerizations, Coprecipitation, hydrothermal synthesis, sonochemical, spark discharge, chemical vapor deposition, physical vapor deposition, and biological synthesis. Of these methods, the hydrothermal method seemed to be the suitable method for synthesis of CoO-ZnO nanocomposite. As it is simple, time efficient and we can control the particle size and morphology to our

Needs Fluoroquinolone anti-microbial Ciprofloxacin is utilized to treat a wide scope of bacterial diseases, including contaminations of the gastrointestinal plot, certain types of infectious diarrhoea, infections of the bones and joints, infections of the skin, typhoid fever, respiratory tract infections, and urinary tract infections. It is one of the most widely used broad spectrum antibiotics. Even though Ciprofloxacin is a very effective antibiotic it has various hazardous side effects on

human body for example risk of tendon rupture, nerve damage, hallucinations, and muscle fatigue. The uncontrolled use of Ciprofloxacin can lead to damage to the ecosystem. Recent studies have shown that ciprofloxacin and other quinolone antibiotics are able to undergo photodegradation.

We have prepared CoO-ZnO@rGO ternary nanocomposite with hydrothermal method. Furthermore characterization studies like FTIR, SEM, X-ray diffraction were investigated. Its photocatalytic activity and efficiency have been improved by the new CoO-ZnO@rGO configuration. The degradation of ciprofloxacin within the sight of noticeable light was utilized to evaluate ternary composites. In comparison with recently reported catalysts, preparation of CoO-ZnO@rGO ternary nanocomposite is simple and eco-friendly and there is no use of toxic solvents used. Moreover the degradation efficiency is high even with less dosage.

### **1.1 HYDROTHERMAL METHOD**

Nanomaterials may be created by hydrothermal synthesis, one of the most prevalent processes. A solution-response model is used. As a result of hydrothermal synthesis, it is possible to synthesis nanomaterials at temperatures ranging from ambient temperature to very high.

It is done in an autoclave, which is a steel pressure vessel loaded up with water and a supplement that helps gem advancement. An upward and downward temperature gradient keeps nutrients from dissolving while encouraging seeds to continue growing at opposing ends of a growing chamber. The aqueous methodology offers various benefits over different strategies for gem improvement, including the ability to create translucent stages that are not steady at the softening point. The aqueous interaction may likewise be utilized to make materials with a high fume strain around their dissolving temperatures. With this process, huge crystals of high quality may be grown while yet allowing for precise control over their composition. An autoclave is required and a crystal cannot be seen as it develops as a drawback of this procedure.

Contingent upon the response's essential constituent's fume pressure, either low or high strain conditions might be used to control the morphology of the materials to be made. With this strategy, a few sorts of nanomaterials have been made. Hydrothermal synthesis has major benefits over other approaches. It is possible to produce nanomaterials that are not stable at high temperatures via hydrothermal synthesis. The aqueous interaction might be utilized to make nanomaterials with high fume pressures with minimal waste. Through fluid stage or multiphase synthetic cycles, aqueous blend takes into consideration exact command over the organization of nanomaterials to be made.

## **1.2 HUMMERS METHOD**

To make graphite oxide, Hummers' technique uses potassium permanganate to add potassium permanganate to a solution of graphite, sodium nitrate and sulfuric acid. Graphite oxide may be reliably produced using this approach by engineers and lab personnel alike.

The oxidation of graphite, which introduces oxygen molecules to the graphene, is the underlying chemical process in the Hummers' technique. Potassium permanganate and sodium nitrate function as catalysts in the reaction between graphene and concentrated sulfuric acid. In this procedure, 100 grammes of graphite create 188 grammes of graphite oxide. To be consistent with graphite oxide, a carbon/oxygen ratio of 1 to 2.1–2.9 has been achieved. Ash and water have been found to be the primary pollutants. Toxicity-inducing compounds such as  $N_2O$  are formed throughout the process.

Numerous specialists and researchers who are keen on involving graphite oxide for different purposes have embraced this interaction since it is the fastest conventional approach to producing graphite oxide while keeping a sensibly high C/O ratio. When chemists and researchers have to introduce a big amount of graphite oxide in a short period of time.

After the 2004 discovery of graphene, scientists' focus turned to graphite oxide. Graphene oxide might be used as a shortcut to mass synthesis of graphene by a

number of research groups. There have been more flaws found in materials made using these techniques than in materials made from graphite alone. Because Hummers' process is so straightforward to use, it remains an important subject of interest in the field of graphite oxide production.

Other organisations have been working to enhance the Hummer's approach in order to make it more effective and ecologically beneficial. One method is to remove  $\text{NaNO}_3$  from the process entirely. It is possible to get suspensions of individual graphite oxide sheets by adding persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) to the process. Beside the advantages of killing nitrate, the expulsion of gases like nitrogen dioxide and dinitrogen tetroxide additionally enjoys benefits.

Scientists have been examining ways of utilizing graphite oxide to accelerate the response speed in the breakdown of water and natural waste in the wake of observing that it is receptive to large numbers of the frequencies of light found in daylight.

### **1.3 ANTIBIOTICS**

Antibiotics are medicine that inhibits the growth of or destroys microorganisms they fight infections caused by microorganisms in humans and animals. In the field of medicine, antibiotics are classified as antimicrobials. Antibiotics are among the most often prescribed treatments for the treatment and prevention of bacterial infections because they are the most effective antibacterial agents available. Bacteria may be killed or inhibited depending on the strength of the agent. Antiprotozoal action is seen in a small number of antibiotics. Cold and flu viruses cannot be treated with antibiotics; instead of antibiotics, medications that block viruses are referred to as antiviral drugs or antivirals. Opposing life is the meaning of the phrase antibiotic. There have been antibacterial agents around since the beginning of time. In the twentieth century, antibiotics transformed medicine. However, antibiotics have been overused and certain bacteria have developed resistance to them because of their efficiency and ease of availability. Because it is occurring today in every part of the globe and might potentially harm everyone of any age in any nation, antimicrobial resistance has been categorised as a major

danger by the WHO. Antimicrobial resistance caused 1.27 million deaths in the world in 2019. Antibiotics may be provided as a prophylactic strategy for non-complicated acute infections in order to avoid surgery. Furthermore, at-risk groups are the only ones that get this treatment. To ensure the safety and efficacy of antibiotics, they are rigorously tested for adverse effects prior to clinical usage. Aside from these side effects, various antibiotics have been linked to a broad range in severity based on the kind of antibiotic used as well as what bacteria are being treated and the specific patient. [Hypersensitivity or allergic responses may be associated with side effects, which may be caused by the antibiotic's pharmacological or toxicological qualities. Unfriendly impacts shift from fever and sickness to genuine unfavorably susceptible reactions, including photodermatitis and hypersensitivity .

Normal unfriendly impacts of oral anti-toxins incorporate looseness of the bowels emerging from unsettling influence of the species arrangement of the gastrointestinal vegetation, driving, for instance, in excess of hurtful microorganisms, for example, *Clostridium difficile*. Antibiotic-associated diarrhoea may be prevented by taking probiotics throughout the duration of antibiotic therapy. Antibacterials may also influence the flora of the vulvo-vaginal region, leading to an overgrowth of candida species of yeast. The mix of a quinolone anti-microbial with a fundamental corticosteroid might bring about extra unfavorable impacts, like the gamble of ligament injury.

A few anti-microbials may likewise hurt the mitochondrion, a microorganisms inferred organelle present in eukaryotic, including human, cells. Fluoroquinolones have been linked to mitochondrial damage, which may lead to oxidative stress in cells. In addition, chloroplasts are known to be affected by them.

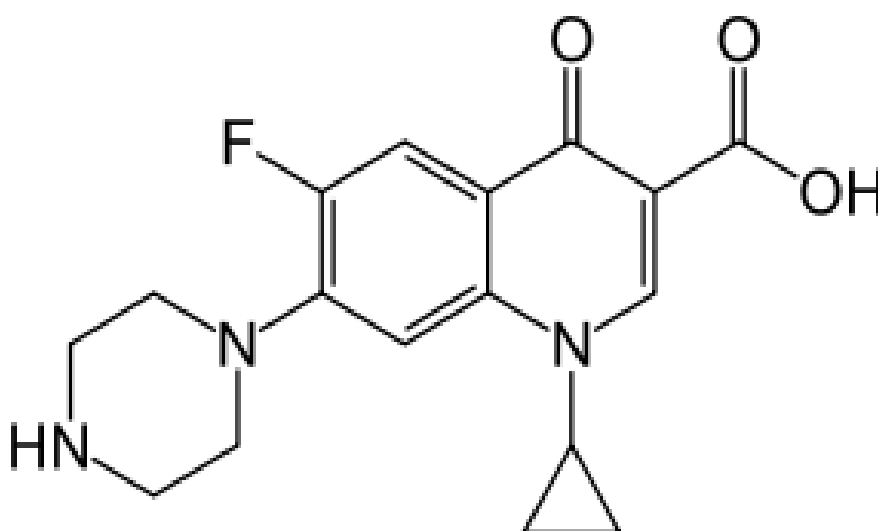
### **1.3.1 CIPROFLOXACIN**

Anti-infection Ciprofloxacin is a fluoroquinolone used to treat a wide scope of bacterial contaminations, including intra stomach diseases and specific sorts of irresistible looseness of the bowels. Ciprofloxacin is quite possibly the most

generally utilized expansive range anti-toxin, and is utilized to treat a wide scope of bacterial diseases.

Major medical organisations have developed treatment recommendations for severe infections, particularly those caused by Gram-negative bacteria such as *P.A. aeruginosa*. Ciprofloxacin plays a significant part here. First-line antibiotics for community-acquired abdominal infections in adults, such as ciprofloxacin and metronidazole, have been endorsed by the Infectious Diseases Society of America (IDSA). There are several treatment recommendations for acute and chronic urinary tract infections, as well as for some forms of endocarditis, certain skin infections, and prosthetic joint infections that include the use of azithromycin.

Even though Ciprofloxacin is a very effective antibiotic it has various hazardous side effects on the human body for example risk of tendon rupture, nerve damage , hallucinations, and muscle fatigue. The uncontrolled use of Ciprofloxacin can lead to damage to the ecosystem Recent studies have shown that ciprofloxacin and other quinolone antibiotics are able to undergo photodegradation.



***Fig 1.1 Ciprofloxacin structure***

Patented in 1980, Ciprofloxacin was introduced to the market in 1987. It is on the list of essential medications maintained by the World Health Organization. Ciprofloxacin has been deemed crucial to human health by the World Health Organization. There are generic versions of this medication. With over 5 million prescriptions written in 2019, it ranked as the 113th most frequently prescribed medication in the United States. Cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(piperazinyl)-3 quinolinecarboxylic acid is the chemical name for the antibiotic Ciprofloxacin. Chemically, it has the formula  $C_{17}H_{18}FN_3O_3$  and a molecular weight of 331.4 g/mole. It's a crystalline substance that ranges in colour from a pale yellow to a light yellow.

Monohydrochloride monohydrate ciprofloxacin hydrochloride is the ciprofloxacin hydrochloride monohydrate salt. Light yellow crystals with a 385.8-g-mole molecular weight are found in it. The empirical formula for this substance is  $C_{17}H_{18}FN_3O_3HCl \cdot H_2O$ .

In order to kill bacteria, the antibiotic ciprofloxacin works by preventing the enzyme DNA-gyrase from doing its job. DNA replication and repair are both carried out by this enzyme. Microorganisms can't fix or duplicate in the event that this catalyst isn't working. Viral contaminations are not treated by Ciprofloxacin; just bacterial diseases are. To prevent the spread of fluoroquinolone resistance, several treatment recommendations propose using older, narrower-spectrum medicines as first-line therapy for less severe illnesses. Even though ciprofloxacin has been licenced by regulatory agencies for the treatment of respiratory infections, most treatment recommendations do not advocate ciprofloxacin for respiratory infections owing in part to its ineffectiveness against streptococcus pneumoniae. Tendons, muscles, joints, nerves, and the central nervous system may all be affected. Because of this, the rate of side effects seems to be increasing. Although most adverse reactions were minor or moderate in intensity, they quickly subsided after the medicine was stopped and did not need any further treatment. As a result of an increased risk of tendinitis and tendon rupture in those over 60, those who take corticosteroids, and those who have kidney, lung or heart transplants,

ciprofloxacin comes with a boxed warning in the United States. In the course of treatment or even months after the medicine has been stopped, tendon rupture might occur. Tendon difficulties were shown to be 1.9 times more common in patients on ciprofloxacin, according to one research. There was a 3.2 percent greater risk for individuals over 60 and a 6.2 percent increased risk for those over 60 and using corticosteroids. Achilles tendon ruptures were found in 38 out of 46,766 people who used quinolones over the course of the research. Ciprofloxacin has adverse effects on blood levels and distribution when used with certain meals and other medications. Overdose of ciprofloxacin may result in reversible renal toxicity.

