Short Communication

Green synthesis of zinc oxide nanoparticles using *Punica Granatum* leaf extract and its application towards photocatalytic degradation of Coomassie brilliant blue R-250 dye

Karanpal Singh[1] · Jagpreet Singh[2] · Mohit Rawat[2]

Abstract

Green synthesis method for nanoparticle synthesis offers many advantages over physical and chemical methods as it does not involve any hazardous chemicals and also it is a one-pot, and economically cheap process. In this regard, the present research describes the green synthesis of Zinc oxide nanoparticles (ZnO-NPs) using *Punica granatum* leaf extract. The various properties such as morphological, structural, and optical properties of green zinc oxide nanoparticles were characterized by Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy, UV–Visible spectroscopy, Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Spectroscopy and X-Ray diffraction (XRD). The XRD pattern revealed the crystalline nature of ZnO-NPs and the average diameter of particles is 20 nm.TEM and FESEM analysis show the spherical shape of ZnO-NPs with size ranging from 10 to 30 nm. The synthesized ZnO-NPs shows the commendable potential towards the photocatalytic degradation of Coomassie brilliant blue R-250 dye under direct sunlight irradiations. Thus, this work provides a positive step in the area of a green photocatalyst to alleviate the noxious dyes from water.

Karanpal Singh and Jagpreet Singh have equally contributed to this work.

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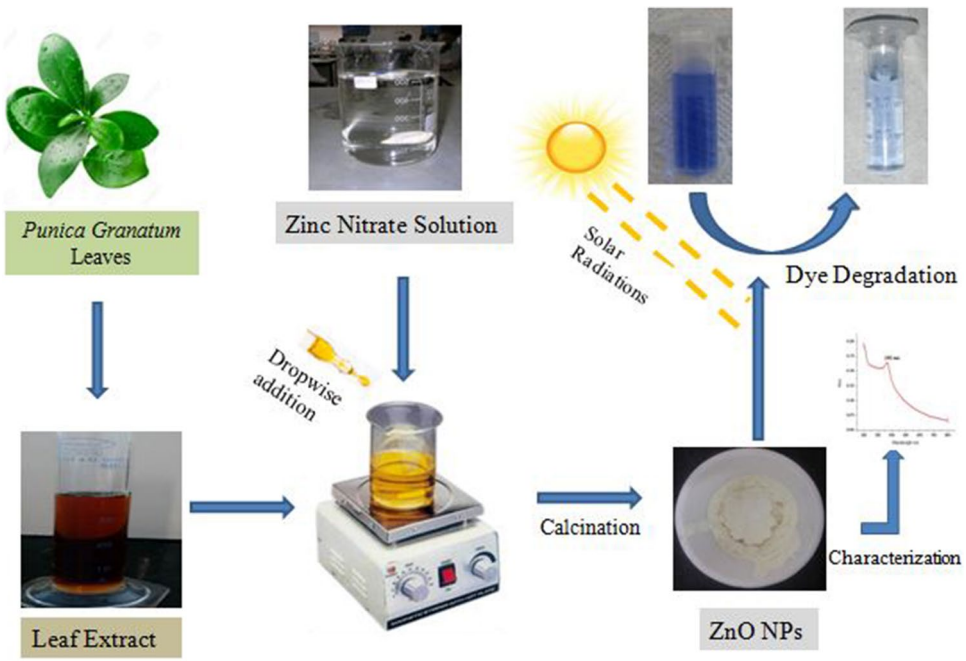
Graphical abstract



Keywords Green synthesis · Zinc oxide nanoparticle · Photocatalytic · Coomassie brilliant blue R-250

1 Introduction

Advances in nanotechnology has led to the production of new nano-sized materials having a range of applications, such as in nanoelectronics, nanomedicine and consumer products [1, 2]. These materials have gained much importance in recent years due to their outstanding physical and chemical properties compared to their bulk counterpart. Nanostructures of many metal oxides have been synthesized having several applications in different fields. Zinc Oxide (ZnO) is a large band gap (3.3 eV) semiconductor. It has applications in solar cells, gas sensors, dye degradation and many more [3]. Zinc oxide nanoparticles have been synthesized using various chemical and physical methods including Sol–Gel [4], precipitation [5], arc discharge [6], hydrothermal [7], pulsed laser ablation [8]. Green synthesis method has been employed to synthesize zinc oxide nanoparticles due to many advantageous over physical and chemical methods as it does not involve hazardous chemicals and is eco-friendly and cost-effective [9, 10]. It uses the biological materials which are easily extractable from plants.

