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RESEARCH ARTICLE

Enhanced Photocatalytic Degradation Properties of Zinc Oxide Nanoparticles Synthesized by using *Turnera subulata* Sm.

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ABSTRACT

Turnera subulata leaf extract has potential efficiency for the formation of biosynthesized Zinc Oxide (ZnO) nanoparticles against dye degradation with various time intervals. The leaves of *T. subulata* were utilized as reducing agent for the formation of metal precursors into metal oxide nanoparticles. *T. subulata* mediated ZnO nanoparticles were confirmed by various analytical techniques such as Ultra Violet–Visible (UV-Vis) Spectrometer, Fourier transform infrared (FT-IR) spectroscopy and morphological studies by Scanning Electron Microscope (SEM). Results show that green synthesized ZnO nanoparticles are directly proportional to reaction time. The phytoconstituents present in leaf extract of *T. subulata* play a major role in ZnO nanoparticles formation by acting as a reducing agent.

KEYWORDS

Turnera subulata, ZnO nanoparticles, Dye degradation, UV-Vis and FT-IR

INTRODUCTION

Nanotechnology (10^{-9}) is a significant branch in the major fields of biology, chemistry, physics and material sciences. Nanoparticles possess a wide array of application in the different fields' viz., medicine, electronics, and therapeutics and as diagnostic agents. The nanomaterials can be synthesized by different methods including chemical, physical, irradiation and biological methods. The development of new chemical or physical methods has resulted in environmental contaminations, since the chemical procedures involved in the synthesis of nanomaterials generate a large amount of hazardous byproducts[1]. Thus, there is a need of "green synthesis" that includes a clean, safe, eco-friendly and environmentally nontoxic method of nanoparticle synthesis. Moreover, in this method there is no need to use high pressure, energy, temperature and toxic chemicals[2,3]. The metal and metal oxide NPs have attractable properties like biological, electronic, magnetic, and photocatalytic activity[4]. Zinc oxide nanomaterials are used in the preparation of substances processing medicinally as well as cosmetically useful properties. Due to its antibacterial properties, zinc oxide is applied on the skin, in the form of powders, antiseptic creams, surgical tapes and shampoos, to relieve skin irritation, diaper rash, dry skin and blisters. Zinc oxide is used along with iron oxide to prepare calamine lotion and with eugenol to prepare zinc oxide eugenol which is used for dental applications[5,6]. Plant extracts mediated synthesis of ZnO nanoparticles has been carried out recently in many plant species like *Camellia sinensis*[7], *Ficus benghalensis*[8], *Punica granatum*[9], *Trifolium pretense*[10], *Hibiscus subdariffa*[11], *Aloe vera*[12], *Citrus aurantifolia*[13], *Parthenium hysterophorus*[14] have been reported

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in Zinc oxide nanoparticles synthesis by different workers[13, 14, 15].

Synthetic Dyes can give color to water bodies even when they exist in small amount. They are widely used in various industries such as textile, plastic, paper and rubber industries[16]. Among these industries, textile industry ranks first in the usage of dyes for coloration of fiber. The textile wastewater is well known to contain strong color, large amount of suspended solids, high fluctuation in pH, high temperature, high COD concentration and other organic contents[17]. Due to the usage of dye and pigments during the dyeing process, the strong color and turbidity of the textile wastewater effluents caused many problems because of its negative visual impact[18]. Some of the dyes are toxic and carcinogenic in nature. Methylene Blue (MB), Methyl Violet (MV), Methyl Red (MR), Eosin (E) and Safranin (S) is a basic dye which is used extensively in the dyeing and printing of cotton, silk *etc.* The high concentration of this dye in contact with the eye can cause corneal injury in human beings. Doses in the range 500 mg can lead to anemia, dizziness, headache, abdominal pain, nausea, profuse sweating and mental confusion[19].

