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UV Accelerated Photocatalytic Degradation of Carbaryl Pesticide Using Nano ZnO

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Abstract

In recent years, nanotechnology has garnered significant attention and recognition due to its multifaceted contributions across diverse disciplines. Nano zinc oxide (ZnO) is a highly promising nano metal oxide that has found application in a wide range of areas, including fire retardancy, wrinkle reduction, and antimicrobial properties, among others. The wet chemical process was employed to synthesise nano zinc oxide, with Zinc nitrate hexahydrate as the precursor. The synthesised nano ZnO powder underwent characterization in order to determine its shape and physical properties. Four analytical techniques were utilised in this study. FTIR analysis was used to identify the functional group, X-Ray Diffraction was employed to determine the crystalline structure, SEM-EDX Analysis was utilised to investigate the

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morphological structure and size of the synthesised nanoparticles as well as to confirm the presence of specific elements, and Transmission Electron Microscopy was employed to determine the size and shape of the synthesised nanoparticles. The synthesised nanoparticles of zinc oxide (ZnO) were employed for the purpose of photodegradation of a solution containing the Carbaryl insecticide. The experiment involved the utilisation of a set concentration of 5 ppm of Carbaryl pesticide. Additionally, a catalyst consisting of 5mg/L of nano ZnO was introduced. The resulting mixture was then subjected to photodegradation through exposure to UV irradiation. The degradation of the pesticide was shown to occur at a rate of 95% within a 60-minute timeframe. The results demonstrate the significant photocatalytic degradation activity exhibited by the nano ZnO particles that were synthesised.

Keywords: Zinc Oxide nano particles, Carbaryl pesticide, photodegradation, and Ultra Violet irradiation.

Introduction

Pesticides are chemical substances that are applied to various settings, including public spaces, agricultural fields, and private gardens, with the aim of eliminating unwanted species. Pesticides have the potential to pollute several environmental components, including water bodies, soil, grass, and vegetation, while also serving their intended purpose of eliminating weeds and insects. Pesticides have been found to pose a significant threat to a diverse array of creatures, encompassing fish, birds, non-target plants, and helpful insects. The potential health consequences of pesticide exposure encompass a range of ailments, including but not limited to blisters, ocular irritation, visual impairment, dermatological reactions, gastrointestinal disturbances, vertigo, queasiness, and chronic conditions such as immune toxicity, developmental and neurological impairments, reproductive damage, congenital abnormalities, carcinogenesis, and disruption of the endocrine system [1-6]. Pesticide contamination is mostly attributed to the extensive utilisation of pesticides, as well as the formation of intermediates resulting from their breakdown and the presence of by-products. The enduring nature of this pollution can be attributed to its notable chemical stability, prolonged presence in the atmosphere, limited biodegradability, and insufficient breakdown through conventional means [7-9]. The escalation in the utilisation of larger quantities of pesticides has emerged as a significant apprehension for the preservation of groundwater, surface water, coastal, and marine ecosystems. The presence of pesticides in water resources has been widely recognised as a potential source of mutagenic agents due to the inclusion of materials that have the capacity to induce genetic alterations in DNA. Consequently, this phenomenon poses significant risks to both living creatures and ecosystems, resulting in substantial harm. According to statistics data from the World Health Organisation, it is observed that around one million individuals experience acute poisoning due to pesticide exposure annually, resulting in a recorded mortality rate ranging from 0.4% to 1.9% [10-11].