Punica grantum plant leaves were used as they are easily available. The pomegranate (*Punica granatum*) is the predominant member of two species comprising the Punicaceae family. The phytochemicals present in this plant leaf extract contains triterpenic acids, alkaloids, tannins, flavonoids [11]. These phytoconstituents act as stabilizing and reducing agents and synthesize metal oxide nanoparticles by chemical reduction. As per our knowledge till date, no report has been found on the use of leaves of *P. granatum* for the synthesis of ZnO-NPs (Fig. 1).

Dyes are organic compounds used in food, paper, leather industries, and textile mills. The effluents from these industries contain dyes that are strongly colored and toxic in nature. The effluents are released into water bodies contaminating surface and ground water, posing potential health hazards to aquatic life, humans, animals and the

Fig. 1 *Punica granatum* plant

environment. The effluent should be treated before discharge to degrade the dye into a non-toxic form. Depending on the nature of pollutant, various purification techniques such as physical, chemical or biological have been developed. ZnO NPs had been successfully used for dye degradation [12–14]. Reactive oxidative hydroxide radicals are formed through catalytic photooxidation using ZnO NPs, that degrade the dyes. Coomassie brilliant blue R-250 is an organic compound classified as a disulfonatedtriphenylmethane dye, reflecting its chemical structure. It was developed for textile industry purposes but are now commonly used for staining proteins in analytical biochemistry. Along with the efficiency of degradation, the catalyst should be stable and reusable as stability and reusability are important tools for industrial applications. As the ZnO-NPs are stable and reusable as revealed by various studies [15, 16].

In the present work, green synthesis method has been employed to synthesize ZnO-NPs using *P. granatum* leaves extract. The green synthesized ZnO NPs are employed towards the photocatalytic degradation of Coomassie brilliant blue R-250 dye under direct sunlight irradiations.

2 Materials and methodology

2.1 Materials

Punica granatum leaves were collected from a nearby garden. Zinc Nitrate Hexahydrate AR (96% purity) was purchased from Merck Chemical Reagent Co. Ltd. India. Deionized distilled water was used throughout the experiment. Coomassie brilliant blue R-250 dye was purchased form the textile industry in Ludhiana, India. All chemicals are used without further purification. Prior to use, all the glass wares were washed first with a freshly prepared Piranha solution (3:1 volume ratio of Concentrated H_2SO_4/H_2O_2), followed by deionized (DI) water of 18.2 MΩ.cm resistivity (Labostar, Singapore) and finally dried in oven.

2.2 Methodology

2.2.1 Preparation of *Punica granatum* leaf extract

Fresh leaves of *P. granatum* were collected from a nearby garden in Fatehgarh Sahib. Midrib of the leaves was removed. The leaves were washed with deionized water to remove dust and then dried in shade for so that all the moisture is removed. *Punica granatum* leaf aqueous extract was prepared. In this, dried leaves were weighed and then ground in a pestle and mortar to get fine powder. Then, the dried fine powder was added in deionized water. The mixture was heated at 60 °C for approximately 3 h, until the green color changes to brownish color as shown in Fig. 3. Allow it to cool for 10–15 min at room temperature. The solution was filtered through Whatman No. 1 filter paper and the filtrate was collected in the flask and the residue was discarded. The aqueous extract was stored at room temperature for further use (Fig. 2).