#### **1.4 PHOTOCATALYSIS**

When a catalyst is present, a photoreaction is speeded up by the process of photocatalysis. Catalyzed photolysis involves the absorption of light by an adsorption substrate with the use of a catalyst. Free radicals (such as hydroxyl radicals:  $\bullet\text{OH}$ ) may conduct secondary reactions when photogenerated catalysis (PCA) is used. PCA is dependent on the catalyst's capacity to form electron-hole pairs. Photocatalysis reactions and photocatalysts are in the same phase in homogenous photocatalysis. When the catalyst and the reactants are in different phases, heterogeneous catalysis is used.

Transition metal oxides and semiconductors are the most frequent heterogeneous photocatalysts. semiconductors, unlike metals, lack energy levels that allow electrons and holes to recombine after photoactivation, while metals have a continuum of electronic states. This area of energy, which stretches from the valence band's uppermost point toward its lowermost point, is referred to as the "band gap." When a lively photon with a band hole bigger than or equivalent to that of the material is taken in by the semiconductor, an energized electron in the valence band moves into the conduction band, where it makes a positive opening. An exciton is a photogenerated electron-opening pair. Recombining the invigorated electron and opening might deliver the energy got through excitation of electron as hotness. An ineffective photocatalyst may be created by excessive

recombination of excitons. There are many approaches that can be used to improve electron-hole separation and extend the lifetime of excitons, in any case, large numbers of them depend on underlying highlights, for example, stage hetero-intersections (for example anatases and rutines), honorable metal nanoparticle, silicon nanowire, and substitutional cation doping to find success. Enabling electron excitation processes to make reduced products with oxidants, as well as holes produced by these reactions reacting with reductants in order to form oxidised products, is the ultimate objective of photocatalyst design. These reactions take happen at the semiconductor surface because of the creation of positive holes and excited electrons.

#### **1.4.1 ZINC OXIDE**

It's easy to see zinc oxide since it's white in colour. This substance does not disperse in water, as previously stated. Zinc Oxide is a semiconductor which shows great potential as a photocatalyst as it is non toxic, cost efficient and has excellent photocatalytic performance. Zinc Oxide have a wide band gap which is crucial for photocatalytic activity. Because photo-induced carriers in photocatalysts quickly recombine, the effectiveness of this approach is considerably reduced. Building heterojunction via semiconductor loading, element doping, and metal ion loading increases photocatalytic performance and reduces recombination of photo-induced carriers efficiently.

#### **1.4.2 COBALT OXIDE**

Atoms of cobalt and oxygen make up the cobalt oxide family of chemicals. Cobalt(II) oxide (cobaltous oxide),  $\text{CoO}$ , is a member of the cobalt oxide family. These nanoparticles of cobalt oxide  $\text{Co}_3\text{O}_4$  are commonly referred to as cobalt oxide nanoparticles, however they may also be cobalt(II,III). An autoclave aqueous blend is many times used to create cobalt oxide.

Starches and metal salts broke up in water at somewhere in the range of 100 and 200 °C are the beginning stage for the aqueous creation of metal oxide empty circles. Carbon circles with metal particles inserted in their hydrophobic shells are

framed because of this cycle. By calcination, the carbon centers are eliminated, leaving empty metal oxide circles. The sugar to metal salt fixation, as well as the response medium's temperature, tension, and pH, and the starting salts' cations, all impact the shell's surface region and thickness. The technique might take anything from a few hours to many days to complete. This technique has a lower yield than other approaches, which is a disadvantage.

Thermal breakdown of organometallic compounds may also be used to synthesise cobalt oxide nanoparticles. The metal salen complex bis(salicylaldehyde) ethylenediaminecobalt(II) ("Co-salen") may be heated to 500 °C in air. Alternatively To make the precursor Co-salen, heat a tetrahydrate of cobalt(II) acetate in propanol to 50 degrees Celsius in nitrogen, add the salen ligand (bis(salicylaldehyde) ethylenediimine), and the reaction is completed. To make the cobalt oxide/graphene composite, heat a tetrahydrate of cobalt(II) acetate in propanol to 45 degrees

In the same way that most cobalt compounds are harmful to people and aquatic life, cobalt oxide nanoparticles also pose a threat. Hyperthermic treatment, gene therapy, and medication administration might all benefit from the ability of cobalt oxide nanoparticles to infiltrate cells. There is, however, the challenge of dealing with their toxicity. Nanoparticles of cobalt oxide have a white powdery appearance and a spinel crystal structure. They are P-type semiconductors and an essential magnetic material. Cobalt metal is formed when nano-cobalt oxide is heated to 900°C (1652°F) in a hydrogen flame. These nanoparticle-producing methods were simple, mild, and inexpensive, making them ideal for large-scale production. Since numerous other metal particles, like Zn(II), Cd(II), Ni(II), Cu(II), and Mn, can undoubtedly shape strong metal salophen intensifies that are leaned to decay into metal oxides after warming, it is all around expected that such methods would be stretched out to get ready numerous other significant semiconducting metal oxide ultrafine powders. Nanoparticles of Co<sub>3</sub>O<sub>4</sub> were also studied for their optical characteristics. They show that the nanoparticles have direct transitions at 1.53 and 2.02 eV, indicating that they are semiconducting. Test results show that the

nanoparticles' absorption peak changes towards shorter wavelength. The quantum effect may also be to blame for the phenomena of the blue shifts.

### **1.4.3 REDUCED GRAPHENE OXIDE**

Reduction of oxygen concentration in graphene oxide (GO) yields reduced graphene oxide (RGO), whereas oxidation of graphite yields graphite oxide, a material with increased interlayer spacing and functionalized basal planes of graphite. According to this definition, graphene oxide has oxygen-containing functional groups, but the reduction of graphene oxide does not contain oxygen-containing functional groups. Carbon, hydrogen, and oxygen atoms make up graphite oxide, a substance often found in pencils and other writing instruments. Reduction of Graphene Oxide in Synthesis (RGO) While swirling at 95°C for four days, 400 mg of XGO was dispersed into an 800 mL of distilled water. There are a slew of low-cost and straightforward approaches of reducing rGO to its final form. RGO does have properties similar to graphene (such as good conductivity), but it tends to have more defects and be of lower quality than graphene made from graphite directly.

## **1.5 ANALYSIS AND CHARACTERIZATION**

### **1.5.1 SEM (Scanning Electron Microscopy)**

Electron microscopes that employ a focussed stream of electrons to create pictures are known as scanning electron microscopes (SEM). The sample's surface topography and composition are revealed via the signals generated by the electrons' interactions with the sample's atoms.

To create a picture, the electron beam moves in a raster pattern and the intensity of the detected signal is merged with its location. An optional electron identifier is utilized to see auxiliary electrons created by particles animated by an electron bar in the most well-known SEM mode (Everhart-Thornley locator).

For instance, example geography influences the quantity of optional electrons that might be identified and henceforth the strength of the sign. One nanometer goal is conceivable utilizing SEM.

Examples might be inspected at an assortment of cryogenic or higher temperatures with expert gear, in low vacuum or wet conditions with variable tension or ecological SEM, or in high vacuum with standard SEM.

### ***1.5.2 FTIR (Fourier Transform Infrared Spectroscopy)***

The infrared spectrum of a solid, liquid, or gas may be obtained using the Fourier Transform Infrared Spectroscopy method. High-spectral-resolution data is collected concurrently by an FTIR spectrometer across a large spectral range. When contrasted with a dispersive spectrometer, which estimates power over a tight scope of frequencies all at once, this has a huge advantage.

FTIR is a method used to decide how much light consumed by a material at different frequencies. By utilizing "dispersive spectroscopy," which includes focusing a monochromatic light pillar on an example, estimating the amount of the light retains and rehashing the cycle for each particular frequency. This method is most easy.

### ***1.5.3 UV-VIS SPECTROSCOPY***

From around 200 nm to 800 nm, UV-VIS measurements cover the whole visible spectrum. Transitions between the molecule's electrical energy levels occur when ultraviolet or visible light is absorbed by the molecule. Characterization may be done on the optical and electrical characteristics of a variety of different materials, including films, powders, monolithic solids, and liquids.

For a wide range of organic and inorganic chemicals, UV-vis spectroscopy is an excellent analytical tool since it is non-destructive, inexpensive, and easy to learn to use. UV-vis spectrophotometers distinguish light ingestion or transmission through a material as a component of frequency.

UV-vis identifiers are utilized in elite execution fluid chromatography and super superior execution fluid chromatography to sort and evaluate the convergence of mixtures in fluid streams. Using mass spectrometry and these approaches, all animals may be identified.

#### UV VIS Spectroscopy Theory :

UV-Vis spectra are produced when incoming light interacts with the electron cloud in a chromophore, causing one or more outer shell or bonding electrons to move from a ground state to a higher energy state.

Most compounds have broad spectral ranges in the ultraviolet and visible ranges of the spectrum. Also, it's possible that it won't be very good at recognising compounds. However, they may be used for quantitative tests and as an alternative method of detection for a number of chemicals. The energy released at each specific wavelength in the radiation emitted by ordinary heated substances is predicted from the principle of chance, which dictates that the radiation has several wavelengths.

When it comes to lighting fixtures, the use of tungsten-halogen lamps has become the norm. The quartz envelope allows radiation to travel well into the ultraviolet range. UV-Visible spectrometers often include a variety of lamps to cover the whole range of wavelengths, the most common of which is the deuterium lamp.

#### **1.5.4 X-RAY DIFFRACTION**

Materials and thin films may be analysed using X-ray scattering methods which provide information about their crystal structure, content and physical characteristics without damaging them. Based on the scattering intensity of an X-ray beam striking the sample as a function of the incident and scattered angle, as well as polarisation and wavelength or energy, these approaches are used.

X-rays are waves of electromagnetic energy, whereas crystals are atoms arranged in a regular pattern. X-rays impacting on crystal atoms are scattered principally by interactions with electrons in the atoms. It's called elastic scattering,

and the electron is referred to as a scatterer. Spherical waves are generated by a systematic arrangement of scatterers. However, Bragg's rule states that although destructive interference cancels out most of these waves, constructive addition occurs in a small number of particular directions:

$$2d\sin\theta = n\lambda$$

There are two diffracting planes separated by a distance of  $d$ ; the  $\theta$   $\{\displaystyle \theta\}$  is the incident angle of the beam's rays is  $n$ ; and the wavelength is  $\lambda$ . Reflections are the diffraction pattern's visual representation of the individual directions. Electromagnetic waves striking a regular array of scatterers produce X-ray diffraction patterns.

When creating diffraction patterns, X-rays are employed since they have the same wavelength  $\lambda$  as the distance between crystal planes,  $d$ . (1-100 angstroms).



## CHAPTER 2

### LITERATURE SURVEY

Sunlight-Driven Photocatalytic Degradation of Ciprofloxacin by Carbon Dots Embedded in ZnO Nanostructures was studied by Indrani Mukherjee, Vatsala Cilamkoti, and Raj Kumar Dutta (2021). The goal of this research was to improve ZnO's photocatalytic degradation by increasing the amount of reactive oxygen species (ROS) on its surface. It took 110 minutes for CIP to be degraded by photocatalysis in the presence of long-wavelength UV and visible light in the presence of ZnO/CD NCs in the presence of optimal circumstances. In comparison to the original ZnO NPs, the photocatalytic degradation rate was three times greater at 0.30 min<sup>-1</sup>. ZnO/CD NCs have a higher deterioration rate because of the increased charge carrier mobility and ROS production. Scavenging investigations on hydroxyl radicals and superoxide radicals have corroborated this. The CDs placed on the ZnO NPs surface prevent charge carrier recombination, resulting in a greater ROS formation. Repeatability tests have shown that ZnO/CD NCs may be used as a photocatalyst. XRD, TEM, and Fourier transform infrared investigations indicated that the ZnO/CD NCs' structure and surface morphology were stable after five cycles of operation. According to the findings, ZnO/CD NCs may be used to enhance the photocatalytic destruction of CIP, a growing pollutant.

