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RESEARCH PAPER

Photo-degradation of methylene blue dye using zinc oxide nanoparticles from citrus limon peel extract

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Abstract

Industrial waste containing organic pollutants must be managed using sustainable and environmentally friendly methods. A range of synthetic dyes discharged by the textile industry poses a significant threat to environmental safety. The use of dyes has increased across various industries, including food, leather, textiles, paper, cosmetics, and pharmaceuticals. However, the improper disposal of dyes into the open environment has led to significant issues affecting human health, aquatic ecosystems, and animal life. The photocatalytic degradation method utilizing metal oxide nanoparticles is the preferred approach among various dye remediation strategies. In this study, zinc oxide nanoparticles were synthesized through a green synthesis method using Citrus limon peel extract, which serves as a reducing agent. Metal oxides are regarded as the best photocatalysts due to their beneficial properties, cost-effectiveness, and durability. Zinc oxide nanoparticles have garnered significant attention for their unique antibacterial, antifungal, and UV-filtering properties, as well as their high catalytic and photochemical activities. The objective of this work is to synthesize zinc oxide nanoparticles and characterize them using scanning electron microscopy and X-ray diffraction. This paper highlights the role of the nanoparticles for eliminating the dyes from the industrial wastewater.

1. Introduction

Nanotechnology has been widely applied in the field of material science over the past decades. The concept was first introduced in a lecture by American physicist Richard Feynman in 1959 (Haleem *et al*., 2023) [1]. Nanotechnology involves the production of materials at the nanometer scale, typically ranging from 1 to 100 nanometers. This includes carbon nanotubes, metals with unique electrical and mechanical properties, and nanoparticles (Mamalis *et al*., 2004) [2]. The rise of nanoscience has led to the emergence of a new interdisciplinary field worldwide, fostering a greater appreciation for science at the nanoscale (Schummer, 2004) [3]. Metal and metal oxide nanoparticles have diverse applications across physics, chemistry, biology, engineering, and material science. The consolidation of nanoscience and biology has attracted many researchers (Chavali & Nikolova, 2019) [4]. The removal of organic contaminants from wastewater, particularly those originating from dyes, remains a significant concern of many countries (Tkaczyk *et al*., 2020) [5]. Indeed, environmental contamination caused by dyes leads to health issues due to their toxicity (Islam *et al*., 2023) [6]. Dyes are organic compounds used in various industries, such as textiles, paper, plastics, leather plastics, food printing and pharmaceuticals, electroplating and agriculture. Freshwater without contamination is essential for not only domestic use but also important in agriculture and industrial use (Mushtaq *et al*., 2020) [7]. Highly contaminated water is discharged from chemical industries due to the high consumption of dyes in these industries. It has been estimated that almost 10 - 15 % of dyes are not bound and discharged into the effluent (Maheshwari *et al*., 2021) [8]. Dyes are more difficult to biodegradable because of their complex molecular structure (Shi *et al*., 2021) [9]. It should be noted that these industries use considerable quantities of water and consequently their wastewater containing dyes in significant