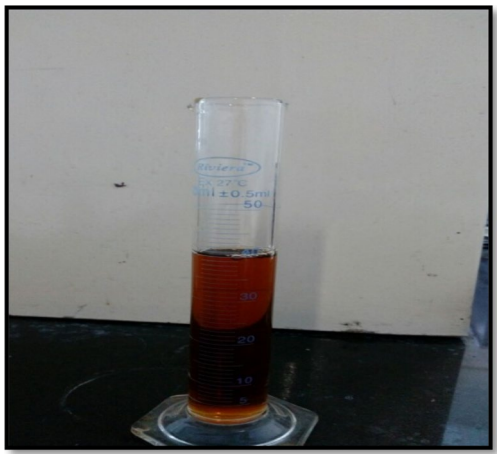


Fig. 2 Sample of leaves extract of *Punica granatum* plant

2.2.2 Green synthesis of zinc oxide nanoparticles (ZnO-NPs)

A solution of (Zn $(NO_3)_2 \cdot 6H_2O$ (0.1 M) was prepared in deionized water. The mixture was stirred without heating on magnetic stirrer to completely dissolve the zinc nitrate powder. After that aqueous leaf extract was added dropwise to the zinc nitrate solution kept on a magnetic stirrer. After the addition of leaf extract, the mixture was heated and stirred for 3–4 h at 60 °C. Then the mixture was heated on a hot plate until the mixture turns into jelly form. The jelly product was taken and put into a crucible. The crucible was kept in the furnace for calcination at 400 °C for 3–4 h. After calcination, zinc oxide nanoparticles were obtained in white colored powder form as shown in Fig. 3.

2.2.3 Photocatalytic activity of ZnO NPs

The photocatalytic activity of the ZnO nanoparticles was determined by the photodegradation of Coomassie brilliant blue R-250 dye in aqueous solution under sunlight. For this the dye which was in powdered form was dissolved in deionized water such that the absorbance of the solution is greater than one. ZnO NPs which act as catalyst were added in the aqueous solution and the solution was

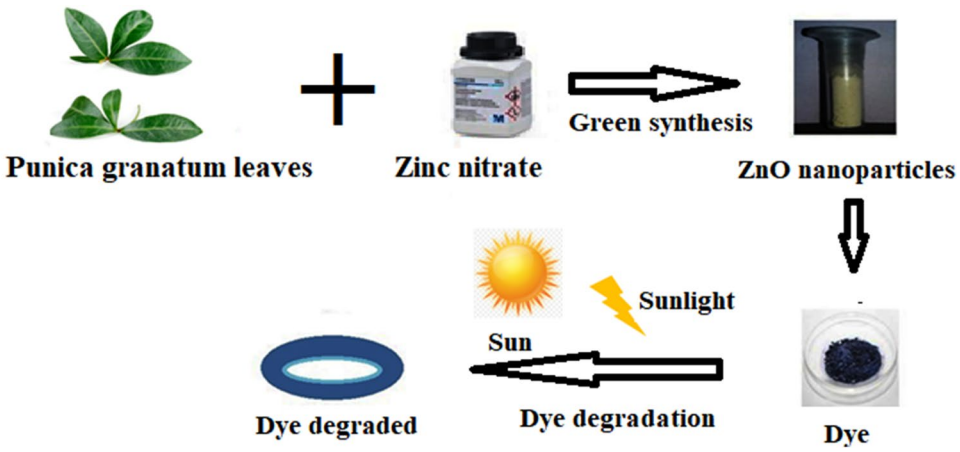


Fig. 3 Stepwise procedure of green Synthesis of ZnO-NPs and dye degradation

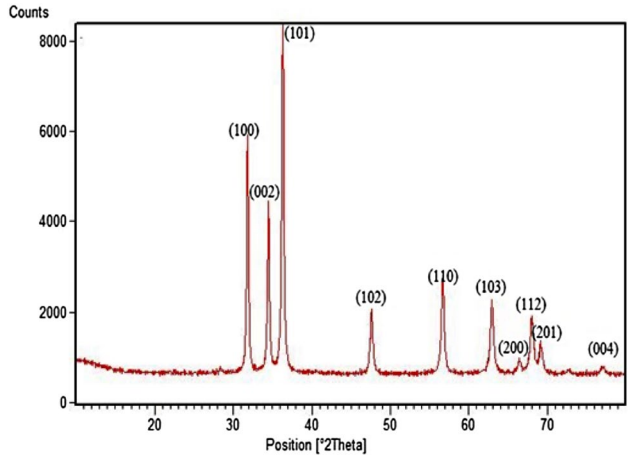


Fig. 4 XRD pattern of the synthesized ZnO nanoparticles using *P. granatum* extract