Tao Zhang, Jianming Pana, Tao Zhang, and Dongya Yang are the members of the XinshanRong group (2016). Studying the production of ZnO-Ag<sub>2</sub>O/porous g-C<sub>3</sub>N<sub>4</sub> composite photocatalyst for the degradation of ciprofloxacin with increased visible light photocatalytic activity. Calcination and hydrothermal methods were used to manufacture ternary photocatalyst, which is a ZnO-Ag<sub>2</sub>O/pg-C<sub>3</sub>N<sub>4</sub> composite photocatalyst. The composite photocatalyst's structure, surface morphology, and chemical composition are studied. DRS and PL tests on optical properties indicated that the generated ZnO-Ag<sub>2</sub>O/pg-C<sub>3</sub>N<sub>4</sub> degraded the fastest (97.4 percent) in comparison to ZnO, porous g-C<sub>3</sub>N<sub>4</sub>, Ag<sub>2</sub>O, and ZnO-Ag<sub>2</sub>O. During photocatalytic degradation, HPLC/MS was used to identify CIP

degradation intermediates. As an added benefit, porous g-C<sub>3</sub>N<sub>4</sub> employed as a support in the combined system increases degrading efficiency while also speeding up response rates when activated by visible light.

Lukasz Wolski, Kalina Grzelak, Malwina Munko, Marcin Frankowski, Tomasz Grzy, and Grzegorz Nowaczyk (2021) carried out research on the photocatalytic degradation of ciprofloxacin over CeO<sub>2</sub>/ZnO nanocomposites: Analyzing chemical routes and figuring out how metal oxides work in concert CeO<sub>2</sub>/ZnO nanocomposites were used to investigate the photocatalytic degradation of ciprofloxacin (CIP). The co-precipitation approach was utilised to manufacture and analyse the catalysts employed in this study. UV–vis and LC-MS methods were used to monitor CIP degradation, while TOC studies were used to measure mineralization efficiency. CeO<sub>2</sub>/ZnO nanocomposites were found to be up to 10 times more active than pure CeO<sub>2</sub> and up to two times more active than ZnO that had not been doped. Photoexcited electrons from the ZnO conduction band move to the CeO<sub>2</sub> valence band, improving the activity of the nanocomposites. A Z-scheme heterojunction was formed. CIP molecules adsorbing on ZnO are immediately oxidised by photogenerated holes (h<sup>+</sup>) in a surface process known as photocatalytic degradation over the nanocomposites. The antibiotic was damaged in two ways: first, by oxidising the piperazine moiety of CIP molecules preferentially with h<sup>+</sup> (route I), and second, by degrading the antibiotic's fluoroquinolone and piperazine moieties simultaneously (pathway II). H<sup>+</sup> and hydroxyl radicals (HO•) were necessary for the latter process.

Attapulgite/Cu<sub>2</sub>O/Cu/g-C<sub>3</sub>N<sub>4</sub> with improved photocatalytic activity for antibiotic degradation was developed by ShixiangZuo, Yao Chen, Wenjie Liu, Chao Yaa, Zhongyu Li, Chaoying Ni XiaohengLiuc (2016). ATP/Cu<sub>2</sub>O/Cu/g-C<sub>3</sub>N<sub>4</sub> photocatalyst was created using a one-pot redox method under anoxic calcination to produce a high-performance photocatalyst with excellent photovoltaic properties. By using FT-IR, BET, TEM, photoluminescence emission (PL), and electrochemical impedance spectra, the composites were evaluated (EIS). Melamine pyrocondensation results in the reduction of ultra-fine CuO nanoparticles on the surface of rod-like attapulgite, which generates both Cu and

a little amount of  $\text{Cu}_2\text{O}$ . In the meanwhile, a Z-scheme  $\text{Cu}_2\text{O}/\text{Cu}/\text{g-C}_3\text{N}_4$  heterostructure is assembled by evenly encapsulating the synthesised  $\text{g-C}_3\text{N}_4$  membrane on the surface of attapulgite/ $\text{Cu}_2\text{O}/\text{Cu}$ . When compared to  $\text{ATP}/\text{g-C}_3\text{N}_4$ ,  $\text{ATP}/\text{Cu}_2\text{O}/\text{Cu}/\text{g-C}_3\text{N}_4$  exhibits better sensitivity to visible light and suppression of hole electrons. Antibiotic degradation photocatalyst was examined using UV–Vis spectrophotometer and liquid chromatograph for photocatalytic performance and mechanism. Reusability and photocatalytic activity of  $\text{ATP}/\text{Cu}_2\text{O}/\text{Cu}/\text{g-C}_3\text{N}_4$  for chloramphenicol are good. Cu species play an important role in the separation of electron-hole pairs and in delaying recombination of  $\text{h}^+$  and OH radicals in the photocatalytic process.

Substance precipitation creation of nanostructure ZnO semiconductor with 2.1 nm width was utilized in an examination on photocatalytic corruption of ciprofloxacin drug in water by Maged El-Kemary, Hany El-Shamy, and Ibrahim El-Mehasseb (2010). X-beam diffraction (XRD), Fourier-change infrared (FT-IR) spectroscopy, filtering electron microscopy (SEM), and transmission electron microscopy were utilized to look at the resultant nanoparticles (TEM). Fluorescence and UV-vis spectroscopy were utilized to inspect the optical attributes. Sharp tops in retention at 334 nm, which relates to the band hole of 3.7 eV, are displayed in the range. Excitonic emanation at the band edge at 410 nm was trailed by a green outflow top at 525 nm, brought about by the change of one electron from the conduction band to a profoundly caught opening after photogeneration. When presented to UV light in watery arrangements of different pH esteems, the created ZnO nanoparticles were tried for their photocatalytic action in the breakdown of the ciprofloxacin drug. When tested at pH 4, the photocatalytic degradation process was found to be sluggish and ineffective. Degradation efficiency was 50% higher at pH 10 after 60 minutes of incubation. Using a pseudo-first order kinetics, the photodegradation of the medication takes place.

$\text{Bi}_2\text{Ti}_2\text{O}_7/\text{TiO}_2/\text{RGO}$  composite was read up for the reproduced daylight driven photocatalytic corruption of ciprofloxacin by WenguangLi, YuanjieZuo, Ling Jiang, Dachuan Yao, Zhongjing Chen, Guangyu He, and Haiqun Chen (2020). By utilizing a straightforward solvothermal approach, analysts tracked down that

titanium dioxide ( $\text{TiO}_2$ ) altered bismuth titanate ( $\text{Bi}_2\text{Ti}_2\text{O}_7$ ) heterojunction was supported on decreased graphene oxide (RGO). It wasn't necessary to use a toxic reductant or toxic solvent. Structural analysis showed that RGO is loaded with spherical  $\text{Bi}_2\text{Ti}_2\text{O}_7/\text{TiO}_2$  nanoparticles. The photocatalytic performance of the produced  $\text{Bi}_2\text{Ti}_2\text{O}_7/\text{TiO}_2/\text{RGO}$  composite is considerably superior than that of each individual component when exposed to simulated sunshine. CIP's degradation efficiency is increased to 95% in 180 minutes employing the catalyst  $\text{Bi}_2\text{Ti}_2\text{O}_7/\text{TiO}_2/\text{RGO}$  composite, and it remains there for 5 photocatalytic reaction cycles. The synergistic impact of  $\text{Bi}_2\text{Ti}_2\text{O}_7$ ,  $\text{TiO}_2$  and RGO<sub>5</sub> is responsible for the composite's enhanced photocatalytic activity. The  $\text{Bi}_2\text{Ti}_2\text{O}_7/\text{TiO}_2/\text{RGO}$  photocatalyst is superior to conventional bismuth-based catalysts in terms of photocatalytic activity, or it demonstrates equivalent activity with less dose. In order to learn more about the photocatalytic degradation process, we performed tests using free radical scavengers.

The Ramezanalizadeh and Rafiee families (2021), It was resolved that an exceptional ternary nanocomposite as an apparent light-determined photocatalyst was answerable for the extremely speedy photodegradation of antibiotic medication. Different characterisation methods, like VSM, XRD, FESEM, UV-Vis DRS, EDX, and ICP-OES, were utilized to concentrate on the straightforward arrangement of the  $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3/\text{BaFe}_{12}\text{O}_{19}$  ternary nanocomposite. Utilizing occurrence apparent light illumination, the as-arranged ternary nanocomposite was utilized to photocatalyze the breakdown of antibiotic medication. The impact of different fundamental and essential boundaries, for example, impetus stacking, pH of the arrangement, TC fixation, brightening time, impetus type, reusability work, arrangement turbidity within the sight of the impetus and scrounger tests were analyzed to explore the adequacy of this examination for the obliteration of antibiotic medication.  $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3$  and  $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3/\text{BaFe}_{12}\text{O}_{19}$  nanocomposites were displayed to have exceptionally comparative photocatalytic movement in parallel and ternary structures, as per tests (around 80% after 15 min under apparent light illumination).  $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{S}_3/\text{BaFe}_{12}\text{O}_{19}$  was picked for additional examination due to its attractive properties and simplicity of partition. Because of

the proficient partition of photograph created electron-opening matches, level band potential, giver thickness, and polarization obstruction of ternary nanocomposite as assessed by Mott-Schottky charts and Nyquist, Bode plots extricated from electrochemical impedance spectroscopy, the photocatalytic execution of ternary nanocomposite can be credited to these variables: However, TC was totally mineralized following photodegradation at pHs 5, 7, and 11 because of its high GC-Mass. Photosynthesized HO• and 1 O<sub>2</sub> were found to be the primary active species in photocatalysis assays. Tests on the durability indicated that after four cycles of usage, there was no significant loss of activity in the Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>S<sub>3</sub>/BaFe<sub>12</sub>O<sub>19</sub>.

S. KALPANA , S. S. KRISHNAN , T. S. SENTHIL , S.V. ELANGO VAN studied the photocatalytic properties of cobalt-doped zinc oxide nanoparticles (2017). Their study tells us Zinc oxide is a inorganic compound which is widely used due to its own specific values. The photocatalytic activity of ZnO nanoparticles in the presence of sunshine is excellent for the elimination of a wide range of drug contaminants. From their study we analyzed various methos for synthesis of ZnO and how the particle size varies with increase of cobalt dopent concentration. Co-precipitation was used to make both pure and cobalt-doped Zinc oxide nanoparticles. According to their findings, decolorization is quite effective at lower pH levels. ZnO's crystal structure was unaffected by the addition of cobalt ions, as shown by the XRD measurements. ZnO is a material with a broad band gap. ZnO nanoparticle structural, morphological, and optical features are investigated in a non-centrosymmetric crystallographic phase. Co doped ZnO nanoparticles exhibit high photocatalytic action within the sight of UV light for the end of methylene blue color when utilized in this examination.. X-beam diffraction studies with Cu K radiation uncover cobalt-doped ZnO nanoparticles. Checking electron microscopy was utilized to analyze the morphology and content of the blended examples (SEM with EDXA). An UV-VIS spectrophotometer was utilized to record the optical ingestion spectra of ZnO nanoparticles. The XRD analysis of Co doped ZnO hexagonal wurtzite without the change in the structure. The Diffraction analysis

provides detailed information on the structural properties. ZnO was used to identify diffraction peaks.

As part of his research, Alaa Qasem Abed-Alkarim Al-Haj Qasem investigated the antibacterial properties of zinc oxide and cobalt oxide nanoparticles in surfactant-/antibiotic shells. (2013). For example, zinc oxide nanoparticles have been shown to have antimicrobial activity, semiconducting capabilities, and many other useful qualities in this study's findings. on the other cobalt oxide nanoparticle have less antibacterial activity. They used chemical reduction method for synthesis of nanoparticles . *S. aureus*, *B. subtilis*, and *E. coli* were used to test the antibacterial properties of produced nanoparticles. Zinc oxide nanoparticles are stabilised using tetra octyl ammonium bromide (TOAB) solution. Zinc oxide nanoparticles (d) have an average particle size of 15.64 nm. *S. aureus* and *E. coli*, with MIC = 165 µg/mL (> 82.0 µg/mL), had better antibacterial activity against ZnO than *B. subtilis*, with MIC = 330 µg/mL (> 165 µg/mL). This results helps us in selecting the ZnO nanoparticle for the removal of ciprofloxacin drug due to its high surface absorption efficiencies. Because of their efficiency on resistant strains of microbial pathogens as well as their low toxicity and resilience to high temperatures these metal oxide nanoparticles ZnO, MgO, TiO<sub>2</sub>, SiO<sub>2</sub>, CuO and CoO may be used as antimicrobial agents... Similarly, Jones et al. found that ZnO nanoparticles had a greater antibacterial impact on *S. aureus* than the other five metal oxide nanoparticles studied. NP combination technique is specifically noteworthy due to the many elements that impact the size, morphology, security, and properties (synthetic and physical) of the metal nanoparticles. These variables include: the exploratory circumstances, the energy of connection of metal particles with lessening specialists, and the adsorption cycles of balancing out specialist on metal nanoparticles. NP synthesis method

Nanoflakes of zinc oxide: cobalt oxide composites by beat laser discontinuity for apparent light photocatalysis were accounted for by Sreed S. Kanackillam, S. Shajia, B. Krishnana, S. Vazquez-Rodrigueza, J.A. Aguilar Martinez, M.I.