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quantities are discharged into natural waters (Kant, 2011) [10]. Moreover, these dyes, preventing the penetration of solar light into water reduce photosynthetic activity and thus cause a disturbance of aquatic equilibrium. The most suitable way to eliminate this waste is their degradation by photocatalysis (Rauf & Ashraf., 2009) [11]. In fact, dyes can be degraded in the presence of photocatalyst when irradiated with visible light due to their absorption in the visible region (Chen *et al*., 2001) [12]. The discharging of the dye from the industries will affect the environment and the living which are surrounding these industries (Khattab *et al*., 2020) [13]. The workers in these industries are the ones who are mainly affected by several problems like allergic reaction in the eyes, skin problems allergies and hair problems etc (Olusegun & Martincigh, 2021) [14]. Direct contact with the dye solvent by the workers in that textiles industries results in causing a carcinogenic effect. From the textiles dye will cause the environment to be polluted and lead to the death of aquatic animals (Gita *et al*., 2017) [15]. The textiles effluent will affect the photosynthetic activity of the plant and also pollute the soil. Hands the toxicity and carcinogenic potential of dyes present in industrial effluent necessary to explore and effective method towards water treatment using highly active and reusable photocatalyst (Ismail *et al*., 2019) [16]. Out of the organic dye methylene blue [MB] placed under cationic dye category and a heterocyclic aromatic compound, has been extensively consumed in textile industries as synthetic coloring agent for cotton, wool and silk. Consequently, discharge of effluent containing methylene blue MB is a cheap root cause for causing harmful effect such as nausea, diarrhea, eye burning, vomiting, etc. In addition, inhalation of methylene blue dye and its contact with skin main cause poisonous effect. Therefore, methylene blue dye from industrial influence is highly decisive to safeguard the environment (Oladoye *et al*., 2022) [17]. The photocatalyst degradation of methylene blue dye using zinc oxide nanoparticles involving using zinc oxide nanoparticles as a catalyst to break down methylene blue under the light irradiation (Jang *et al*., 2006) [18]. This process utilizes the semiconductor properties of zinc oxide to generate electron hole pairs upon light absorption, which then react with the dye two degrade it (Lam et al., 2012) [19]. This process often called photocatalysis is an environment friendly way to remove dyes from waste water (Bal & Thakur, 2022) [20]. Dyes are more difficult to biodegrade because of their complex molecular structures. Effluents from the industries containing reactive dyes causes serious environment pollution because the presence of dyes, in water is highly visible and affects their transparency and aesthetic even if the concentration of dyes is low. Lemon is an important medicinal plant of the family *Rutaceae*. (Mohanapriya *et al*., 2013) [21]. It is cultivated mainly for its alkaloids which are having anticancer activities and the antibacterial potential in crude extracts of different parts of lemon against clinically significant bacterial stain have been reported (Ewansiha, 2020) [22]. The synthesized nanoparticles were yellowish white and their UV-vis spectra showed the characteristics maximum peak at 332 nm which affirmed the formation of zinc oxide nanoparticles (Aldalbahi *et al*., 2020) [23]. Zinc oxide nanoparticles showed excellent catalytic activity of 50.25% photodegradation of methylene blue dye under natural sunlight irradiation for 120 minutes (Nnodim, 2022) [24].

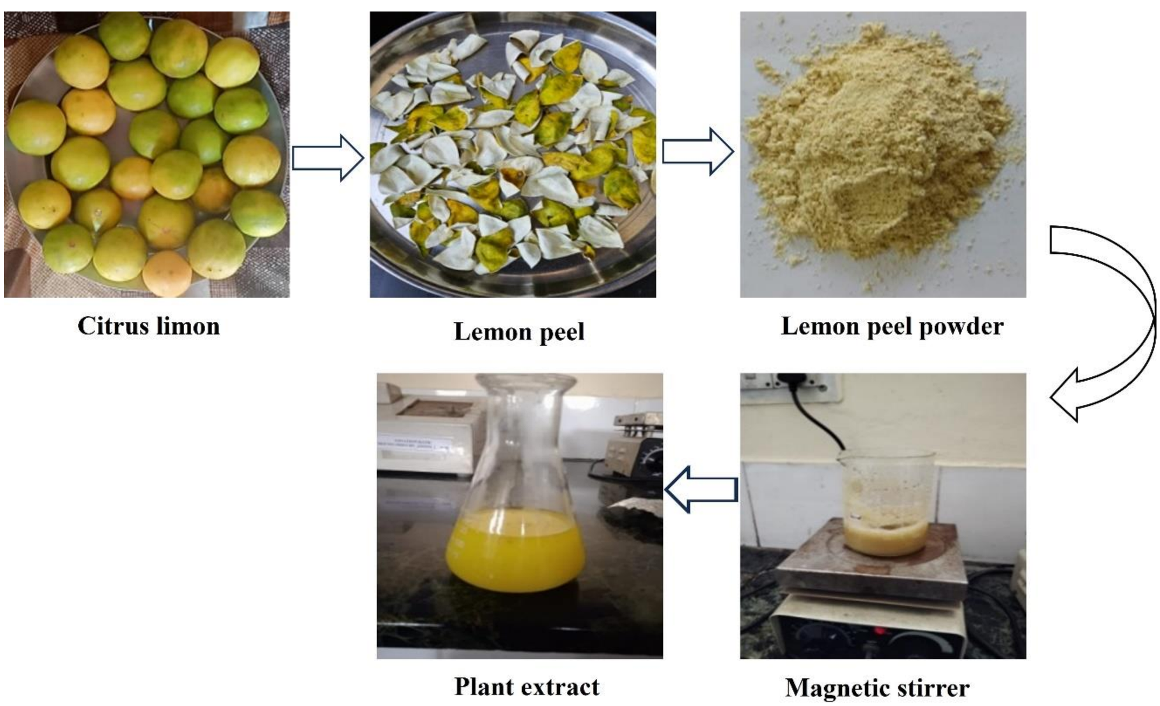

Figure 1: Flowchart of preparation of plant extract.