sonicated. Then the solution was kept in sunlight with continuous stirring. After 30 min of time interval; 4 ml of the solution was centrifuged to pellet down the catalyst and the absorbance of the supernatant was measured using UV–Vis spectrophotometer. After each interval the absorbance decreased, indicating the degradation of dye by ZnO NPs.

2.2.4 Characterization of ZnO NPs

X-ray diffraction of powdered zinc oxide nanoparticles was performed using a PANalytical X-ray diffractometer. Transmission Electron microscopy analysis was done using a Hitachi HF 3300 TEM machine. The UV–visible spectrum of zinc oxide nanoparticles was recorded using Shimadzu UV 2600 spectrophotometer. Fourier transform spectroscopic measurements were done using a Bruker Alpha FTIR spectrometer. Chemical purity and stoichiometry of the samples were investigated using Oxford instruments EDX. The particle dimensions and morphology of the prepared ZnO nanoparticles was examined by Carl Zeiss Field emission scanning electron microscope (FESEM).

3 Results and discussion

3.1 X-Ray diffraction analysis

Figure 4 represents the X-Ray diffraction pattern of zinc oxide nanoparticles in powder form. The sample was characterized using PANalytical X-Ray diffractometer. The sample was analyzed at a range of angles from 0° to 100°. The prominent x-ray diffraction peaks exhibited by ZnO nanoparticles are at $2\theta = 31.81°$, 34.49°, 36.28°, 47.62°, 56.63°, 62.91° and 67.97° and could be indexed as (100), (002), (101), (102), (110), (103) and (200) respectively. The XRD pattern revealed orientation and crystalline nature of ZnO-NPs. The XRD pattern has been compared with JCPDS data sheet/ICDD no. 36-1451. This clearly confirms that ZnO-NPs have been successfully synthesized by green synthesis method confirming the formation of crystalline and wurtzite hexagonal structure. The particle diameter of ZnO-NPs was calculated from the highest peak (101) in the XRD graph according to Debye–Scherrer's Equation given below:

$$d = K\lambda/\beta \cos\theta$$

where, d is the crystallite size, λ is the diffraction wavelength, β is the corrected FWHM, θ is the diffraction angle and K is a constant and is close to unity i.e. 0.94.

The average particle diameter of ZnO-NPs came out to be around 20 nm. Phase purity of ZnO-NPs is confirmed as no diffraction peaks of other phases are detected.

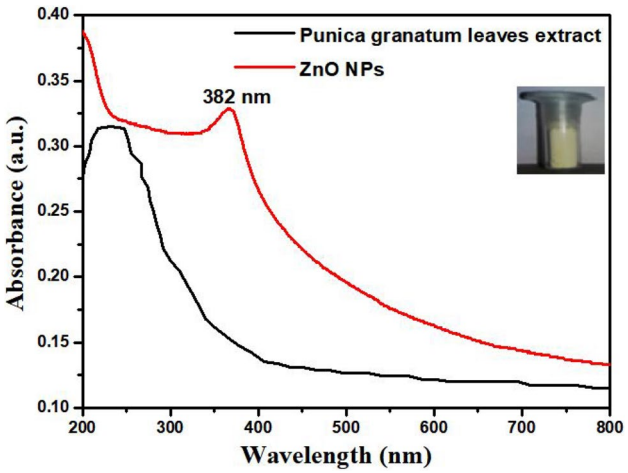


Fig. 5 UV–visible spectrum of ZnO NPs and *P. granatum* leaves extract. (inset: photograph of synthesized ZnO NPs)