Carbaryl compounds are a class of insecticides that share structural and mechanistic similarities with organophosphate insecticides (OPs). The approval for its usage in insecticides dates back to 1959. Carbaryl, also known as 1-Naphthyl-N-methylcarbamate, is a widely used active ingredient that is commercially accessible in many trade names (Figures 1, 2). In addition to various other outdoor pests, this method is commonly employed for the control of ticks, aphids, fire ants, spiders, fleas, and other pests. Furthermore, it finds application in certain gardens to regulate the density of flowers on fruit trees. Carbaryl is classified as a cholinesterase inhibitor and poses a significant risk to human health. The classification of being a potential human carcinogen has been assigned to it by the United States Environmental Protection Agency (EPA). Contact with some substances has the potential to induce irritation on the skin and eyes, leading to the manifestation of a rash or a sense of burning. Exposure to some substances has the potential to induce poisoning, resulting in symptoms such as impaired visual acuity, feelings of nausea, excessive perspiration, emesis, and discomfort in the stomach region. The potential adverse effects of carbaryl include the manifestation of headaches, weakness, and respiratory difficulties, as well as its impact on the neurological system, kidneys, reproductive health, and potential carcinogenicity [12-17].

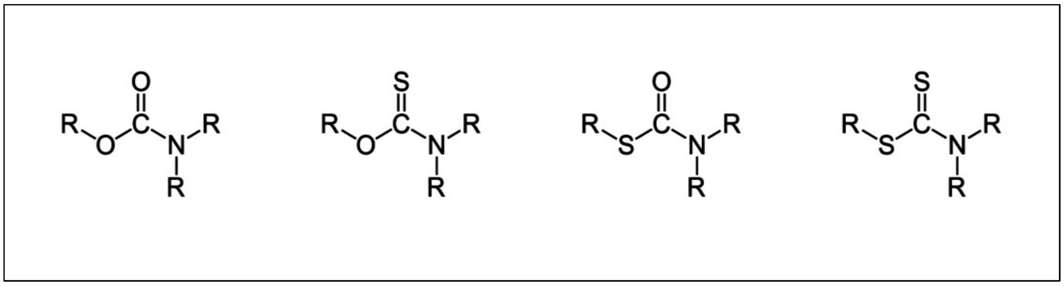

Figure 1: General structure of Carbamate molecules

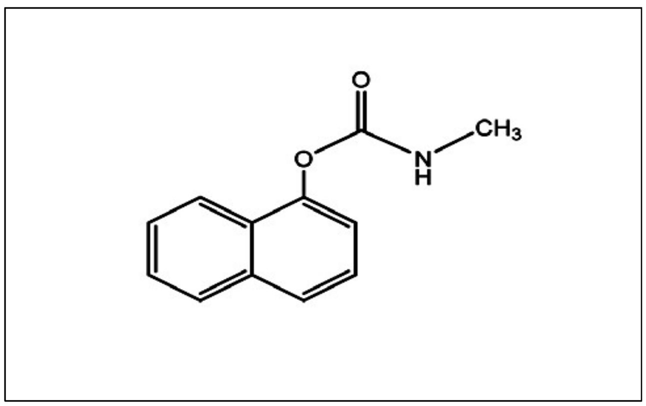

Figure 2: Structure of Carbaryl Pesticide

Given the aforementioned circumstances, it is imperative to advance the development of novel technologies that facilitate the efficient breakdown of these bio-recalcitrant molecules. In recent times, there has been a significant surge in the attention given to photo catalysis due to its advantageous characteristics such as affordability, environmental compatibility, and absence of secondary contaminants during the degradation of pesticides, organic pollutants, textile colours, and industrial waste. The utilisation of advanced oxidation processes (AOPs) has proven to be an effective approach in achieving the mineralization of such compounds, therefore offering considerable potential. The distinguishing characteristic of these AOPs is their ability to generate highly reactive free radicals with strong oxidising properties when dissolved in aqueous solutions. Heterogeneous photocatalysis has been proposed as an effective advanced oxidation process (AOP) for the removal of organic pollutants in water, as evidenced by several successful studies [18-21]. Nano metal oxides are materials of great importance that have a diverse variety of uses, including but not limited to energy production, medical technology, manufacturing of personal care products, water purification, and organic molecule synthesis [22]. There is a significant amount of research being conducted on semiconductor nano materials with the aim of effectively eliminating organic pollution compounds from bodies of water [23]. Zinc oxide, a semiconductor, has garnered significant interest due to its environmentally friendly nature, abundant availability, and lack of harmful constituents. Due to its appealing characteristics, such as photocatalysis, solar cell production, sensor applications, electrical device manufacture, and optical coatings [24-27], this substance has found widespread utilisation in various products. The objective of this research endeavour is to create economically viable photo catalytic nanoparticles and establish an efficient degradation technique for the rapid removal of carbaryl pesticide from water through the utilisation of Ultra Violet irradiation. In this study, nano zinc oxide particles were utilised as a highly efficient photocatalyst for the breakdown of carbaryl insecticide when exposed to Ultra Violet irradiation.