2. Material and methods

2.1 Chemicals

Zinc acetate hexahydrate, Sodium hydroxide, Methylene blue dye and Ethanol were used as purchased. Distilled water will be employed to prepare all solution.

2.2 Instrument

Digital weighing balance, hot air oven, magnetic stirrer centrifuge, sonicator, autoclave, digital pH meter, X-ray diffraction, UV visible spectrophotometer, scanning electron microscope, Transmission electron microscope and FTIR employed as major instrument.

2.3 Preparation of plant extract

Firstly, healthy lemon fruits were collected from local market. Green and yellow fruits peels were used for the synthesis of zinc oxide nanoparticles (ZnO NPs). The peel was washed with double distilled water to remove external impurities present on the peel and left in shadow for 10 days to dry up. Dry peel was crushed in a mixture grinder to obtain its powder form. About 5 gm of powdered peel were taken in hundred ml of distilled water and then boiled at 80^0 C for 20 minutes and filtered through whatman 41 filter paper to remove insoluble impurities. The resultant filter was stored at 4^0 C (Fig. 1).

2.4 Green synthesis of Zinc oxide nanoparticles

In the synthesis of zinc of zinc oxide nanoparticles lemon peel extract was used as a reducing agent. 0.93 gram of zinc acetate dissolve in 50 ml of the deionized water using a magnetic stirrer for 10 minutes at 40 degree celcius .Then ,2gm NaOH mix in 50 ml distill water at room temperature using a magnetic stirrer for 10 minute .Both the solution mix properly and keep it for 1 hour at magnetic stirred. Then ,a milky colour appear . After 1 hour add 25 ml plant extract and put the solution at magnetic stirrer for 3 hour. The yellowish precipate was observed ,which was collected by centrifugation at 8000 RPM and washed with ethanol for further purification . The prepared nanoparticles were dried in an oven at 80^0 C for 8 hour and stored in an air tight vial (Fig. 2).