3.2 UV–visible analysis

The absorbance pattern of nanoparticles is different as compared to their bulk counterpart because of surface plasmon resonance and by UV–visible analysis synthesis of nanoparticles is confirmed. Figure 5 represents the UV–visible absorption spectrum of ZnO-NPs. UV–visible spectrum was measured in a quartz cuvette using Shimadzu UV spectrophotometer by analyzing the sample in the range of 200–800 nm. The addition of *P. granatum* leaf extract to zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$] solution resulted in color change of the solution from white to brown due to the formation of ZnO-NPs. The color changes arise from the excitation of surface plasmon vibrations with the zinc oxide nanoparticles. It was observed that the absorbance peak was centered near 382 nm, indicating the reduction of zinc nitrate hexahydrate into ZnO-NPs [17–19].

3.3 TEM analysis

Transmission Electron microscopy analysis was done using a Hitachi HF 3300 TEM machine. Figure 6 shows the TEM images of the synthesized zinc oxide nanoparticles. TEM images reveal that green synthesized ZnO-NPs are polycrystalline with spherical structure and the size of the nanoparticles was found to be in the range of 10–30 nm which is close to the value obtained from the XRD data. The TEM images at higher resolution also give information that nanoparticles are not in physical contact but are separated by uniform inter-particle distance.

3.4 FESEM and EDX analysis

There are varieties of ZnO nanostructures that had been discovered such as nanospheres, nanorods and many more. FESEM is used to visualize and analyze every small topographic detail and thus used to determine the particle dimensions and morphology. The particle dimensions and morphology of the prepared ZnO nanoparticles was