Materials and Methods

All the chemicals utilized in this work are Analytical-grade and utilized directly without any additional purification. Zinc nitrate and Sodium hydroxide are acquired from Sigma Aldrich and throughout the experiment, doubly distilled water is utilized whenever required. Zinc oxide nano particles are synthesized by the wet chemical method using Zinc nitrate hexahydrate as a precursor. The reason for choosing the wet chemical method for the synthesis of nano ZnO is to achieve nano particles of appropriate size of nano particles. The technical grade of Carbaryl pesticide available commercially is used for the degradation studies in this work.

Result and Discussion

Procedure for the Synthesis of Nano ZnO

All the reactions were conducted in an ambient conditionat room temperature. 0.2 M solution of $Zn(NO_3)_2$ and 0.4M NaOH were employed to synthesize nano ZnO particles by the wet chemical process. In a 500 ml of a beaker Zinc nitrate was dissolved in water, and added Sodium hydroxide drop-wise at room temperature by stirring continuously to form metal hydroxides. The stirring procedure was continued at 85 ^{0}C for 6 hours to obtain as-synthesized powder. Thus, the synthesized powder was calcined in a Muffle furnace at 600 ^{0}C for 2 hours and the furnace cooled. The resulting product was characterized by XRD, SEM, and EDAX [28].

Characterization of Catalyst

FTIR (Fourier Transmission Infrared) spectroscopy (Perkin Elmer-Spectrum RX-IFTIR) was employed to identify the functional groups present in the synthesized product. The X-Ray diffraction patterns were recorded on Bruker X-Ray Diffractometer using graphite filtered CuK radiation (λ=1.54 Å) at 40 KV with a scanning rate of 3/min (from 2θ=20-80°). Optical absorption spectra were recorded on a UV-Vis spectrometer (Shimadzu). The morphology and Size of the particles were determined by the 200 KeV Transmission Electron Microscope (TECNAI 200 Kv TEM- Fei, Electron Optics). The elemental composition of particles was determined by using SEM-EDAX (JEOL JSM 5600, EDS Model: INCA Oxford).

Fourier Transform-Infra Red Spectroscopy (FT-IR)

FT-IR analysis was done using optimized parameters to determine the bond structure and related functional groups of the synthesized ZnO nano particles. The FTIR absorption spectraof the synthesized particles were identified in the 4000-400 cm-1 wavenumber range (Figure 3). The band located at 436 cm-1 is attributed to the Zn–O stretching mode of the ZnO lattice [29-33]. The bands at 3466 cm-1 are attributed to the O-H mode of vibration. C=O exhibiting a strong asymmetric mode of vibration between 1633 and 1558 cm-1. The symmetric stretching occurs between 1508 and 1378 cm-1 because of the presence of C-O. C-O-C peak is also present there.