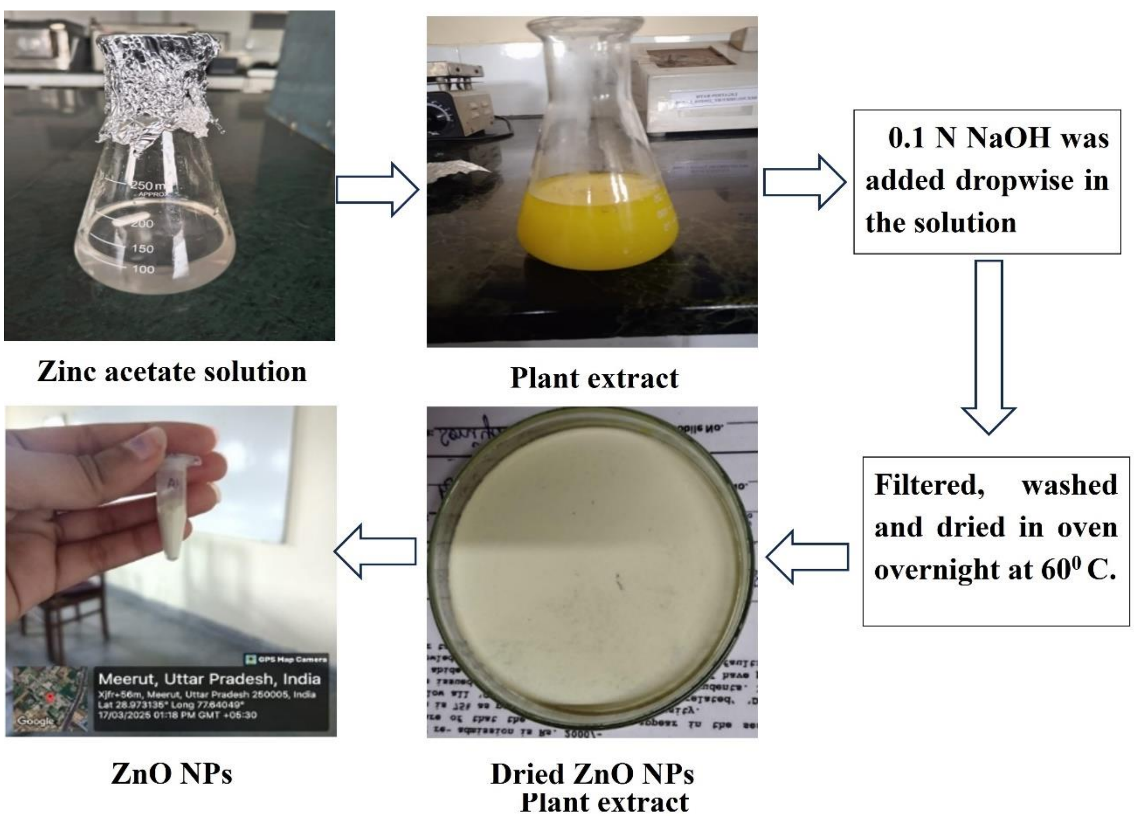

Figure 2: Flow chart of green synthesis of zinc oxide nanoparticles (ZnONPs)

2.5 Preparation of methylene blue dye solution

10 PPM of methylene blue dye aqueous solution were prepared by dissolving 5mg of methylene blue powder in 500 ml volumetric flask containing deionized water .The resulting mixture was magnetically stirred on a magnetic stirring hotplate for 30 minutes to ensure homogenous dye solution (Fig. 3).

Figure 3: Photocatalytic degradation of methylene blue

The photodegradation of Methylene blue was detected in the presence of zinc oxide nanoparticles under sunlight exposure and the decrease in absorbance was determine by using a UV-vis spectrophotometer. In an aqueous solution of methylene blue 10 PPM, photocatalyst prepared from different concentration of mass 5 mg was added separately. At regular interval of time, the reaction was observed spectrophotometrically at room temperature. Reaction mixture color started to fade revealing that degradation had started (Fig. 4).

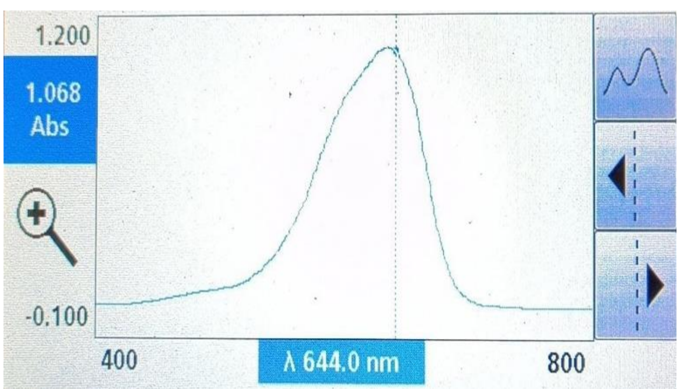

Figure 4: Absorption peak of methylene blue dye

3. Result and Discussion

3.1 Phytochemical screening of lemon peel extract

The term phyto is derived from the Greek word which means plant. The naturally occuring chemical substance present in plant are called phytochemicals (Doughari, 2012) [25]. The phytochemicals have either favourable or unfavourable effects on human health (Dillard & German, 2000) [26]. The phytochemicals ingredient in a plant determine its medicinal value. Personally, plants were utilized directly but currently active ingredient have been detected and extracted in the purest form. Different solvent used for the extraction process are ethanol, water, benzene, and methanol. The detection of phytochemicals in plant assists in the prediction of any plant in the application of pharmacology (Doughari, 2012) [25].
The phytochemical screening is observed in aqueous extract. Various phytochemicals present in the aqueous extract were alkaloid, flavinoid, cardiac glycosides, saponins and reducing sugar. UV visible absorption spectra of zinc oxide nanopartcles.

3.2 UV -visible absorbtion spectra of ZnO NPs

UV –vis spectroscopy serves as one of the best method for characterizing nanoparticles . UV –vis spectra of lemon peel extract showed a strong peak at 331nm at pH 9. The result in entirely according to the Mostafa *et al*., 2021 [27] in which AgNPs using orange peel extract. The UV –vis absorption of all three combination of zinc oxide also so the strong peak at 332 nm. UV-vis spectroscopy was carried out to confirm the formation of the nanoparticles of zinc oxide and to estimate the band gap value (Hamam & Alomari, 2017) [28]. Optical absorption of bioreduced zinc oxide nanoparticles was study by UV visible spectrophotometer and to recorded absorbtion spectrum of zinc oxide and a particles is given below. ZnONPs display its characterstics absorption band at 352 nm that has stretched to blue region with respect to bulk absorption is (app. 400 nm) of zinc oxide nanoparticles due to nanosizes effect. Band gap energy of zinc oxide (ZnO) linked to photon and absorbance energy was determined from intercept of tangent to the plots of photons energy and it was found to be 3.16eV (Siahsahlan et al., 2025) [29].