In the present study, we have synthesized Zinc oxide nanoparticles via green routes using *T. subulata* leaf extract, giving a special emphasize on growth of nanoparticles at different temperatures. Photocatalytic properties of the synthesized nanoparticles were measured using visible spectroscopy. The synthesized NPs were characterized by spectrometry, FTIR and SEM was used to investigate the particle size.

MATERIALS AND METHOD

Collection of Plant Materials

The flowering plants of *Turnera subulata* Sm. was collected from the Bishop Heber College campus, Tiruchirappalli. The Plant was identified using the Flora of the Tamilnadu Carnatic[20] and authenticated by the Department of Botany, Bishop Heber College, Tiruchirappalli, India.

Preparation of the Leaf Extract

Ten grams of fresh *T. subulata* leaves was ground using mortar and pestle added to 100 ml of distilled water and stirred at slow heat. The extract was filtered through muslin cloth and then extract was filtered through Whatmann No.1 filter paper, stored at room temperature in order to be used for further studies.

Synthesis of Zinc Oxide

Zinc Oxide was prepared using the precipitation method[21]. Zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) and Sodium hydroxide (NaOH) were the two starting materials for the synthesis of ZnO nanoparticles. 0.025 M Zinc sulfate heptahydrate and 0.05M Sodium hydroxide in aqueous solutions. 50 ml of the alkali solution (NaOH) with an approximate rate of 5ml/min was slowly dropped into the Zinc Sulfate Solution[22]. The solution is stirred under heat vigorously the temperature of 60ºC. The precipitates derived from the reaction between the Zinc sulfate and Sodium hydroxide solution were collected by filtering and were rinsed three times with distilled water by centrifugation devices. Then, the final precipitates were collected for the synthesis of ZnO.

Characterization of ZnO NP

UV-visible spectra were recorded using a spectrophotometer Cary E 500 in a range from 280–800 nm for the confirmation of NP formation. The characterization involved Fourier transform infrared spectroscopy (FTIR) analysis of the dried powder of the synthesized ZnO NPs by Perkin Elmer Spectrum 1000 spectrum in attenuated total reflection mode, and using the spectral range of 4000–400 cm^{-1} with the resolution of 4 cm-1. The size and morphology of the ZnO NPs were examined by scanning electron microscopy (SU3500, Hitachi).

Photocatalytic Degradation of Dye

The photocatalytic activity of biosynthesized ZnO NPs was studied by degradation of Methylene Blue (MB), Methyl Violet (MV), Methyl Red (MR), Eosin (E) and Safranin (S)

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under solar irradiation. The dye solution was prepared by dissolving 1mg powder of Synthetic dyes in 100 ml distilled water. 10 ml ZnO NPs with leaf extract was added to 5 ml of prepared synthetic dye solutions and the mixer was stirred magnetically for 30 min in shadow before exposing to sunlight. The colloidal suspension was then put under solar irradiation with constant stirring. The average temperature of the atmosphere during the experiment found to be 30 °C with 2 hrs mean shine duration. At every 30 min, 5 ml of suspension was collected from the colloidal mixer. The collected suspension was then look over at wavelength from 520 nm using the Systronics type-104 Vis spectrophotometer, to study the dye degradation in presence of ZnO NPs.

RESULTS AND DISCUSSION

UV-Visible Analysis

The UV–visible spectroscopy is a commonly used techniques for optical properties of ZnO nanoparticles[23] (Pal *et al.*, 2007) were characterized. The UV–Vis absorption curve of ZnO NPs is shown in Fig. 1. Zinc oxide formation was confirmed as the absorption peak (lambda max) was found near 350 nm. The results showed that the prepared ZnO NPs with *T. subulata* exhibit an highest absorbance peak (0.500653318 AU) at minimum range 358nm and lowest absorbance peak (0.112728986 AU) at maximum range 1046.7nm (Table 1), which correlates with the already reported results, in which absorption peak was found near most at 360 nm[24].