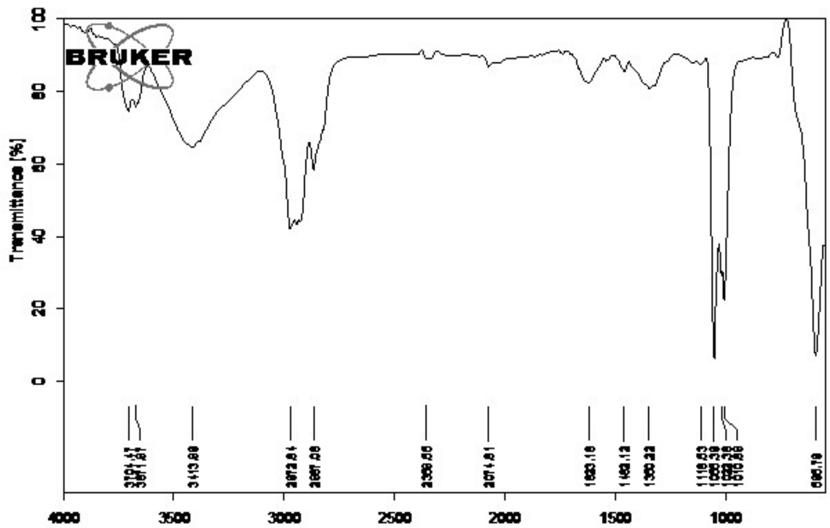

Figure 3: FT-IR spectrum of nano ZnO

X-Ray Diffraction (XRD)

Figure 4 shows the XRD spectrum of Zinc Oxide. The sharp diffraction peak determines about crystallinity and good size of the particles. The diffraction angle of 2θ scanned in the range of 20-80°. The peaks showed at 31.71, 34.37, 36.19, 47.49, and 56.51, determining the reflecting planes at (100), (002), (101), (110), and (200) respectively. All the diffraction peaks show a strong resemblance with the reported JCPDS (Joint Committee on Powder Diffraction Standards) belonging to the hexagonal wurtzite crystal phase of Zinc oxide

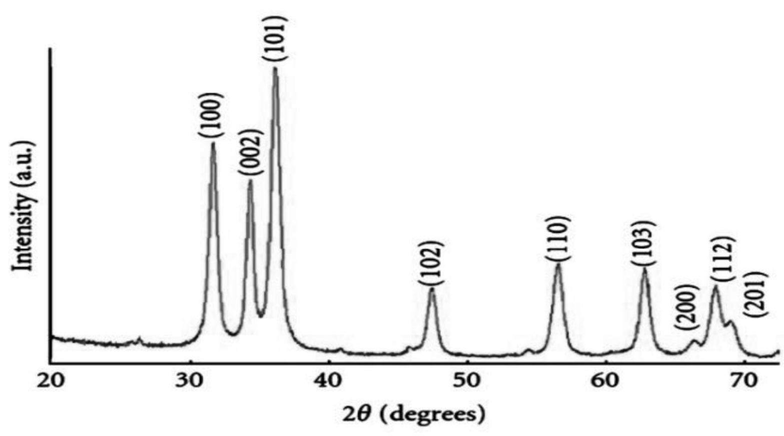

Figure 4: XRD pattern of Nano ZnO

UV-Visible Spectroscopy

Figure 4 shows the UV-Visible spectrum of nano Zinc oxide which is useful to determine the light-absorbing capacity of the synthesized particles. The synthesized Nano ZnO shows a notable high absorption peak at 364 nm. The UV-Visible spectrum showed that the synthesized nanoparticles had the ability to absorb visible light [34, 35]. The high absorbance intensity and the wider absorbance region reveal the effective photocatalytic behaviour of the synthesized nanoparticles when exposed to light.