3.3 Determination of Percentage of Degradation

By using absorbance obtained from the Cmax in visible region of the dye solution , MB dye solution is at 664nm respectively , the percentage of the dye degradtion was estimated using the formula below ;
Percentage of dye Degradation = [Ci –Cf]\Ci X 100 where,
Ci = Initial absorbance of dye solution
Cf = Absorbance of dye solution at a given contact time .

3.4 Photocatalytic activity

The photocatalytic activities of the synthesized zinc oxide ZnO nanoparticle were evaluated via the phoyodegradation of methylene blue (MB) under sunlight irradition (Atchudan et al., 2016) [30]. Prior to illumination, 10 mg photocatalist was added to the dye aqueous solution (10 mL,10 ppm). The solution was stirred in the drk for 20 minutes in order to achive absorption-desorption equilibrium, then the photocatalytic reaction was started. The photocatalyst will then be exposed to the sunlight for the desired time at 40^0 C. UV-Visual is absorption spectra of MB absorbance with respect to time for ZnO-80 and ZnO-180. The aqueous solution of the MB molecules exhibits two peaks, one at 664 nm has a progressively blue shift to shorter wavelength (Fig. 5(a) because of hypochromic effect (Mantasha et al., 2020) [31]. In the presence of ZnO-80, the absorption of MB decreased sharply after 30 min. Initialy, the absorption peak at 664 nm was much large than the absorption peak at 615 nm which gives a big difference between their intensities. After 30 min, this difference is attenuated, thus indicating that the rate of degradation of the monomers is much higher than that of the dimers . In addition to the decrease in the intensities of the two peaks , a slight shift towards the blue of the bands located at 664 nm also observed . This is caused by the N-demethylated degradation concomitant with the degradation of phenothiazine.

