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Novel Biogenic Synthesis of Stable Monodispersed Zinc Oxide Nanoparticles for Photocatalytic Degradation of Methylene Blue

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Abstract

Greener methodology for the synthesis of Zinc oxide Nanoparticles (ZnO NPs) is the most preferred method owing to its facile, simple, economical and non-hazardous properties. In this research work, ZnO NPs were synthesized by adopting a novel facile biogenic route in the presence of *Gentiana kurroo* plant extract, which acts as a capping as well as reducing agent. Optimization of ZnO NPs was done by controlling various parameters including pH, incubation time, temperature, salt and plant extract concentration etc. Additionally, the successful formation of ZnO NPs has been investigated using UV/VIS and FTIR analysis techniques. The photocatalytic efficiency of ZnO NPs showed excellent photocatalytic degradation of Methylene Blue (MB). The photodegradation performance was 89% which was achieved in 90 min.

Introduction

Nanotechnology has gained huge importance due to its potential applications in different fields of life including catalysis, agricultural products, food applications and medical treatments [1,2]. The nanoscale particles (1-100nm) showed excellent performance in different applications as compared to the micro-sized particle mainly due to greater surface area. Among different nanomaterials, ZnO NPs have been considered as highly promising and greatly versatile nanomaterial [3]. ZnO NPs are semiconductor material and possess a wurtzite structure. ZnO NPs can be used in different fields including optoelectronics, sensing, medical field and energy generation [4,5]. ZnO NPs can be synthesized by different physical and chemical approaches like thermal evaporation [6], pulsed laser deposition (PLD) [7], ion implantation [8], reactive electron beam evaporation [9], co-precipitation method [10], sol-gel technique [11], hydrothermal method [12], thermal decomposition [13], and green synthesis [14]. Among all the synthetic methodology green synthesis of ZnO NPs are of considerable importance due to its ecofriendly and cost-effective approach. Additionally, enzymes, proteins, plants, fungi, bacteria, and algal extract have been used for the biogenic synthesis of NPs [15-19]. These biogenic extracts act as both reducing and stabilizing agents [20]. Bhuyan et al. [21] synthesized ZnO NPs through a biogenic route in the presence of *Azadirachta indica* extract that acts as a stabilizing and reducing agent. They used this photocatalyst for photodegradation of MB dye and in antibacterial activity. Ngoepe et al. [22] used *Monsonia burkeana* plant extract for greener synthesis of ZnO NPs and found that ZnO showed good antibacterial activity. Numerous other plant extracts have been used for the biogenic synthesis of ZnO NPs but still no study has reported the synthesis of ZnO NPs in the presence of *Gentiana kurroo Royle* extract.

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Gentiana kurroo (family Gentianaceae) is commonly known as "Nilkanth" in Kashmir Himalayas. The phytochemical studies showed the presence of Tannins, Alkaloids, Saponins, Glycosides (Gentiopicrine, Gentianine), Terpenes, Flavonoids, Phenolics, Carbohydrates, Genianic Acid, Pectin iridoid glycosides, the alkaloid Gentianin in the root and rhizome of plant [23,24]. The roots of the plant are used as a bitter tonic, antiperiodic, expectorant, astringent, stomachic, anthelmintic, antipsychotic, anti-inflammatory, antioxidant and anti- bacterial [25]. The chemical composition of the extract was dominated by the presence of sulphur-containing compounds like dimethyl sulphide, 2-methyl sulphide, 2-ethylfuran and 2pentylfuran constituting 36.1% of the total identified components [26]. The presence of antioxidants in the *Gentiana kurroo Royle* extract imparted excellent reducing properties which significantly affect the preparation of metal nanoparticles. Hence, this study was an attempt to make use of *Gentiana kurroo* Royle plant roots as a raw material for the preparation of ZnO NPs and photocatalytic efficiency was investigated by using MB as a model contaminant.