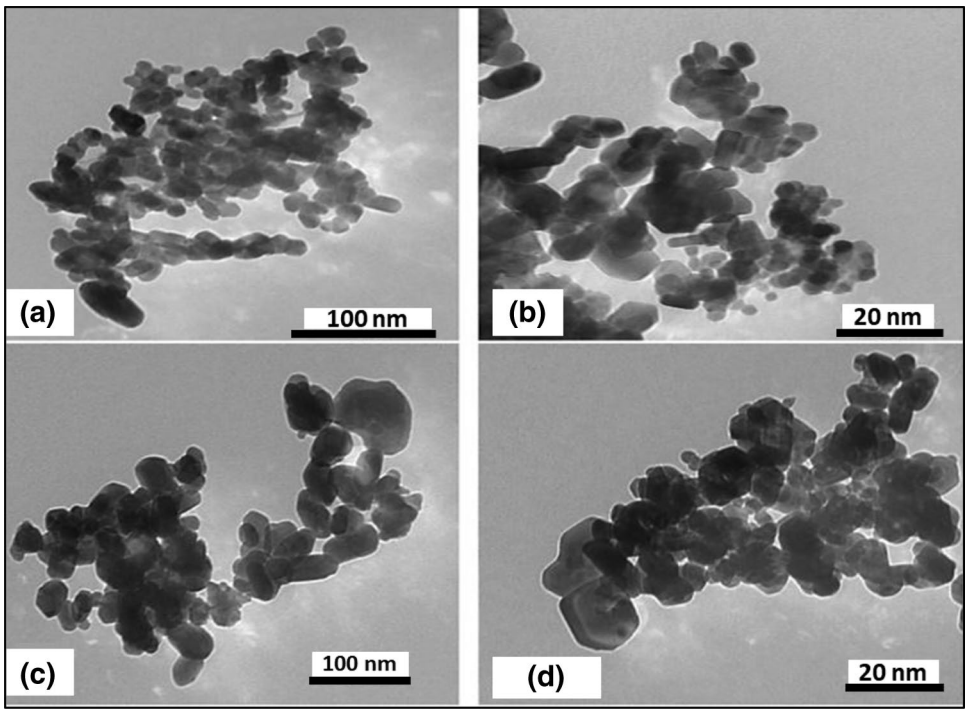


Fig. 6 Schematic shows TEM images of ZnO NPs

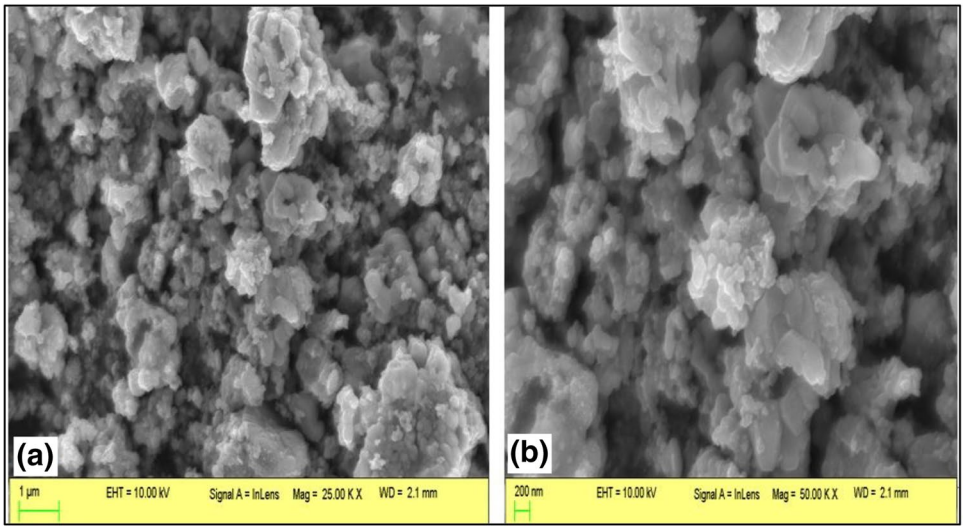


Fig. 7 FESEM images of ZnO NPs

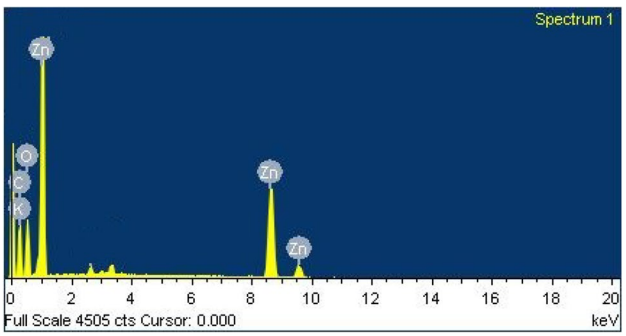


Fig. 8 EDX spectrum of ZnO NPs

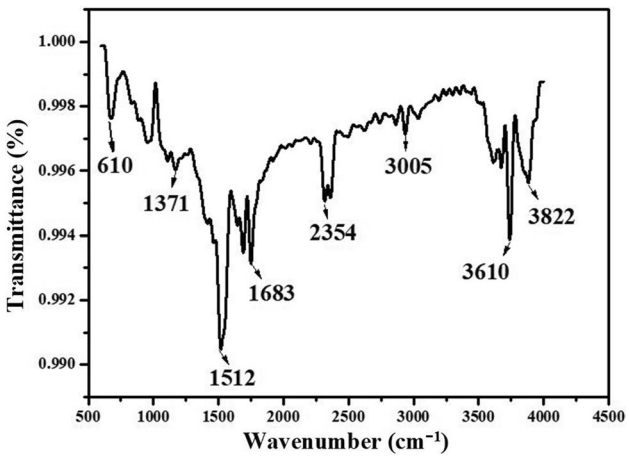


Fig. 9 FTIR spectrum of ZnO NPs

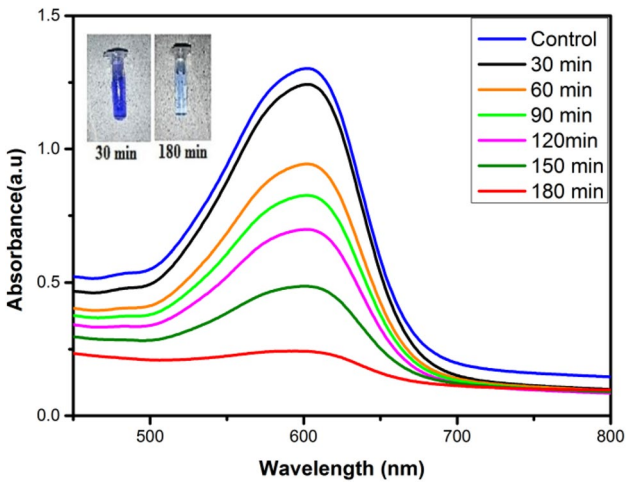


Fig. 10 UV–vis absorption spectum showing photocatalytic degradation of Coomassie brilliant blue R-250 dye using Zinc oxide nanoparticles at different time intervals