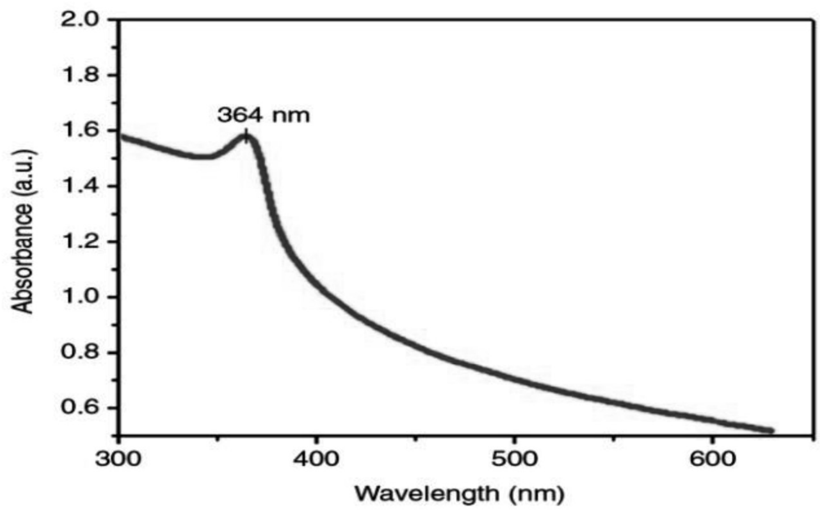

Figure 5: UV-Visible spectrum of nano ZnO

Scanning Electron Microscopy- Energy Dispersive X-Ray Analysis (SEM-EDX)

Figure 6 & 7shows the SEM and EDX of the synthesized nano ZnO respectively. The Morphological structure of the synthesized Zinc oxide nanoparticles was confirmed by SEM (Figure 6) and the elemental composition of the synthesized nanoparticles was confirmed by EDX (Figure 7[36-38]. The EDX spectra determine the presence of Zn and O and there is no other impurities were detected.