Experimental

Materials

Zinc chloride ($ZnCl_2$, 97%), Sodium hydroxide (NaOH, 98%), Sodium Borohydride ($NaBH_4$, 97%) Ammonia (NH_3, 98%), Methylene blue (98%) were purchased from Sigma Aldrich. All chemical were used as received no need to use further purification processes. Other material used here includes *Gentiana kurroo roots*. *Gentiana kurru* plant was taken from the Botanical Garden of University of Punjab, Lahore, Pakistan.

Preparation of plant extract

Roots of *Gentiana kurru* plant were washed with tap water and then distilled water, dried and fully ground to obtain a fine powder. 10g of *Gentiana kurru* plant powder was added into 300-400 ml of distilled water and boiled for about 4-5 hr which then centrifuged at 4000 rpm for 20 min. The extract was then filtered and centrifuged for 20min to obtain a clean extract.

Synthesis of ZnO NPs

For ZnO NPs synthesis hydrothermal synthetic route was adopted. For this purpose, 8ml metal precursor salt (1mM) solution was taken and pH (12) was maintained with the addition of drop wise 3M NaOH solution till solution become turbid. Then whole mixture was refluxed at a temperature of 100^{O}C for a period of 2h. Then mixture was centrifuged at 4000 rpm/25 min and dried in an oven for a period at 90 ^{O}C/6 hr. Synthesized ZnO NPs were then calcined in a muffle furnace at 600 ^{O}C/1 hr.

Biogenic synthesis of ZnO NPs

In three necked round bottom flasks 24 ml aqueous solution of 1mM Zinc Chloride solutions, 3ml of 2.5% rhizome extract of *Gentiana kurroo* royle and 3M sodium hydroxide solution were mixed and the sample was refluxed for 2 hr at 100 ^{O}C. This product was then centrifuged for 25 min at 4000 rpm, washed with deionized water and dried in an oven 6 hr/90 ^{O}C. These synthesized precipitates were then calcined in a muffle furnace at 600 ^{O}C/1 hr.

Protocol to investigate photocatalytic performance of ZnO NPs

The photocatalytic performance of ZnO NPs was investigated by using MB as a model reaction. Photocatalytic decolorization of methylene blue dye was not observed in the absence of photocatalyst due to the high activation energy barrier. The same experiment was performed in the presence of photocatalyst by adding 30 mg of ZnO NPs, 1 ml (10 ppm) of MB solution, 1ml of deionized water in quartz cuvette and the sample was then sample scanned at a various interval of time. A decrease in the absorption spectra peak from 665nm was observed which indicates the degradation of MB.

Characterization

Ultraviolet-visible spectrophotometer analysis was performed by using UVD-3500 Lambda, Inc. USA used to explain the optical properties of ZnO NPs. Functional group analysis was done by FTIR spectrophotometer.

Result & Discussion

The successful synthesis of ZnO NPs via the hydrothermal method (ZnO_1 NPs) and through facile novel biogenic route in the presence of *Gentiana kurroo* Royle stabilizing agent (ZnO_2 NPs) have been investigated using UV/VIS spectrophotometer (Figure 1,2). Figure 1 shows that ZnO_1 NPs have λ_{max} at 370 nm and 380 nm before and after calcination while ZnO_2 NPs exhibited a distinctive peak at 360 nm. The peak noticed in Figure 2 showed increase in wavelength and red shift after calcination mainly due to large particle size at higher temperature. Additionally, absorbance values show decline with the decrease in particle surface area. The UV-Vis spectra of ZnO_2 NPs showed the sharpness of the peak indicates the monodispersity of ZnO NPs. Table 1 showed the change in particle size before and after calcination. Sangeetha et al. [27] also reported the synthesis of ZnO NPs by chemical as well as green method. The particle size of nanoparticles can be calculated as follow

$$r(nm) = \frac{-0.3049 + \sqrt{-26.23012 + \frac{10240.72}{\lambda_p}}\ (nm)}{-6.3829 + \frac{2483.2}{\lambda_p}\, nm} \quad \text{(Eq 1)}$$

Here, r is the size of nanoparticles in nm while λ_P is value of absorbance at maximum wavelength (nm).