FTIR Analysis

FTIR analysis was performed to determine the functional groups responsible for the synthesis of ZnO NPs in *T. subulata* leaf extract. The FTIR spectrum of *T. subulata* leaf extract is shown in Fig. 2, which shows absorption bands at 675.9 cm^{-1} (due to overlap of C-H and Zn-O stretching), 1124 cm^{-1} (C-O Stretch in alkoxy aromatic), 1203 cm^{-1} (C-O Stretch in ester-acyl, strong), 1273 cm^{-1} (C-O Stretch in acid-acyl, strong), 1346 cm^{-1} (O=N-O-R nitro symmetric), 1385 cm^{-1} (Aromatic amine), 1638 cm^{-1} (due to overlap of C=C and C=O stretching), 2076 cm^{-1} (C≡C stretch) and 3437 cm^{-1} (OH stretch) (Figure 2). The peak at 675.9 cm^{-1} corresponds to ZnO bonding which confirms the presence of NPs were coated with the polymers.

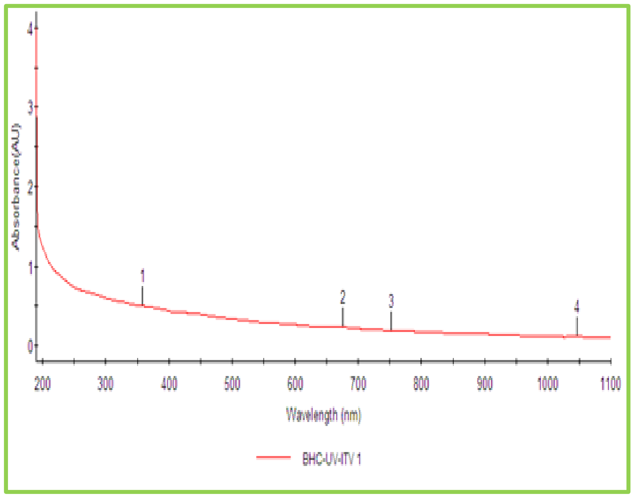

Figure 1: UV-Visible Absorption Spectra of ZnO NPs Synthesized using *T. Subulata.*

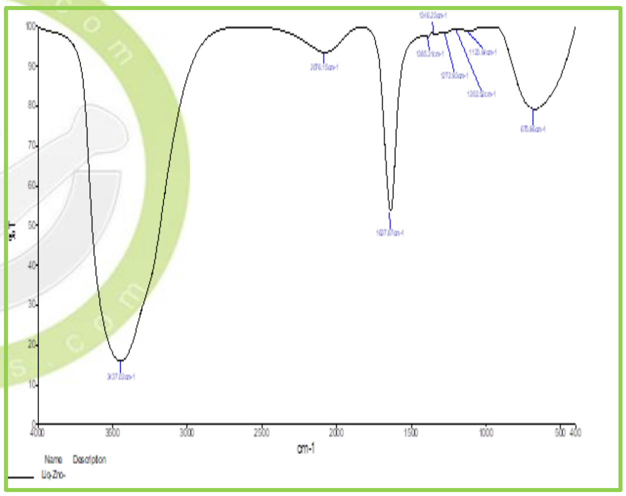

Figure 2: FTIR Graph of ZnO NPs Synthesized from T. subulata

Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (SEM) photographs of ZnO nanoparticles at different magnifications was shown in fig 3. SEM image has shown individual ZnO nanoparticles as well as a number of aggregates. SEM image showed that spherical-shaped nanoparticles and most of the particles exhibit some faceting. SEM results which coincides with results already reported, which shows formation of spherical shaped NPs and aggregated molecules in Calotropis leaf extract[25, 26].