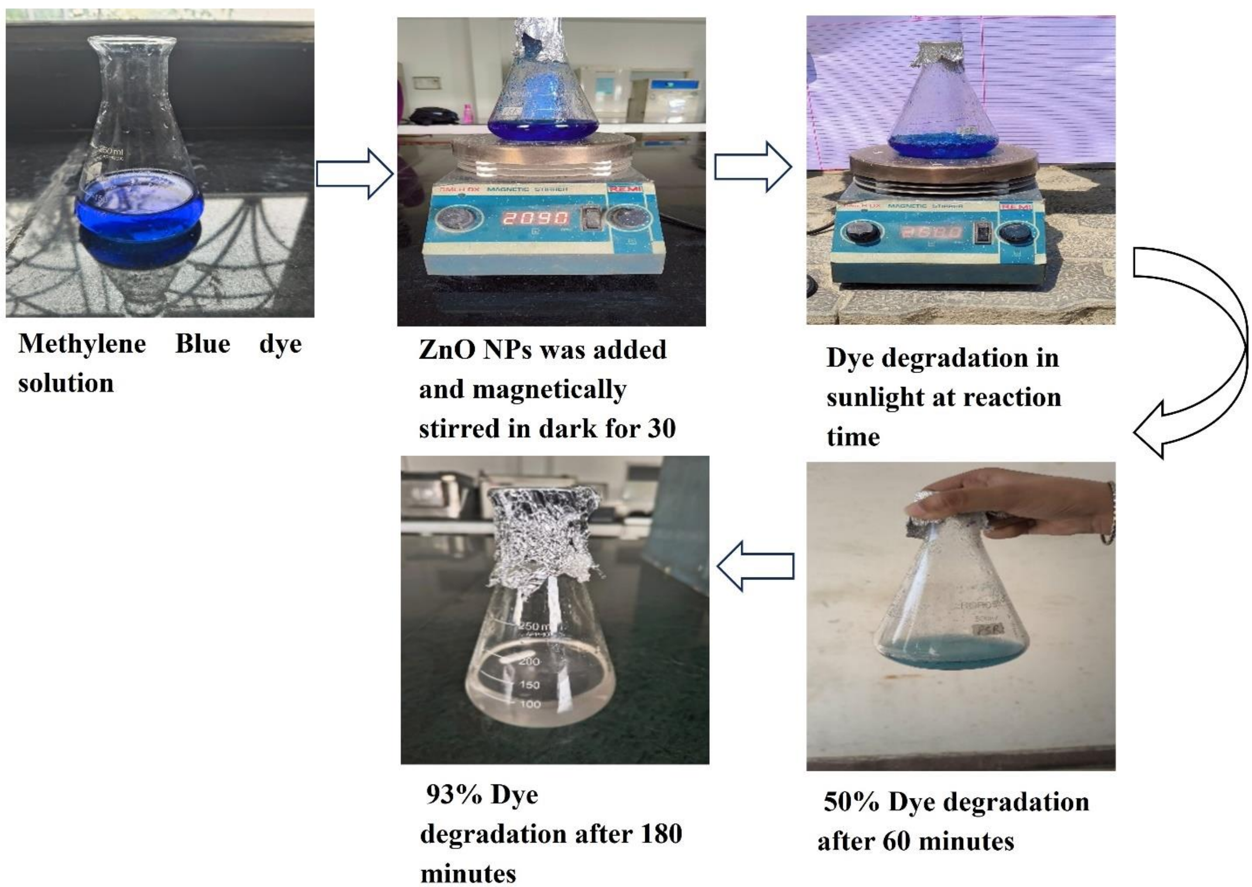

Figure 5: Flowchart of photo-degradation of methylene blue Dye with respect to time

Fig. 5 illustrates the UV-Vis absorbance spectra of methylene blue (MB) dye during the photocatalytic degradation process facilitated by zinc oxide (ZnO) nanoparticles. The absorbance peak observed at 644.0 nm corresponds to the characteristic absorption wavelength of MB. Initially, the absorbance is 1.068 Abs, indicating a high concentration of MB in the solution. As the photocatalytic reaction proceeds under light irradiation, the intensity of the peak decreases significantly, which signifies the reduction in MB concentration over time. Complete degradation of MB is observed after irradiation for 60 to 180 minutes using ZnO nanoparticles. This implies that the ZnO nanoparticles act as effective photocatalysts, accelerating the breakdown of MB molecules. The consistent decrease in absorbance with time confirms the photocatalytic activity of ZnO NPs, making them highly suitable for wastewater treatment and dye removal applications. Additionally, a comparative analysis (as presented in the associated table, not shown here) highlights that the ZnO nanoparticles synthesized in this study outperform other reported ZnO-based photocatalysts in terms of degradation efficiency and time. This clearly establishes the superior performance of the current ZnO nanoparticles, making them a promising material for photocatalytic environmental applications.In fact the photocatalyst degrade almost 100 percent of MB in a shorter period of time than the zinc oxide nanoparticles synthesized by using various plant extract (Table-1).

Table 1: Degradation of methylene blue dye at a particular time interval

S.No	Photo- catalyst	Pollutants	Initial Dye concentration	Time in minutes	Final Dye concen-tration	Degradation efficiency % =((Ci-Cf) / Ci) x100
1	ZnO	Methylene Blue(MB)	0.421	15	0.415	1
2	ZnO	MB	0.421	30	0.402	4
3	ZnO	MB	0.421	45	0.361	14
4	ZnO	MB	0.421	60	0.308	26
5	ZnO	MB	0.421	75	0.295	29
6	ZnO	MB	0.421	90	0.291	30
7	ZnO	MB	0.421	105	0.171	58
8	ZnO	MB	0.421	120	0.164	61
9	ZnO	MB	0.421	135	0.112	73
10	ZnO	MB	0.421	150	0.065	84
11	ZnO	MB	0.421	165	0.051	87
12	ZnO	MB	0.421	180	0.029	93

4. Conclusion

Using an eco-friendly method, ZnO nanoparticles were successfully synthesized utilizing Citrus limon (lemon) peel extract. Waste lemon peel was successfully utilized in the synthesis of ZnO nanoparticles. The synthesized ZnO nanoparticles exhibited a yellowish-white mass in the reaction mixture, confirming their formation. The successful synthesis of the desired nanoparticles was confirmed using standard characterization techniques, including UV-vis spectroscopy, FE-SEM, HR-TEM. FTIR, and XRD analysis. The UV-vis spectroscopic analysis showed the absorbance peak at 332 nm which indicated the formation of ZnO NPs. FE-SEM revealed irregular shape of nanoparticles without distinctly defined morphology. The synthesized ZnO NPs by using optimum concentration of precursor, when used in optimum dose, resulted in notable degradation of 50 percent to 93 percent under solar irradiation. It is anticipated that the as synthesized photocatalyst will be a valued agent for the photocatalyst removal of persistent water pollutant dyes and assist in environment detoxification.

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