Table 1: Showed the change in particle size of ZnO NPs before and after calcination.

Sample name	*Particle size* (before calcination)	*Particle size* (after calcination)
Chemical method ZnO_1	2.73 nm	3.07 nm
Green method ZnO_2	2.29	1.4M

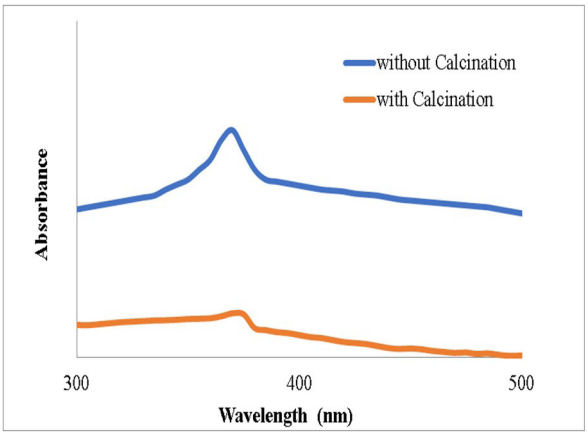

Figure 1: UV/Vis of ZnO NPs synthesized in the absence of stabilizer.

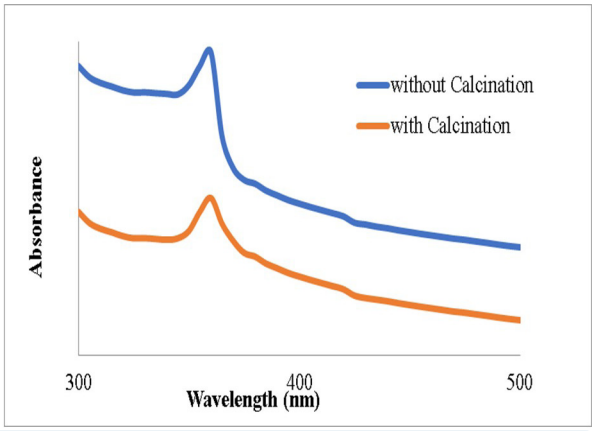

Figure 2: UV/Vis analysis of ZnO NPs synthesized by using rhizome extract of Gentian kurroo royle.

Optimization parameters for ZnO NPs

ZnO NPs prepared at various amount of $ZnCl_2$ salt solution like 0.01M, 0.05M and 0.1M etc. The UV-Vis spectra of synthesized ZnO NPs at a varying concentration of $ZnCl_2$ are shown in Figure 3 (A) which revealed that higher concentrations of salt show a significant increase in the size of ZnO NPs [28]. It has been observed that the optimum value of salt concentration for fabrication of ZnO NPs was 0.01M. Additionally, pH is another factor significantly affecting the formation of ZnO NPs. Figure 3 (B) shows that optimum pH was 12 because the peak intensity specifies high monodispersity of nanoparticles. Moreover, compounds are in protonated form at low pH, which indicates less reducing and stabilizing capacity of biomolecules, whereas deprotonation of many functional groups occurs at higher pH. Additionally, the more concentrated the *gentian kurru* plant extract is more it will be reducing and stabilizing agent which highly promotes metal ion reduction. The absorption spectra ZnO NPs fabricated by different salt to extract ratio i.e. 8:1, 12:1 and 16:1 is shown in Figure 3 (C) and the λ_{max} at 365 nm, 375 nm and 380 nm values due to increase in particle size with increases in number of Zn^{2+} ions. Figure 3 (D) showed that the quality of ZnO nanoparticles was greatly influenced at different temperature values such as 80°C, 100°C and 120°C. Additionally, at high temperature value i.e. 100°C particle size of nanomaterials decrease as nucleation process dominates growth of nanomaterials. However at 120 °C the intensity of λ_{max} was found to lower due to the dominancy of crystal growth rate over the nucleation process [29]. UV/VIS spectra of ZnO NPs at various time interval was observed and λ_{max} was found to be at 360 nm, 370 nm and 370 nm, respectively. However, the absorption intensity decreases at more incubation time due to a slow heating rate with refluxing temperature of 100°C that leads to allow the diffusion process to contribute to grain growth [30].