Mendivil Palma, and D.A. Avellaneda (2019). For the last two decades, ZnO nanoparticles have been well-known as a photocatalyst. When it came to examining these nanocomposites' shape, structure, optical characteristics and content, they employed a new method called pulsed laser fragmentation (PLF). Chemical methods such as hydrothermal method, co-precipitation method, and chemical bath deposition were the most often used synthesis procedures. In photocatalytic research using a solar simulator (220W), visible light is produced using the contaminating dye methylene blue. Colorless or white ZnO powder and black cobalt oxide were the only commercially available ZnO products. Stability and cyclic photocatalytic activity of nanocomposites under visible light irradiation were shown. We may conclude that it has a crystalline structure based on XRD measurements. ZnO and Co<sub>2</sub>O<sub>3</sub> cryomilled samples morphologies were found to be identical in agglomerated form in all three combinations of ZnO and Co<sub>2</sub>O<sub>3</sub>. TEM studies validated the flake nanostructure and cobalt oxide, zinc oxide planes. Morphologies like circular or bar like designs were not unequivocally perceived. Results from XRD, SEM, and XPS show the example's very proficient noticeable light photocatalytic exercises. Metal oxide nanocomposites made by heat laser fracture show expanded and cyclic noticeable light photocatalytic movement. 3.3 eV was the bandgap of ZnO, though the bandgaps of Co<sub>2</sub>O<sub>3</sub> went from 1.3 to 2.4 eV. The outcomes from XRD, SEM, and XPS show that the example ZC<sub>20</sub>, which has superb crystallinity, a functioning surface shape, and a uniform dispersion of the pertinent parts on a superficial level, has very effective noticeable light photocatalytic exercises.

Three scientists in India studied several ways for making nanocomposites: Krishnasamy Ravichandran of Tamil Nadu, Prabhakaran of Tamil Nadu, and Thirumurugan Arun of Tamil Nadu. Nanoscale (1–100 nm) resizing of one of the components in the composite results in an additional improvement in characteristics. Fillers are added into a nanocomposites matrix depending on the qualities to be enhanced. s. Multiphase solid materials are used to make nanocomposites, which are made up of a continuous phase and a discontinuous phase, at least one of which is on the nanoscale. in this study we came to know

about various synthesis processes of various nano composites such as polymer nanocomposite, bypolymer nanocomposite, ceramic nanocomposite using mechanochemical synthesis, Self-Propagating High-Temperature Synthesis (SHS). They gave a clear idea about solgel method, coprecipitation method, spray decomposition solution combustion, liquid- phase processes, solid-phase processes, deposition techniques and many more. We decided to use the hummers technique for the production of CoO-Zno@rGOterinary nanocomposite after evaluating all of these approaches. Nanocomposite may be made in a variety of ways using these methods.

An investigation on the synthesis and electrochemical characteristics of carbon nanoparticles/zinc oxide/zinc cobalt oxide composite was carried out by Hamid M. Shaikha, Nadavala Siva Kumar, and Asif Mahmood (2020). RuO<sub>2</sub>, MnO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> are examples of carbon-based metal oxides that show the combined effects of electric double-layer capacitance and electric double-layer capacitance (EDLC). A CNP/ZnO/ZnCo<sub>2</sub>O<sub>4</sub> synthesis combining CNP and ZnO/ZnCo<sub>2</sub>O<sub>4</sub> has been investigated. For the CNP/ZnO/ZnCo<sub>2</sub>O<sub>4</sub> combination, two hydrothermal steps were used. Nanocomposite creation from ZnO and ZnCo<sub>2</sub>O<sub>4</sub> mixed phases has been validated by XRD analysis, and the nanocomposite has been created. In order to do FE-SEM analysis, CNP/ZnO/ZnCo<sub>2</sub>O<sub>4</sub> composite and virgin CNP were studied for their morphology. by use of a two-step hydrothermal synthesis process CNP/ZnO/ZnCo<sub>2</sub>O<sub>4</sub> composite was synthesized. Supercapacitors might benefit from this study since the CNP/ZnO/ZnCo<sub>2</sub>O<sub>4</sub> composite material has been demonstrated to be a low-cost and simple to produce electrode material with a good electrochemical performance. An good EC and a quick charge transfer rate made the CNP/ZnO/ZnCo<sub>2</sub>O<sub>4</sub> composite the most accurate electrode in terms of capacitance behaviour. In terms of high-performance supercapacitors, this study offers a potential contender.

## CHAPTER 3

### AIM AND SCOPE

#### AIM

- Synthesis of using hydrothermal method
- To conduct characterization studies of synthesized nanocomposite using XRD, FTIR, UV~VIS spectroscopy, SEM
- To study degradation efficiency of pharmaceutical drug using synthesized nanocomposite

#### SCOPE

- The main scope of this project is to Remove ciprofloxacin drug pollutants from water source using **CoO-ZnO@rGO** nanocomposite and to investigate its properties such as removal efficiency, structure and morphology

## CHAPTER 4

### MATERIALS AND METHODS

#### 4.1 MATERIALS USED

##### *4.1.1 Synthesis of CoO-ZnO nanocomposite*

Cobalt acetate ( $C_4H_6CoO_4$ ), Zinc Acetate( $C_4H_6CoO_4$ ), sodium hydroxide( $NaOH$ ), cetyl trimethyl ammonium bromide( $C_{19}H_{42}BrN$ ), distilled water.

##### *4.1.2 Synthesis of Reduced Graphene Oxide (rGO)*

potassium permanganate ( $KMnO_4$  ), Natural flake graphite (NFG), sodium nitrate( $NaNO_3$ ), hydrogen peroxide( $H_2O_2$ ), sulfuric acid(  $H_2SO_4$  ), phosphorus pentoxide( $P_2O_5$ ), Potassium persulfate( $K_2S_2O_8$ ), distilled water.

#### 4.2 METHOD OF SYNTHESIS OF CoO-ZnO@rGO ternary nanocomposite

##### *4.2.1 Preparation of CoO-ZnO nanocomposite*

Add 4 gm of cobalt acetate to 40 ml water. Place it on a magnetically stirrer and continuously stirred at room temperature. Slowly add 4 gm of zinc acetate until it is completely dissolved in cobalt acetate solution. 1 gm of cetyl trimethyl ammonium bromide was added slowly until it is completely mixed forming a gel. Resulting gel is placed in a digital ultrasonic cleaner for sonication for 20 minutes. Prepare 2 gm sodium hydroxide in 40 ml water and mix continuously. 10 ml of the ammonium hydroxide solution is added dropwise to gel in the digital ultrasonic cleaner and continue the sonication process. The suspension is then placed in the

muffle furnace at 170 °C for 15 hours. We then dried the precipitate after washing it in distilled water and filtering it. It is further calcined at 550°C for 3 h .



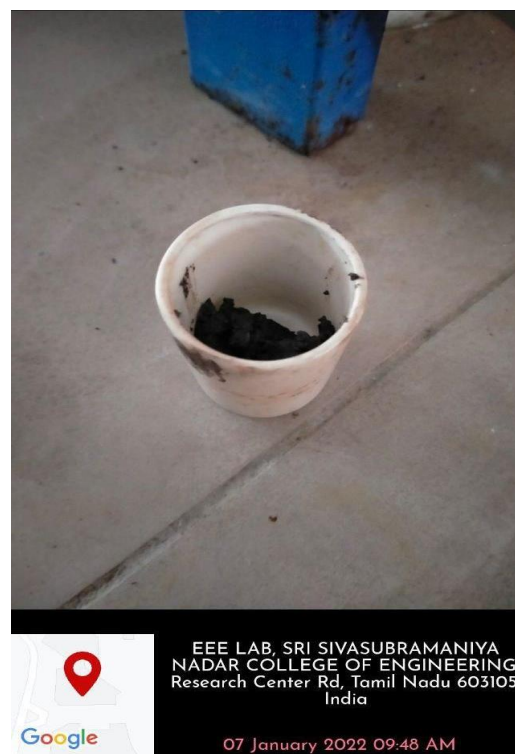
***Fig 4.1: Magnetic stirrer hydrothermal***



***Fig 4.2 : Sample before process***



**Fig 4.3 Hydrothermal apparatus**



**Fig 4. 4 CoO-ZnO nanocomposite**

#### **4.2.2 Preparation of Reduced Graphene Oxide rGO**

A combination of 4 gm NFG, 12 ml  $\text{H}_2\text{SO}_4$  and 8 gm  $\text{P}_2\text{O}_5$  should be prepared. Magnetic stirring for six hours was followed by the addition . 12 ml of  $\text{H}_2\text{SO}_4$  and 8 gramme of  $\text{K}_2\text{S}_2\text{O}_8$  to the filtrate. For six hours, this mixture was agitated by magnetic force. After the liquid had cooled to room temperature, it was diluted with 300 ml of distilled water to make it easier to pour. It was then heated in a muffle furnace at 60 degrees Celsius for two hours to dry the filtrate. 7.2 grammes of the pre-oxidized graphite powder are added to 92 millilitres of  $\text{H}_2\text{SO}_4$  and 12 millilitres of  $\text{KMnO}_4$  in a water bath while being constantly stirred. After 15 minutes, 2 gramme of  $\text{NaNO}_3$  is added to the solution. After 2 hrs of stirring at room temperature, the solution is ready. After 15 minutes of stirring, 200 ml of distilled water is added to the solution. A 30 percent  $\text{H}_2\text{O}_2$  solution and 560 ml of distilled water are added to the solution in steps, respectively. HCl is used to wash the filtrate (10 percent ). Thirty minutes in a muffle furnace at 60 degrees Celsius heats the suspension, which is then allowed to cool overnight in the open air.

For one week, use distilled water to remove any remaining metallic ions and acids.

It was necessary to dry the filtrate over night before sonicating it for five hours with  $\text{H}_2\text{O}_2$ . To eliminate the contaminants, warm water may be used up to three times.

After 4 hours of heating the filtrate to  $60^\circ\text{C}$ , the dry GO powder is produced.

To get rGO from GO, The dried GO powder is administered in an empty beaker with 10 mg of the substance. The beaker was put in a hood on a hot plate heated to  $350^\circ\text{C}$  for 10 minutes and covered with aluminium foil that had numerous perforated pores. The resultant rGO black powder was then removed from the beaker and stored in a vial.

### 4.2.3 Synthesis of Ternary nanocomposite

A certain amount of reduced graphene oxide was ultrasonically treated in 30 ml distilled water. To this solution equal amount of CoO-ZnO was added. The resulting mixture is continuously stirred. Hydrothermal reaction at 180°C for 6 h, The resulting mixture is filtered, washed in distilled water and dried to obtain CoO-ZnO@rGO ternary nanocomposite.



**Fig. 4.5 : CoO-ZnO and rGO before Ultrasonication**



**Fig. 4.6 : Digital Ultrasonication**



**Fig. 4.7 : CoO-ZnO and rGO  
after ultrasonication**



**Fig. 4.8 : Hydrothermal apparatus**



**Fig. 4.9 : CoO-ZnO@rGO ternary nanocomposite**

### **4.3 CHARACTERIZATION**

For the study of the ternary nanocomposite's crystal structure and crystalline phase, powdered CoO-ZnO@rGO was powdered and XRD patterns were studied in a range of 5 to 80° with a duration time of 4deg/min. Scanning Electron Microscope (SEM) measurements were taken in order to images of sample. A powdered CoO-ZnO@rGO ternary nanocomposite's FT-IR spectra were collected in the 400 to 4000 cm<sup>-1</sup> range. A UV-vis spectrometer was utilised to examine the deterioration rate.