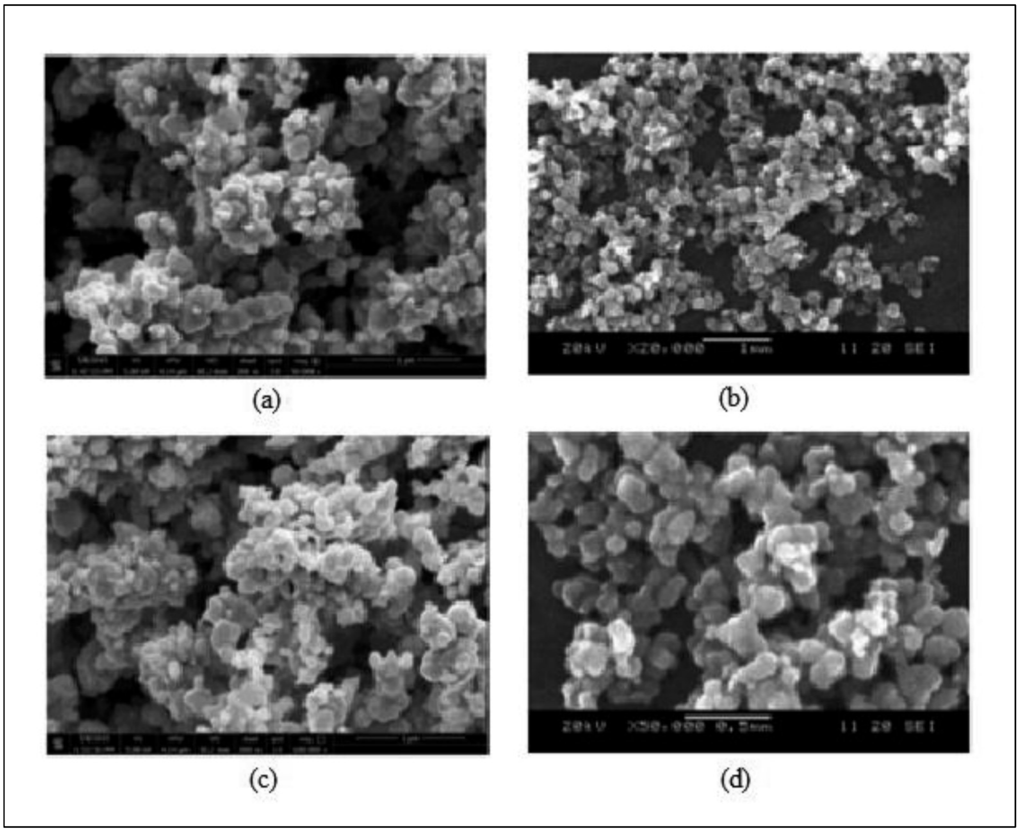

Figure 6: SEM images of nano ZnO

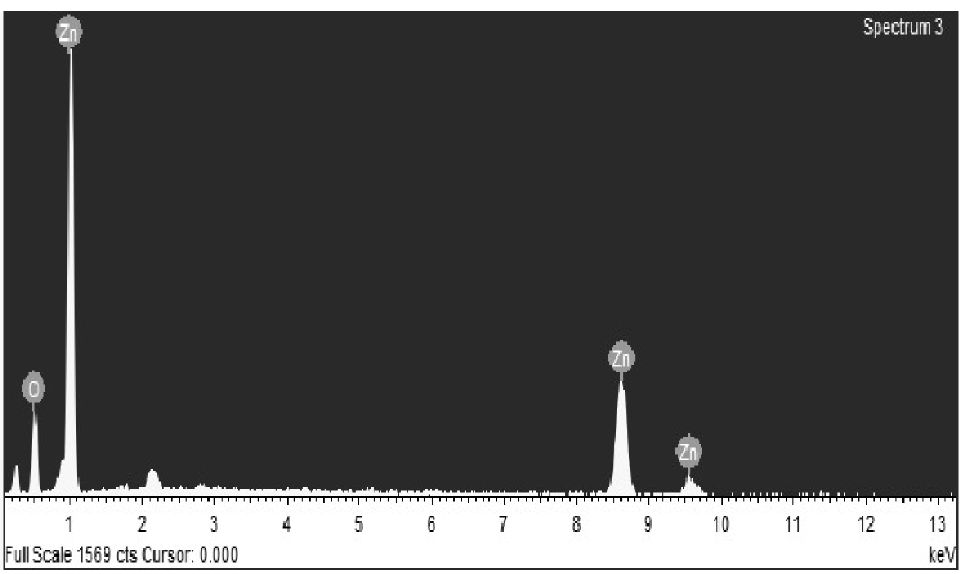

Figure 7: EDX spectrum of nano ZnO

Transmission Electron Microscope (TEM)

Figure 8 shows the Transmission Electron Microscope of nano ZnO. The samples were systematically analysed by TEM to notify the morphology and actual size of the particles. The TEM image of nano ZnO shows the presence of hexagonal wurtzite accumulated with a dimension of ~50 nm. The existing size of the nanoparticles was found to be around 30 nm. TEM image reveals that the morphology of the nanoparticle was hexagonal wurtzite.