FTIR analysis was used for functional group identification and chemical structure of ZnO NPs. FTIR spectral bands of *Gentiana kurroo* rhizome extract appeared at 3300 cm^{-1} due to the presence of OH^- groups in a molecule and bands at 1116 or 1101 cm^{-1} appeared due to the stretching vibrations of C-OH and C-H (Figure 4A). Additionally, the band appeared at 1644 cm^{-1} showed the C=C stretching of aromatic ring. The peaks appeared in Figure 4A showed the presence multiple phytochemicals like phenol or flavonoids etc. of plant extract that help in reduction and stabilization of ZnO NPs. More specifically the bands of ZnO NPs were observed at 3400 cm^{-1} were assigned to the stretching mode of hydroxyl group (Figure 4B). The peaks observed at 1579 and 1383-1340 cm^{-1} are designate asymmetrical and symmetrical stretching of Zn-O. Additionally, ZnO NPs show peak at 884, 840 cm^{-1} related to alkyl halides.

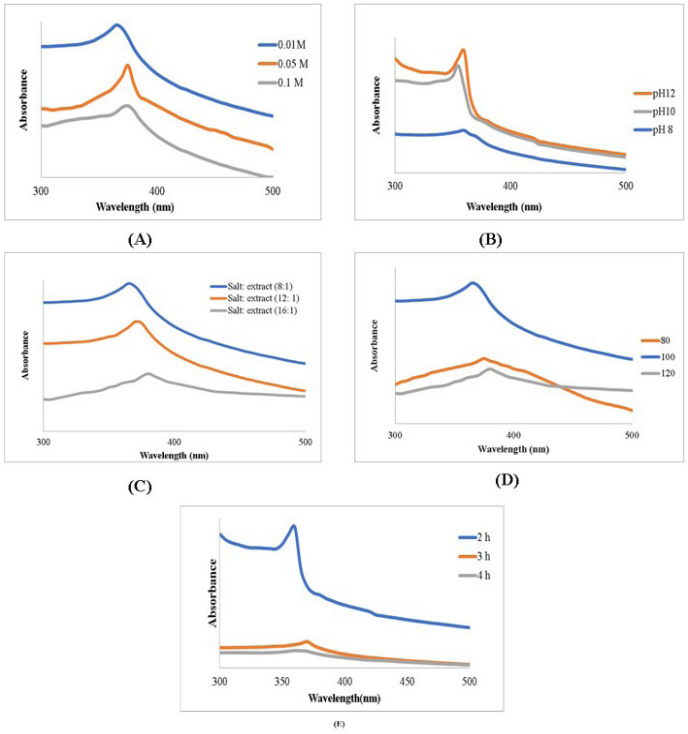

Figure 3: UV/Vis spectra of ZnO NPs at different **(A)** salt concentration, **(B)** pH, **(C)** volume ratio of salt to extract concentration, **(D)** temperature, **(E)** incubation time.

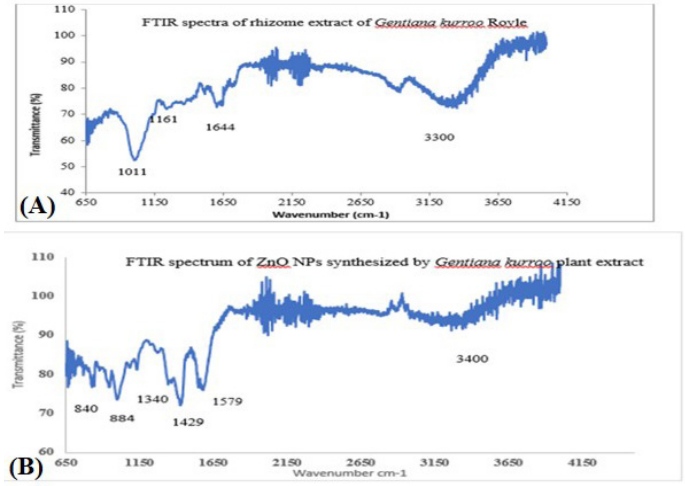

Figure 4: **(A)** FTIR spectra of Gentiana kurroo Royle rhizome extract, **(B)** FTIR spectra of biogenic ZnO NPs.