examined by Carl Zeiss Field emission scanning electron microscope (FESEM). Figure 7 shows FESEM images of green synthesized ZnO nanoparticles. From this image, it is clearly judged that the particle is in nanostructure form. All the nanoparticles are in spherical shape and the average particle diameter is 20 nm which corresponds to the XRD result.

The element analysis or chemical characterization of green synthesized ZnO nanoparticles was done using EDX. Chemical purity and stoichiometry of the samples were investigated using Oxford instruments EDX. Figure 8 shows the EDX spectrum of ZnO nanoparticles. The EDX spectrum confirms the presence of ZnO and O ions in ZnO nanoparticles synthesized using *P. Granatum*. The elemental analysis showed 76% of Zinc and 15% of oxygen, respectively suggesting that the ZnO powder has good purity and very little impurities can be seen. Theoretically expected the stoichiometric mass percent of Zinc and Oxygen are 80.3% and 19.7%.

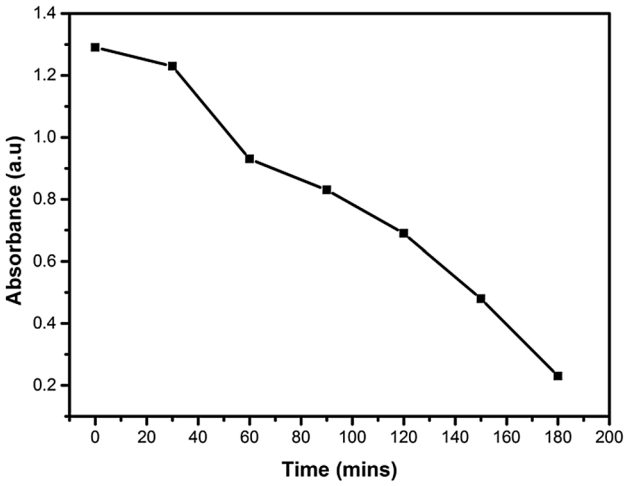


Fig. 11 Schematic shows the reduction of Coomassie brilliant blue R-250 dye intensity with time

3.5 FT-IR analysis

FT-IR spectroscopy measurements are carried out to confirm the presence/formation of Zn–O bond and to identify the phytoconstituents that are capped on ZnO-NPs surface. Fourier transform infrared spectroscopy was done using a Bruker Alpha FTIR spectrometer. FT-IR spectrum of green synthesized ZnO-NPs is shown in Fig. 9. The spectral peaks 3610 cm^{-1} and 3822 cm^{-1} are due to O–H stretching. The peak around 2354 cm^{-1} is due to C–H stretch. The peak around 1512 cm^{-1} is due to the C=O stretching. The peaks at 1683 cm^{-1} corresponds to ZnO bending deformation vibrations. The strong vibrational bands at 610 cm^{-1} are assigned to the stretching modes for the formation of ZnO nanoparticles. Hence FT-IR study reveals that ZnO-NPs are protected from being aggregated by the phytoconstituents of *P. granatum* by stabilizing the surface of nanoparticles during the synthesis process [17–19].