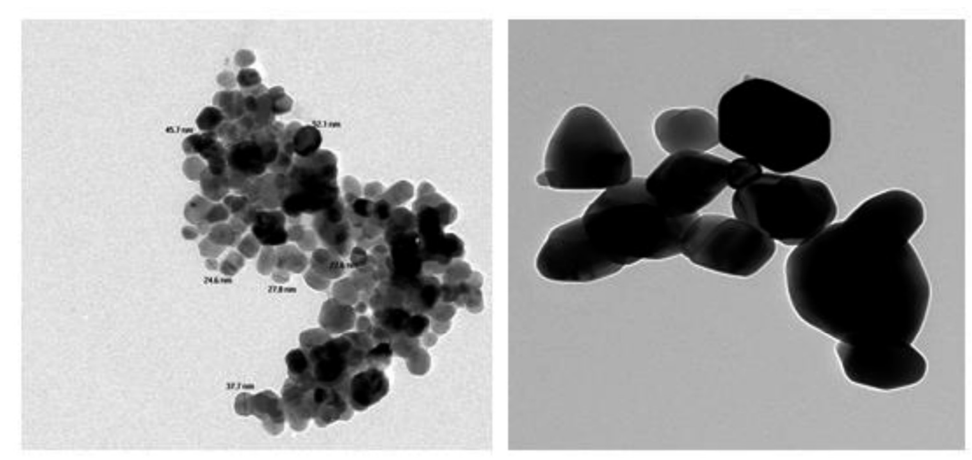

Figure 8: TEM images of nano ZnO

Experimental Section

Photocatalytic Degradation Studies

In the current study, the photodegradation of pesticides has been studied in aqueous dispersion under Ultra Violet irradiation using nano ZnO as a catalyst. The photocatalysis result indicates that the Zinc Oxide nano particles show good degradation efficiency. A volume of 250 ml of stock solution of 5 ppm concentration is prepared, and transferred into the reactor and 5 mg of nano ZnO was added as a photocatalyst. The suspension was initially stirred for half an hour under a completely dark environment to achieve the adsorption maximum. A stirring rate of 500 rpm was continued for the entire experiment. Later the solution was introduced to a UV chamber for UV irradiation with vigorous stirring for a fixed time. Within 60 minutes of the test solution being exposed to radiation, it was discovered that its colour had changed from a light blue to a clear, colourless liquid. The degradation efficiency of carbaryl was determined by the UV-VIS spectrophotometer. To measure the concentration of pesticide solution after being exposed to UV irradiation for each 10 minutes, approximately 5 ml of the test solution was taken out and centrifuged to remove the catalyst particles from the suspension. Using the provided formula, the percentage of degradation was determined.

% of degradation = (Co-C)/Co X 100

Where, Co is the initial concentration of the test solution and C is the concentration of the solution after photocatalytic degradation.

General Mechanism involved in Photodegradation

Photocatalysis involves the acceleration of a sequence of chemical events under the influence of light [39]. Photocatalysis is a contemporary oxidation process that relies heavily on hydroxyl radicals to facilitate the degradation of organic molecules inside aqueous environments [40]. When a photocatalyst is exposed to a photon possessing an energy level exceeding its band gap, the ensuing photocatalytic reaction is promptly initiated. When the electrons residing in the valence band undergo excitation and transition to the conduction band, the initiation of an electron-hole pair formation can be observed. Subsequently, oxygen molecules actively seek for the electron residing within the conduction band of the photo catalyst in order to form superoxide ions. The degradation of organic contaminants ultimately occurs through a continuous assault by hydroxyl radicals and superoxide ions [41]. The photocatalytic degradation process holds greater significance in comparison to alternative methods of degradation due to its enhanced effectiveness, absence of sludge formation, and ability to facilitate the environmentally acceptable elimination of organic contaminants from water [42]. The process described entails the creation of electrically charged particles in the presence of light using semiconductor materials. This, in turn, initiates a sequence of chemical events including the oxidation of heavy metals, the alteration of organic pollutants through redox reactions, and the reduction of carbon monoxide [43-45].

COD (Chemical Oxygen Demand) Analysis

The COD analysis typically provides a measure of the organic strength of industrial effluents. This analysis can estimate the total amount of oxygen required for the oxidation of organic compounds into carbon dioxide and water. Before and after degradation, the pesticide solution's COD was calculated. The pesticide contaminant's initial and final COD values were determined to be 11614 mg/L and 162 mg/L, respectively. The drop in COD values proved that both the colour and the pesticide molecules had broken down [46].

Total Organic Carbon (TOC) Analysis

TOC estimates the total amount of organic carbon for this degradation research. It is frequently employed to estimate the amount of organic carbon present in industrial effluent streams. Because it may be used to evaluate cutting-edge oxidation processes like photocatalysis, which was developed to decompose various inorganic and organic pollutants, it is seen to be more important [45]. It has been designed to break down a variety of organic and inorganic. Using nano ZnO through photo degradation, almost 95% of the organic carbon was removed from the carbaryl pesticide solution in forty minutes. This analysis shows that nano ZnO works well as a photocatalyst to break down pesticide contaminants. The catalyst's capacity for recycling. The photo catalyst's capacity to be recycled greatly increases the catalyst's application cost and stability [47]. The chosen nanocomposite was removed from the test solution by centrifugation after the degrading process was finished in order to test the manufactured nanoparticles capacity for recycling. The retrieved nanomaterial was cleaned in double-distilled water, filtered, dried, and used for the subsequent carbaryl pesticide degradation cycle. Further cycles of this method were carried out, and data on UV-Visible absorbance show that the degrading efficiency of carbaryl pesticide remained constant for five cycles. The fortunate recycling ability of the produced nano ZnO has thus been clearly specified.