### **4.4 PHOTOCATALYTIC DEGRADATION OF CIP**

The degradation of Ciprofloxacin by the nanocomposite's photocatalytic activity was investigated in the presence of visible light. The photocatalytic reaction was conducted under direct sunlight.

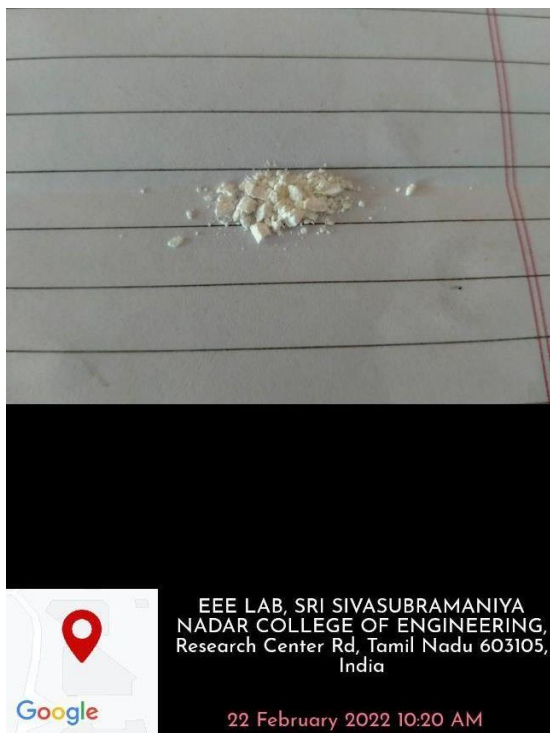
After preparing CoO-ZnO@rGO ternary nanocomposite solution and CIP solution are undergone ultrasonication for 30 min afterwards the solution are mixed according to various parameter pH (3-9) ,Time (5-105 mins), Drug pollutant concentration ( 3 to 13 ppm). For adsorption-desorption equilibrium to develop and reduce the likelihood of inaccuracy, the sample solution is held in the dark for 30 minutes prior to the first reading after mixing.

For the same length of time, the catalysts were bombarded with visible light to examine their optical characteristics. The level of deterioration was determined by keeping the time constant. The drug solution was isolated from the main solution using the photocatalytic procedure and centrifugation. It was necessary to utilise a UV–Vis spectrophotometer in order to accurately assess the absorption.

It is possible to calculate CIP photocatalytic degradation efficiency using the equation CoO-ZnO@rGO.

$$\% \text{ Photocatalytic activity} = \frac{C_o - C_t}{C_o} \times 100$$

Where,  $C_0$  and  $C_t$  represents equilibrium concentration and concentration at a particular irradiation time  $t$  respectively.



**Fig 4.10: Ciprofloxacin drug**



**Fig.4.11: Sample before  
photocatalytic studies**



***Fig. 4.12 : Sample after photocatalytic studies***

## **CHAPTER 5**

### **RESULTS AND DISCUSSION**

#### **5.1 STRUCTURE AND MORPHOLOGY**

The Measured XRD patterns for newly synthesized CoO-ZnO@rGO ternary nanocomposite acquired phase, purity and crystallinity are investigated. As shown in Fig 5.9 from the XRD data the weak prominent peak at  $2\theta=26.46$  indicates reduced graphene oxide. Peaks at  $2\theta= 31.84, 34.554, 36.354, 44.64, 47.63, 56.68, 62.96, 65.10, 67.92, 69.09, (100), (002), (110), (1103), (112)$  and  $(201)$ , which correlate to ZnO's hexagonal wurtzite crystalline structure, obviously match. It is clear that the ZnO nanoparticle possesses the wurtzite phase based on the diffraction patterns seen, which are compatible with the JCPDS card number 36-1451. No additional impurity phase was discovered, which implies that Co ions occupy lattice sites rather than interstitial ones, based on the diffraction patterns.

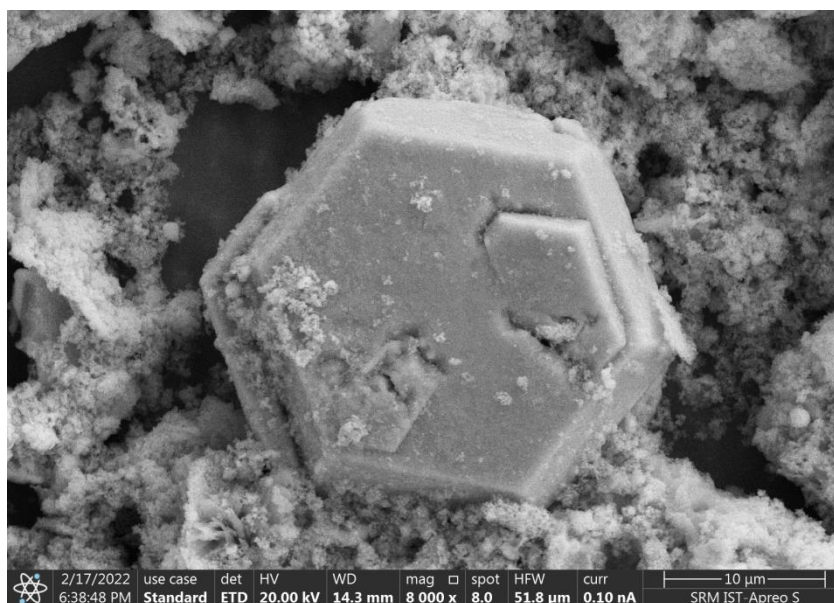
SEM was used to investigate the nanocomposites' structure and morphology, which are shown in Figs. 5.1 and 5.3. SEM image of CoO-ZnO nanocomposite Fig. 5.1 confirms the hexagonal structure of ZnO, the spore-like structures accompanying the ZnO supports that the CoO is incorporated successfully. As shown in Fig. 5.2, CoO-ZnO nanocomposite is made of zinc, cobalt, and oxygen. EDS analysis confirms this. Due to the fact that no impurity-related peaks were seen during the EDS analysis, the newly synthesised ternary structure is entirely composed of Zn, O, Co, and C.

As shown in Figure 5.3, SEM images of the ternary nanocomposite CoO-ZnO@rGO clearly demonstrate the ternary arrangement among the selected parts, with rGO interspersed with the CoO-ZnO@rGO nanocomposite. The EDS analysis, shown in Fig.5.4, was also carried out to verify the ternary framework's

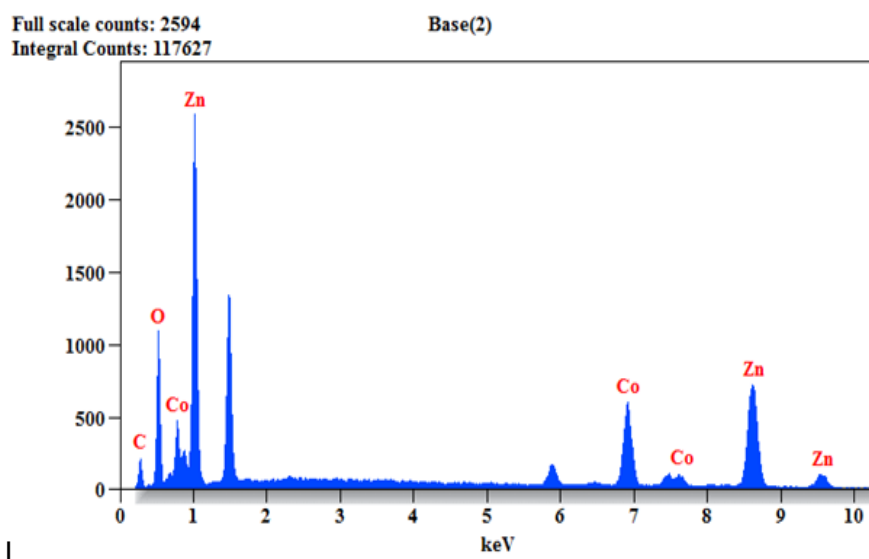
elemental composition. Analysis of the ternary nanocomposite by EDS proved that it is made of zinc, cobalt, oxygen, and carbon, and nothing else. Fluorine impurities were found during EDS analysis, although it is obvious that the newly synthesised ternary structure is Zn, O, Co and C-rich rather than fluorine-rich.

Analysis of the sample's FT-IR spectra confirmed the chemical composition.

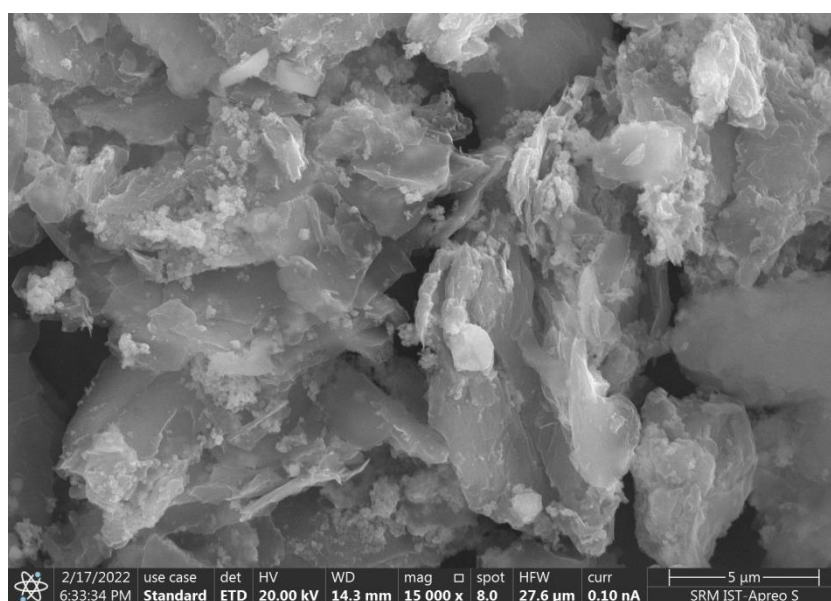
The peaks at  $1162\text{ cm}^{-1}$ ,  $1399\text{ cm}^{-1}$ , and  $1632\text{ cm}^{-1}$  in Fig. 5.6 of the CoO-ZnO@rGO ternary nanocomposite are attributable to metal oxides. The O–H stretching of the hydroxyl group is responsible for the  $3423\text{ cm}^{-1}$  absorption band.  $2849\text{ cm}^{-1}$  and  $2917\text{ cm}^{-1}$ , respectively, correspond to symmetric and asymmetric C–H bonds. Products with C–H bonds may be found. Asymmetric and symmetric C=O stretching is responsible for the  $2378\text{ cm}^{-1}$  peaks. The stretching mode of Metal oxide stretching is responsible for the peaks at  $481\text{ cm}^{-1}$  and  $681\text{ cm}^{-1}$ .