3.6 Photocatalytic activity

The photodegradation of Coomassie brilliant blue R-250 dye under sunlight was studied by measuring the decrease in the absorbance of the dye in the presence of the prepared ZnO nanopowders. The absorbance of the dye solution decreased with increasing time of exposure, indicating a decrease in the concentration of Coomassie brilliant blue R-250 dye. It was clearly observed that with time the intensity of the blue color of the dye solution decreased gradually and became light at last. The time-dependent degradation of Coomassie brilliant blue R-250 for the samples under sunlight is shown in Fig. 10. The optimum absorbance peak of Coomassie brilliant blue R-250 was found to be 600 nm. It also shows that the ZnO-NPs can degrade the pollutant drastically in the 3 h.

3.6.1 Recyclability and photostability

The recyclability of the photocatalyst has been checked through three cycles of the photocatalysis process. It was observed that the negligible decline in the photocatalytic degradation efficiency of ZnO NPs as shown in Fig. 11a. Also, XRD results after photocatalysis process indicate that the crystal structure of ZnO remains same as before the photocatalytic process as depicted in Fig. 12b.

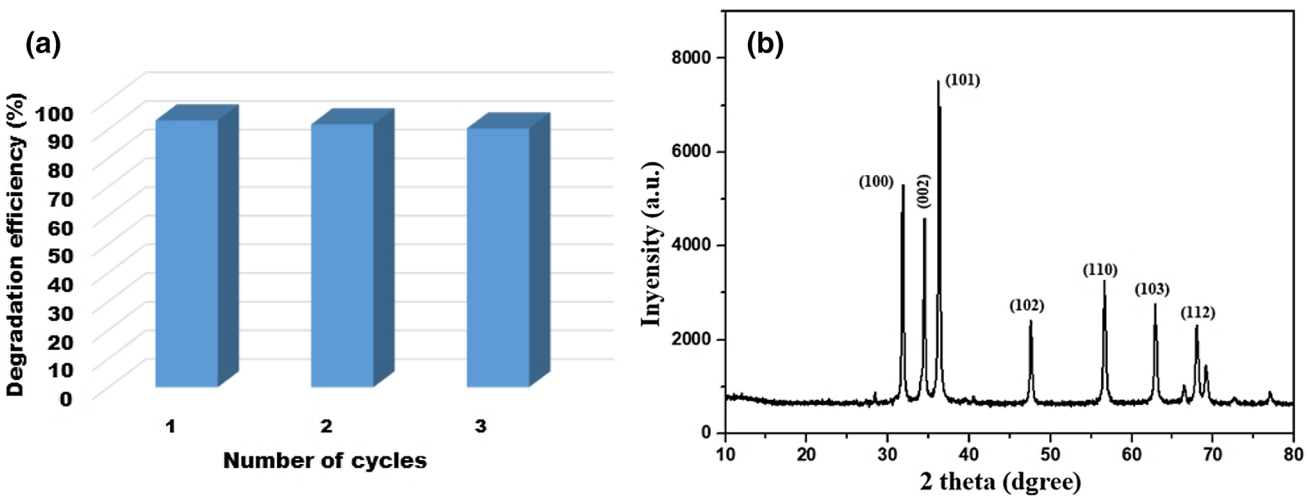


Fig. 12 Schematic shows the **a** degradation efficiency after three cycles and **b** XRD pattern of ZnO NPs after photocatalytic process

4 Conclusion

In the present research, ZnO-NPs have been successfully synthesized via a green synthesis method using an aqueous leaf extract of *P. granatum*. The spherical, polydispersity of ZnO-NPs of particle sizes ranging from 10 to 30 nm with an average size of 20 nm are obtained. All the nanoparticles are in the spherical shape and the average size of particles is 20 nm. The EDX analysis showed 76% of Zinc and 15% of oxygen, respectively suggesting that the ZnO powder has good purity and very few impurities. The photocatalytic study shows an effective photodegradation of Coomassie Brilliant Blue dye R-250 by the biosynthesized ZnO-NPs with degradation efficiency ~ 93%. Thus, this study signifies that the non-toxic, cheap, simple and eco-friendly method to synthesize ZnO-NPs using the leaf extract of *P. granatum* and their effective utilization as a green photocatalyst for practical applications in wastewater treatment.

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Compliance with ethical standard

Conflict of interest The authors declare that there are no conflict of interest regarding the publication of this manuscript.

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