Absorption Spectral Analysis

The photocatalytic degradation reaction was carried out employing nano ZnO as a photo catalyst in the presence of UV light. In order to track the degradation of carbaryl pesticides, the absorption spectra are periodically monitored. The photodegradation procedure is now more effective because it was possible to ascertain from this measurement how well the pesticide molecule relates to the nanoparticles. Figure 9 exhibits the outcomes. In the presence of nano ZnO, the highest absorption peak for the pesticide pollutant at 205 nm has been reduced at an astounding pace and has nearly vanished during thirty minutes of light illumination [48].

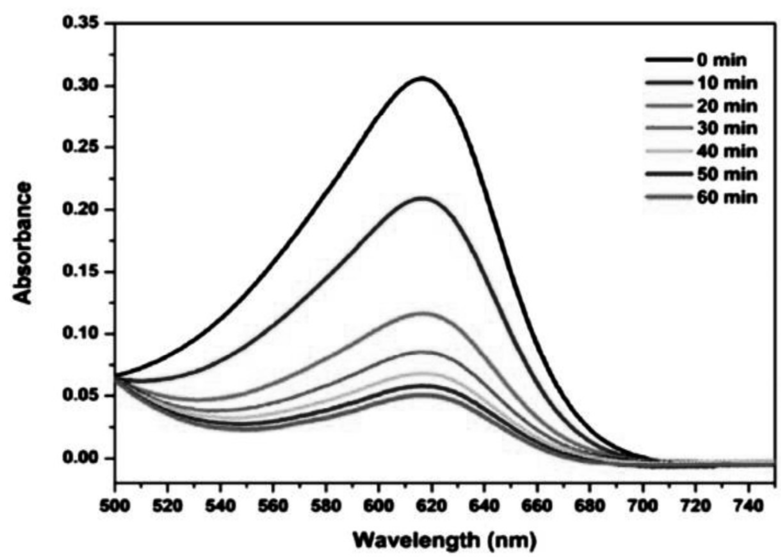

Figure 9: UV-Visible absorption spectrum for the degradation of carbaryl pesticide at different time intervals

Recycling Ability of the Catalyst

The recycling capability of the photocatalyst significantly enhances both the cost-effectiveness of its application and the stability of its performance. Following the completion of the degradation process, the nanoparticles that were chosen were separated from the test solution through the utilisation of centrifugation. This was done with the purpose of evaluating the recycling potential of the produced nanoparticles. The nanoparticles that were retrieved underwent a cleaning process using double-distilled water, followed by filtration and drying. These treated nanoparticles were then utilised in the subsequent cycle of carbaryl pesticide degradation. The aforementioned procedure was iterated for subsequent cycles, and the collected UV-Visible absorbance data indicates that the degradation efficacy of carbaryl exhibited a consistent trend over the course of five cycles. The recycling efficiency of the generated nano ZnO particles has been clearly demonstrated.

Conclusion

The wet chemical procedure was utilised to synthesise nano zinc oxide particles, and further characterisation confirmed that the size of the ZnO particles falls inside the nano range, around 50 nm. Additionally, the particles were seen to possess a spherical shape and a hexagonal wurtzite crystal structure. The experimental findings demonstrate the strong photo catalytic efficacy of nano zinc oxide when exposed to ultraviolet (UV) light. A significant reduction of 95% has been successfully attained in the overall organic carbon content of the carbaryl test solution, which initially contained 5 parts per million. The results obtained provide evidence for the significant photocatalytic degradation capabilities exhibited by the nano ZnO particles that were synthesised. The recycling capacity of the synthesised nanoparticles exhibits a notable capability in maintaining the purity of the catalyst. The current investigation has substantiated that the utilisation of nano ZnO for photo degradation, coupled with UV irradiation, represents a highly successful and economically viable approach for the expeditious remediation of wastewater and other organic contaminants prevalent in aqueous environments.

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