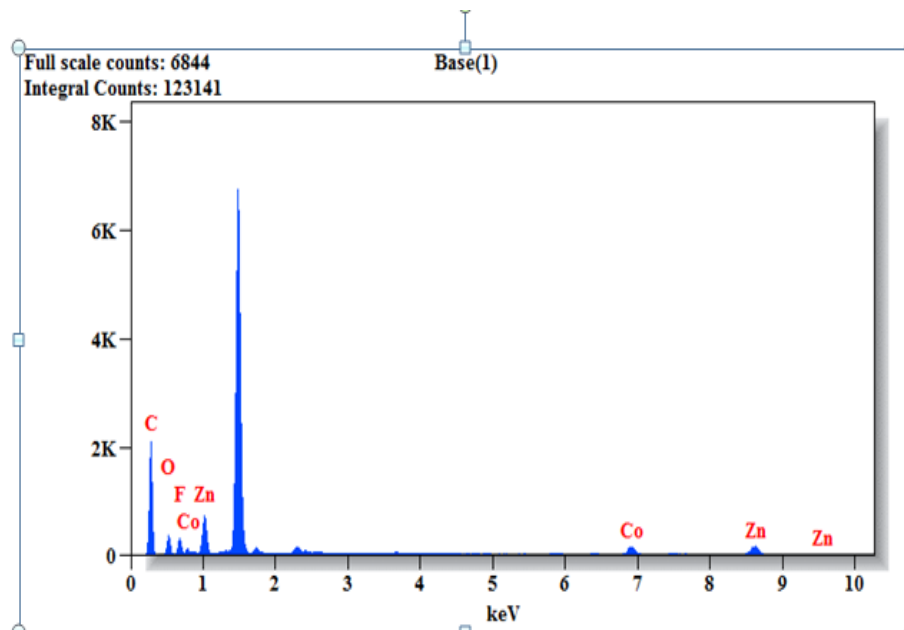
**Fig 5.1 : SEM Image of CoO-ZnO Nanocomposite**



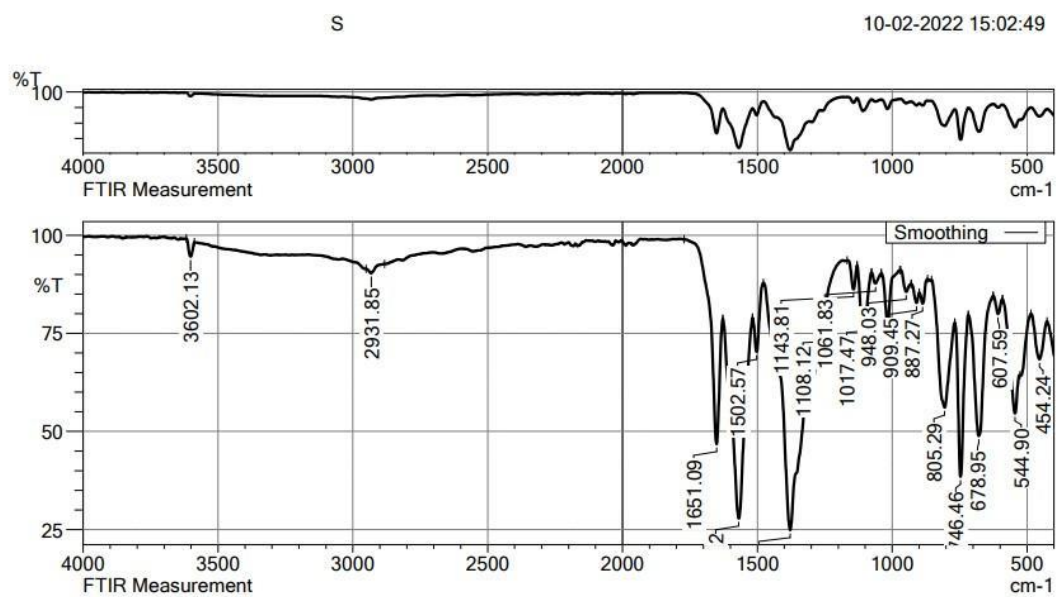
**Fig 5.2: EDS Elemental Analysis of CoO-ZnO Nanocomposite**



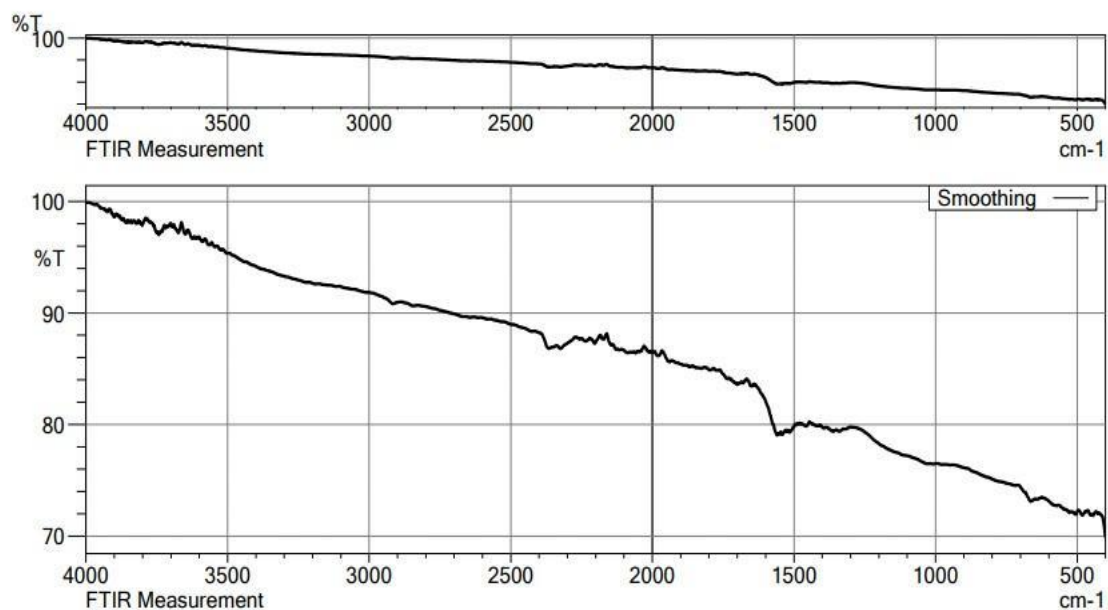
**Fig 5.3 : SEM Image of CoO-ZnO@rGO Ternary Nanocomposite**



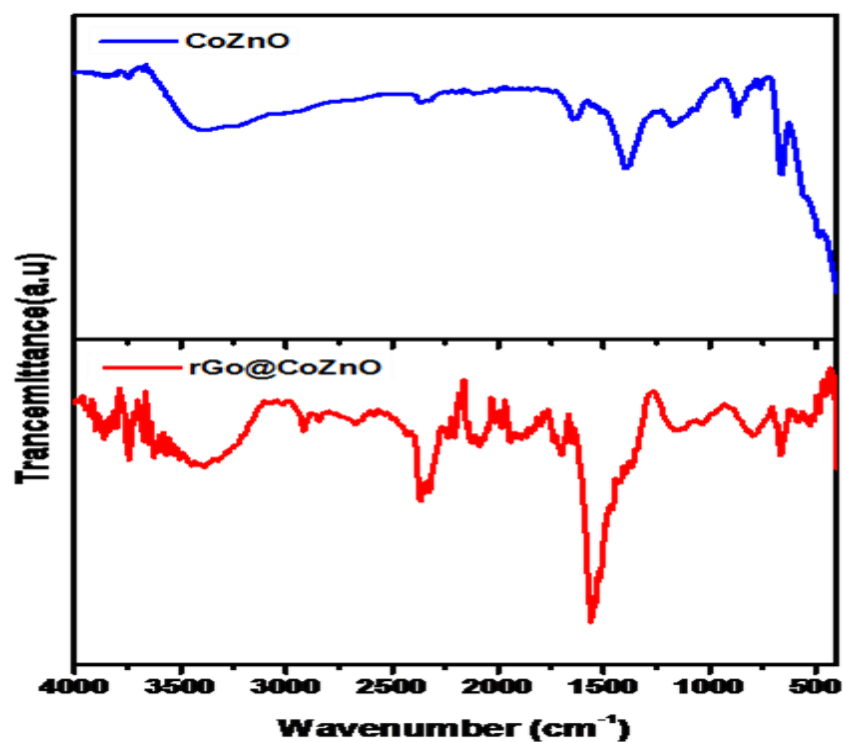
**Fig 5.4 : EDS Elemental Analysis of CoO-ZnO@rGO Ternary Nanocomposite**



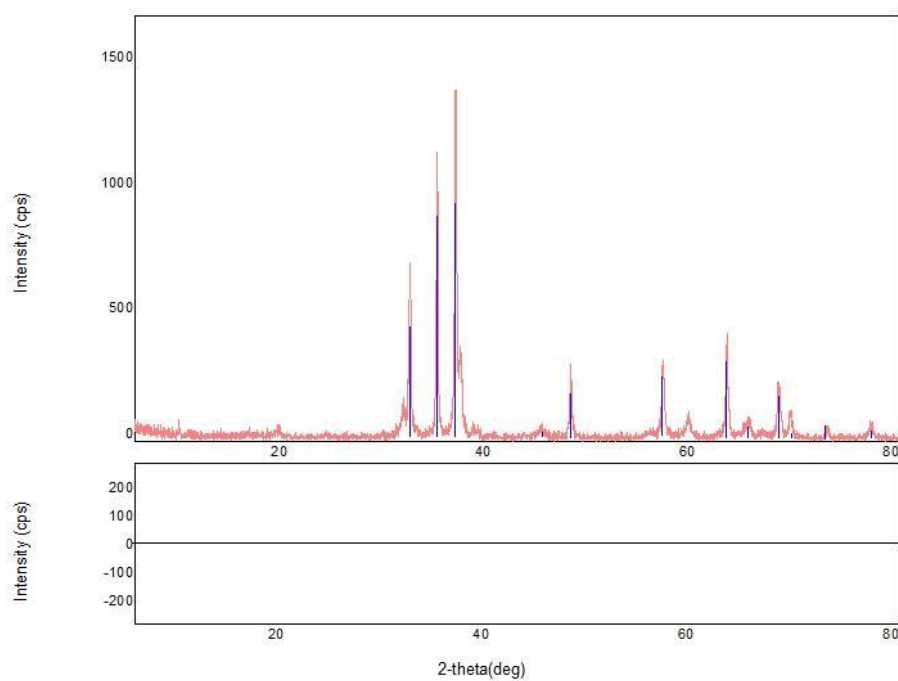
**Fig 5.5 : FTIR Measurement of CoO-Zn Nanocomposite**



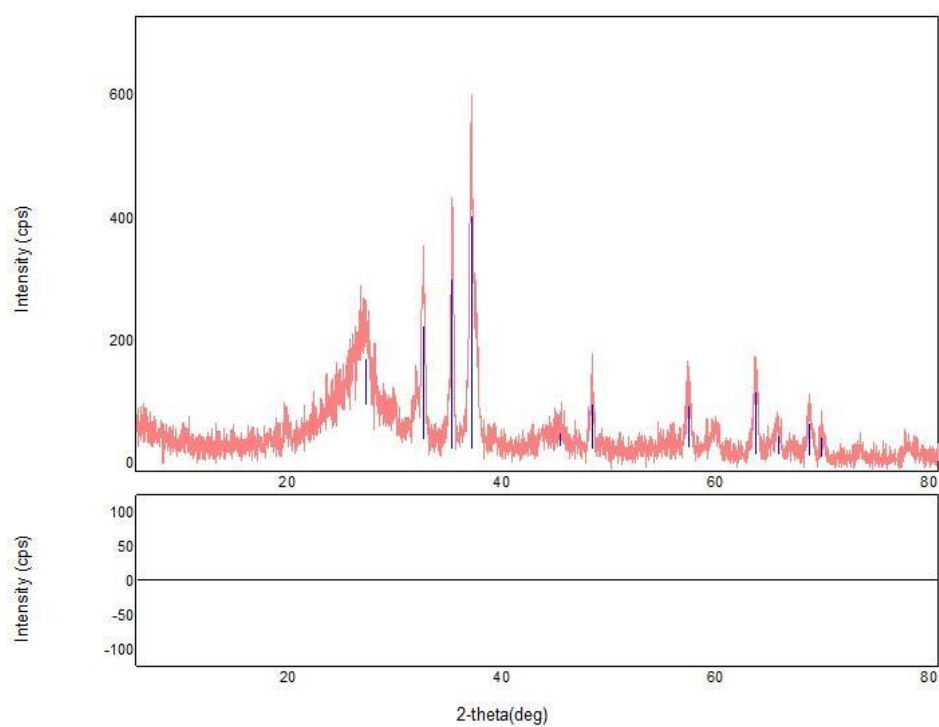
**Fig 5.6 : FTIR Measurement CoO-ZnO@rGO Ternary Nanocomposite**



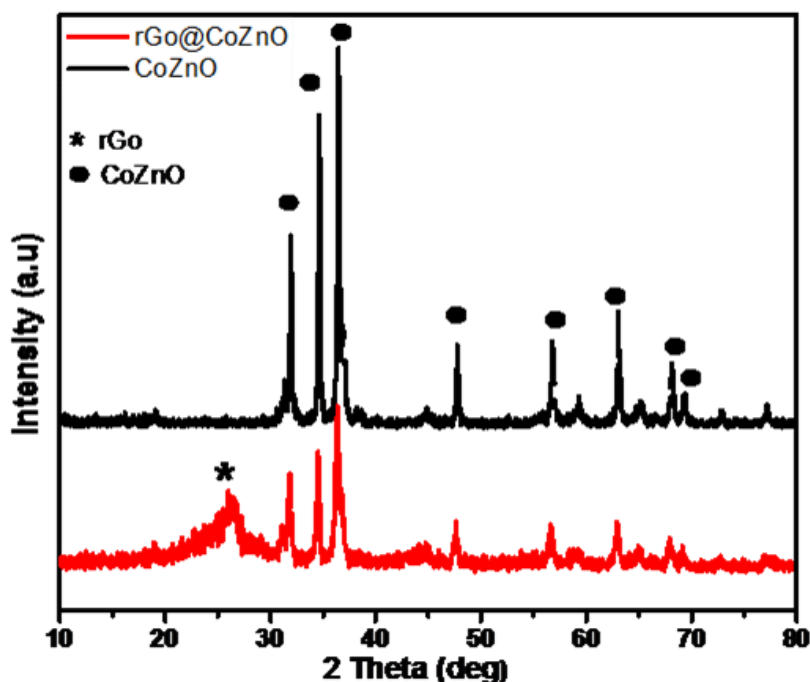
**Fig 5.7 : FTIR Comparative Measurement Data of CoO-ZnO and CoO-ZnO@rGO Ternary Nanocomposite**



**Fig 5.8: XRD Data of CoO-ZnO**



**Fig 5.9 : XRD Data of CoO-ZnO @rGO Ternary Nanocomposite**



*Fig 5.10 : XRD Comparative Data of CoO-ZnO and CoO-ZnO@rGO Ternary Nanocomposite*

## 5.2 PHOTOCATALYTIC DEGRADATION MECHANISM

In order to create photoexcited electrons and holes in the conduction band and valence band, the CoO-ZnO@rGO ternary nanocomposite photocatalyst absorbs sunlight with an energy larger than its band-gap. In order for photocatalytic degradation to work, the photocatalyst must be able to prevent the recombination of excitons so that they may be used to generate ROS. There are at least two key functions for the rGO implanted on the CoO-ZnO surface.