Photocatalysis of MB

The photocatalytic performance of biogenically synthesized ZnO NPs using MB as a model contaminant. Figure 5 (A) shows the significant increase in the photodegradation of MB with time due to the presence of a photocatalyst. Moreover, photocatalysis of MB follows pseudo first order kinetics which means that reaction rate mainly depends on the initial concentration of dye as shown in Figure 5 (B). The %age photodegradation rate of MB can be calculated via the following equation.

$$\%\text{ age degradation} = \frac{C_O - C_t}{c_t}) \times 100$$

Here C_t represents *dye* concentration after time *t,* C_o showed initial concentration of dye *t is the* time required and *K* is the rate constant.

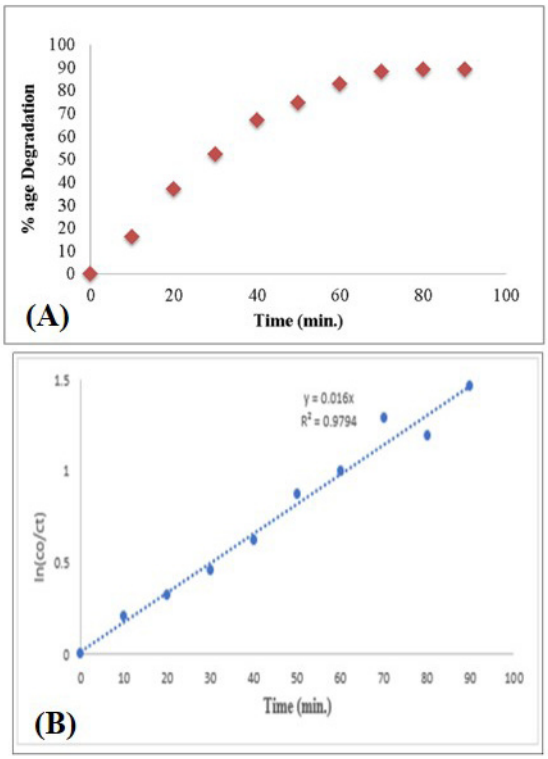

Figure 5: (A) Showed degradation rate of methylene blue with ZnO NPs, **(B)** Showed kinetic study for photodegradation of MB in the presence of ZnO NPs.

Adsorption of reactant occurs on the photocatalyst surface through $\pi - \pi$ stacking interaction which also acts as an excellent substrate for the transfer of electron from reducing agent to pollutant. Through electron transfer super oxide radical and oxidizing agent generated leading to the decolorization of methylene blue dye.

Conclusion

ZnO NPs were prepared through biogenic facile novel approach in the presence of *Gentiana kurroo Royle* rhizome extract and Zinc precursor salt. The successful synthesis of ZnO NPs has been attained by varying the factor affecting the synthesis of ZnO NPs at 2.5% plant extract with 0.01M $ZnCl_2$, 12 pH, 100°C, and 2 hr irradiation time. FTIR analysis confirmed the successful synthesis of ZnO NPs in the presence of *Gentiana kurroo Royle* rhizome extract as the phytochemical groups have been identified from spectra of plant extract. Additionally, the UV/VIS analysis also confirmed the formation of NM and showed a maximum peak at 360 nm. However, the photocatalytic performance of ZnO showed higher photodegradation performance with 89% efficiency in 90min. Hence, the greener route synthesis suggested that ZnO NPs can be used as a safer photocatalyst in different applications.

Declaration of Interest: NO.

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