Aside from absorbing long-wavelength UV light, it also aids in the generation of free excitons through absorption of visible light. CoO-ZnO@rGO ternary nanocomposite's absorption of visible light in the 400-550 nm region would benefit the up-conversion characteristics of rGO. CoO-ZnO@rGO ternary nanocomposite is able to absorb more sunlight because of the spectrum conversion phenomena.

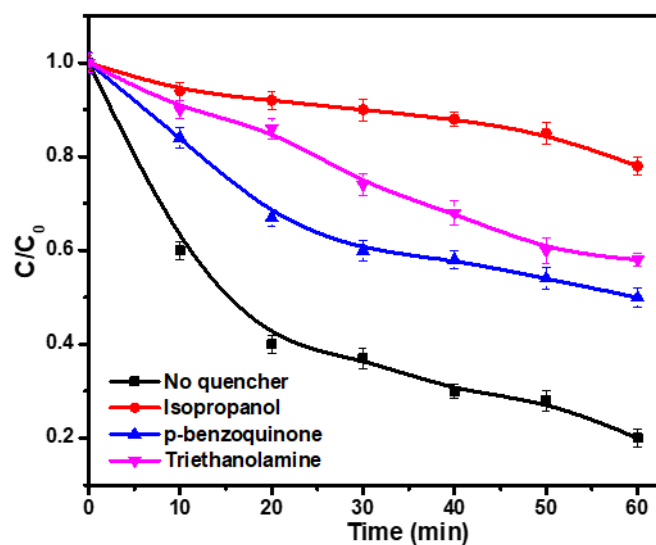
As a result, the CDs efficiently segregate the electron-hole pairs formed by the CoO-ZnO@rGO ternary nanocomposite to increase the photocatalytic degradation efficiency.

The charge carrier recombination was inhibited because of the greater defect concentrations in the CoO-ZnO@rGO ternary nanocomposite. Photoexcited charge carriers will thus spread to heterostructure's surroundings and interact with molecule oxygen and H<sub>2</sub>O to form ROS as a consequence. Second, the rGO are well-known for their high-quality electron and hole acceptors. The photoexcited electrons and holes might be trapped by the rGO placed on the ZnO surface. As a result, the photoexcited electrons and holes have a longer lifespan, giving them more time to carry out certain photochemical reactions and generate diverse ROS, resulting to a quicker rate of photocatalytic destruction of the pollutant molecule.

### **5.2.1 Role of the Reactive Species in Photocatalytic Mechanism**

The possible degradation route of CIF was first proposed. The photochemical degradation reaction is hypothesised to be triggered by the absorption of light energy by molecules, which causes them to enter excited states and initiate a variety of reactions. Photolysis, also known as direct photolysis, is a photochemical event in which antibiotic molecules directly absorb light. Ciprofloxacin (CIF) is degraded and mineralized as a result of photocatalytic degradation, which results in the formation of carbon dioxide and water. Afterwards, the most prevalent active species in the photocatalytic CIF degradation process in the CoO-ZnO@rGO nano-composite were identified and identified as follows: In free radical trapping assays, isopropanol (IPA), a scavenger of hydroxyl radicals ( $\cdot\text{OH}$ ), inhibited the photocatalytic degradation of CIF by 14.5 percent. This suggests that the predominant reactive species is  $\cdot\text{OH}$ . While TEA (triethanolamine) and BQ (1,4-benzoquinone) had suppressed the photocatalytic degradation of CF to 52 and 31 % respectively. They were used as the scavenger of superoxide radicals ( $\cdot\text{O}_2^-$ ), holes ( $\text{h}^+$ ) and hydroxyl radicals ( $\cdot\text{OH}$ ), correspondingly. These results demonstrate that  $\cdot\text{O}_2^-$ ,  $\text{h}^+$ , and  $\cdot\text{OH}$  are the active species for the CoO-ZnO@rGO sample in the photo-catalytic process, while

$\cdot\text{OH}$  makes a major contribution to it. Moreover, the sequence of effects is as follows:  $\cdot\text{OH} > \text{h}^+ > \cdot\text{O}_2^-$ . These data demonstrate that the active species in the photo-catalytic process for the CoO-ZnO@rGO samples are  $\cdot\text{O}_2^-$ ,  $\text{h}^+$ , and  $\cdot\text{OH}$ . It is identified that  $\cdot\text{OH}$  accounting for a large portion of the total contribution for photo-catalytic degradation. Furthermore, the reactivity of species are in sequential order as follows:  $\cdot\text{OH} > \text{h}^+ > \cdot\text{O}_2^-$ .



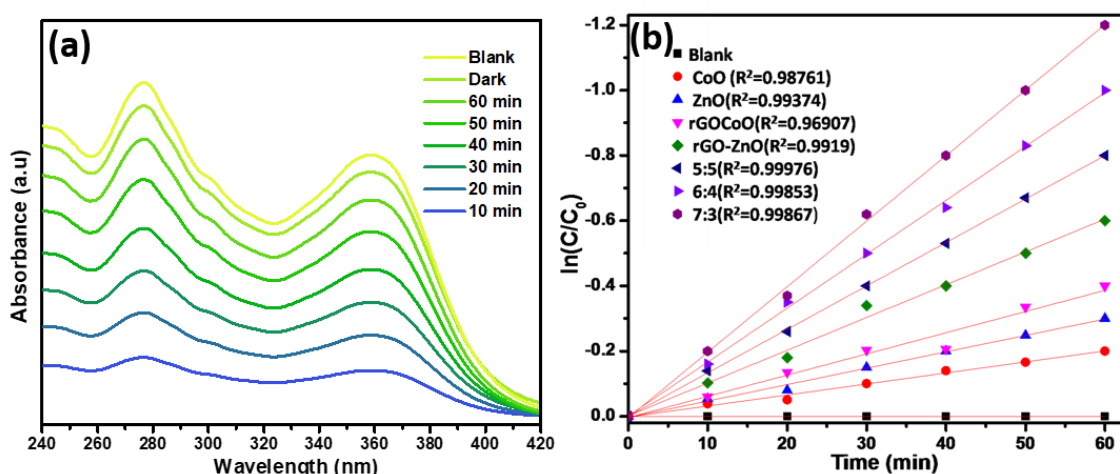
**Fig.5.11 : Degradation of CF by CoO-ZnO@rGO Nano-composite in the Existence of Visible Light was Studied using Species Trapping**

### 5.2.2 Photocatalytic Activity for CIP

The following figures depict the photocatalytic efficiency of CIF antibiotics as well as their kinetic research: Fig depicts that, as compared to other composites and bare semiconductors, CIF degradation occurs over a CoO-ZnO@rGO nano-composite with enhanced photocatalytic activity to CIF degradation (CIF degradation over other composites and semiconductors is shown to be 93.15 percent ). (a). The rate kinetic performance of CIF degradation is shown in Fig. 11(c) as a plot of  $C/C_0$  vs time (min), which is consistent with pseudo-first-order reaction kinetics and is explained by the following equation to characterise the removal efficiency:

$$\ln \frac{C}{C_0} = -kt$$

As shown in the graph, C indicates the concentration of pollutants at time t,  $C_0$  denotes the starting CIF concentration, and K represent the reaction rate constant.

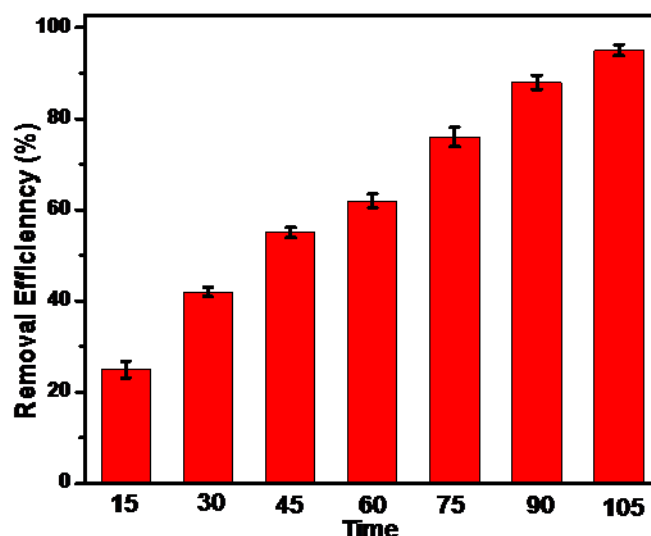


**Fig.5.12 : CIF photocatalytic degradation using Co-OZnO@rGO (3:7:40) Nanocomposite.  $\ln(C/C_0)$  vs time pseudo-first-order kinetic graphs for synthesised nanocomposite**

### 5.3 PHOTOCATALYTIC DEGRADATION STUDIES

#### 5.3.1 Influence of Time

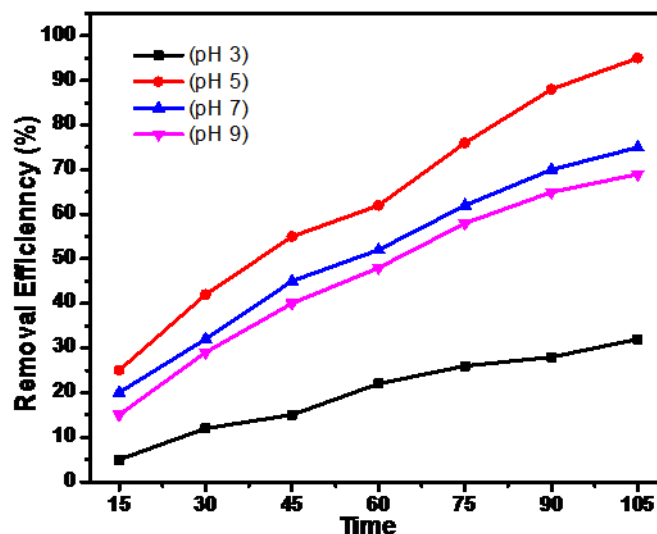
At constant room temperature, constant ciprofloxacin drug concentration and constant catalytic concentration and constant pH range under varying time photocatalytic degradation is studied. Photocatalytic degradation takes place under sunlight. From the graph we can calculate the removal efficiency of the sample at different time intervals. Drug concentration is maintained at 0.4mg/L, pH value is at 7 and catalyst concentration is 0.8mg/L and time ranges from 15min to 105min. As shown in Fig 5.11 the maximum efficiency of the sample is observed at 105minutes and the minimum efficiency is observed at 15 minutes. From the graph we can conclude that sample working efficiency increases with increase in time.



***Fig 5.13 : Photocatalytic degradation of ciprofloxacin with CoO-ZnO@rGO ternary nanocomposite at different time period***

### ***5.3.2 Influence of pH***

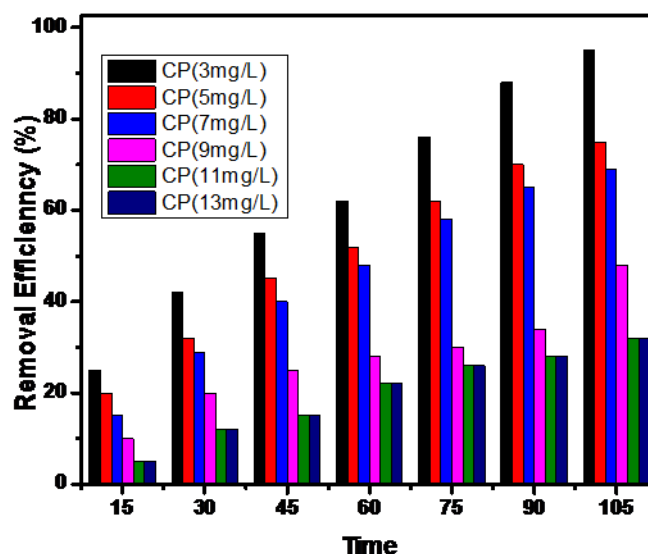
At constant room temperature, constant ciprofloxacin drug(0.4mg/L) concentration and constant catalytic concentration (0.8mg/L) under varying time and pH photocatalytic degradation is studied. photocatalytic degradation takes place under sunlight . From the graph we can calculate the removal efficiency of the sample at different time intervals and different pH levels. time ranges from 15min to 105min and pH ranges from 3 to 9 . As shown in Fig. 5.12 The maximum efficiency of the sample is observed at 105minutes time for pH range 5 and the minimum efficiency is observed at the pH range of 3. From the graph we can conclude that sample works efficient for the pH range of 5.



**Fig. 5.14 : Photocatalytic Degradation of Ciprofloxacin with CoO-ZnO@rGO Ternary Nanocomposite Studies at Different pH**

### 5.3.3 Influence of Drug Concentration

At constant room temperature, constant pH and constant catalytic concentration (6 mg/L) under varying time and concentration of drug photocatalytic degradation is studied. photocatalytic degradation takes place under sunlight. From the graph Fig 5.13 we can calculate the removal efficiency of the sample at different time intervals. Drug concentration varies from 3 mg/L to 13 mg/L and time ranges from 15 min to 105 min. The maximum efficiency of the sample is observed at 105 minutes time for 3 mg/L concentration is about 96%.

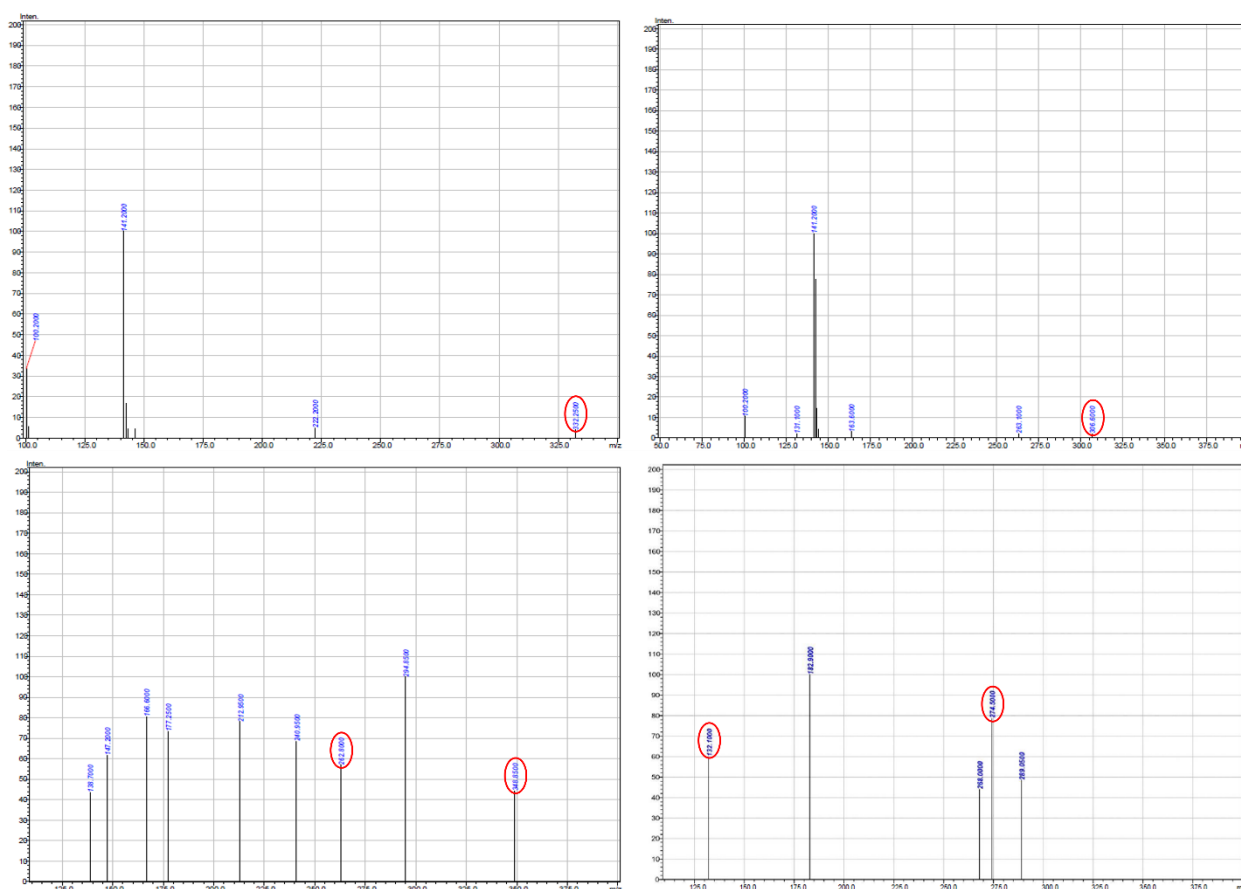


**Fig 5.15 : Photocatalytic Degradation of Ciprofloxacin with CoO-ZnO@rGO Ternary Nanocomposite Studies at Different Concentration of Ciprofloxacin**

#### 5.4 LC-MS Analysis for CF Degradation Intermediates

In three different techniques, the degradation intermediates for Ciprofloxacin (CF) were discovered, and three likely degradation routes were hypothesised based on the LC-MS results for Ciprofloxacin (CIP) degradation that corresponded to their  $m/z$  values for Ciprofloxacin (CF). Intermediates are produced by a variety of methods, the most prevalent of which being piperazine moiety breakdown and decarboxylation. [66] CIP fragmentation routes involving the aromatic ring's electron-withdrawing carboxyl and fluorine groups are frequently encountered. Perhaps the byproducts produced are same or comparable to one another. Since the severe assault, Diethylene Ciprofloxacin (B) was the most often encountered breakdown product in all procedures. Based on their  $m/z$  values, these CF degradation intermediates were found for three techniques, and plausible degradation pathways were given for each technique. Piperazine moiety breakdown and decarboxylation are two prevalent pathways for the creation of mediating agents. The carboxyl and fluorine groups on the aromatic ring, which

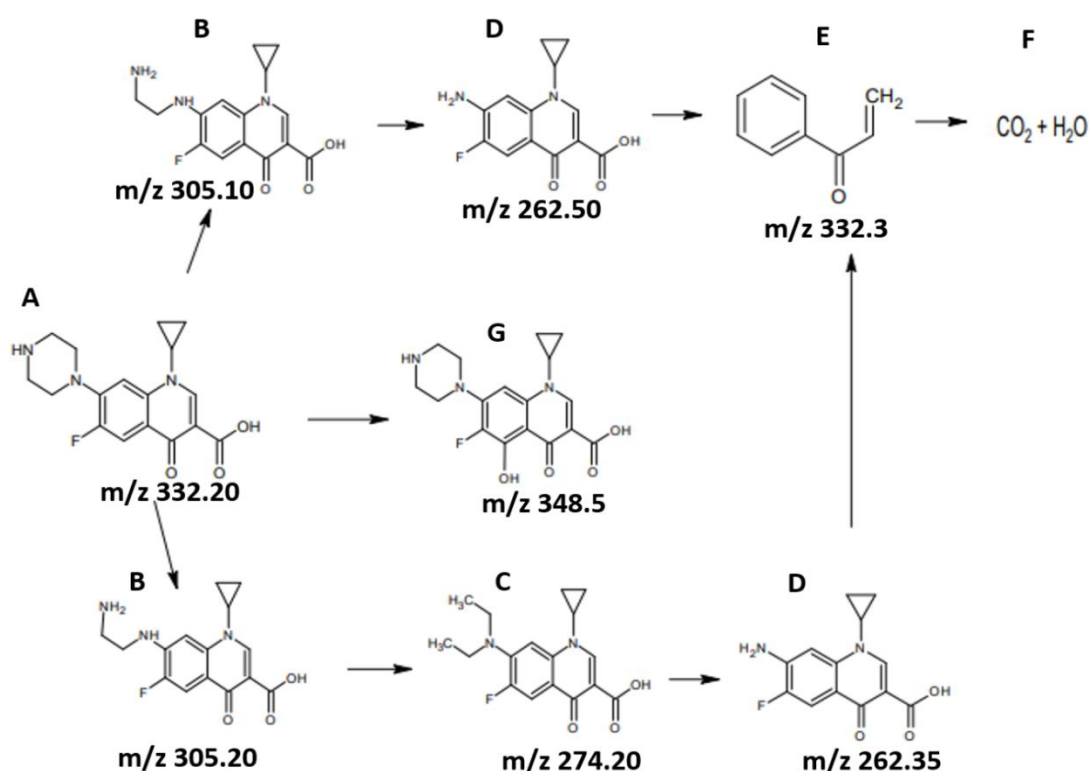
act as electron-withdrawing groups, are also involved in the CF fragmentation routes. There is a possibility that the byproducts created will be the same or quite similar to one another. Because of the attack of strong OH radicals on the piperazinyl substituent, diethylene Ciprofloxacin (B) was the most significant degradation product in all techniques, resulting in the loss of  $C_2H_2$  as a result of the loss of  $C_2H_2$ .



**Fig. 5.16: LC-MS spectral analysis for the identification CF degradation intermediate product in the existence of the CoO-ZnO@rGO nano-composite for irradiation time of 60 minutes.**

In Figure 15, you can see the photocatalytic degradation route that has been

proposed for CF. The piperazine ring is more susceptible to reactive species than the quinolone moiety, which indicates that it is more reactive. On the basis of the available data, three probable degradation mechanisms have been presented. In this reaction, the piperazine ring of the CF molecule is first cleaved, followed by defluorination, resulting in an end product with a mass spectral value of 274.5. (C). In the second case, the addition of a mono-hydroxyl group to the parent molecule CIP, resulted in the discovery of an intermediate compound G ( $m/z$  of 348.8), which was used as a starting point for further research. The third approach, after a percent, generates fragmentation products with  $m/z$  values of 306.6 (B), 274.5 (C), 262.8 (D), and 132.2 (E), respectively (E). OH radical assault on the piperazine ring and formation of the intermediates discussed above may result in additional attack and breakdown of the piperazine ring into smaller molecules or mineralization of the piperazine ring into  $H_2O$  and  $CO_2$ . The fragmentation patterns of all of the transformation products discovered were similar to those of CF, showing that the quinolone core structure had not been altered during the transformation process.



**Fig. 5.17 : CoO-ZnO@rGO (3:7:40) Nano-composite with the Integrated**

***Photocatalytic System were used to Demonstrate a Probable  
Degradation Pathway for Ciprofloxacin (CIP) and the Formation  
of Primary Intermediate as photoproduct.***

**SUMMARY AND CONCLUSION**

CoO-ZnO NC was successfully prepared using hydrothermal method rGO was prepared using modified Hummers method and later rGO was incorporated into CoO-ZnO NC using hydrothermal method to synthesize CoO-ZnO@rGO ternary NC. The structure and morphology and chemical properties were characterized by X-ray diffraction analysis (XRD), Fourier-transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). Photocatalytic studies were investigated using UV-vis spectroscopy. The photocatalytic efficiency of the synthesized CoO-ZnO@rGO ternary nanocomposite was examined for the degradation of CIP before the test sample was which was mixed with CIP was kept in dark for 30 mins for adsorption desorption equilibrium later test was conducted under visible light irradiation under various time, drug concentration and pH. The results shows a good potential photocatalytic degradation of CIP for the synthesized ternary nanocomposite. Maximum removal efficiency of 96% was observed under pH 3, time 105, drug concentration 3mg/L.

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