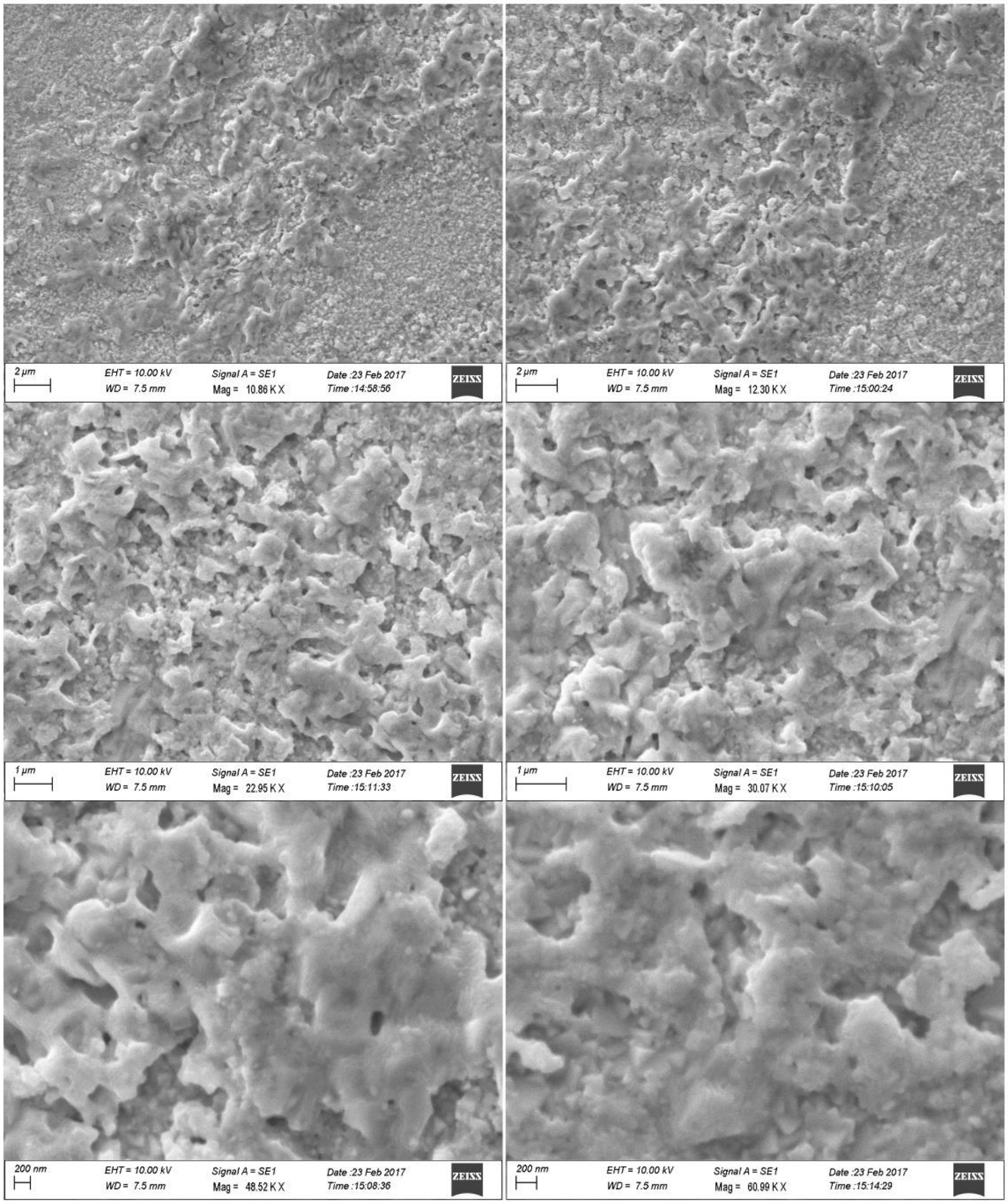

Figure 3: SEM photographs of ZnO NPs in different magnification

Photocatalytic Degradation of Dye

Photocatalytic activities of biosynthesized ZnO NPs with leaf extract of T. subulata was evaluated using synthetic dyes such as Methylene Blue (MB), Methyl Violet (MV), Methyl Red (MR), Eosin (E) and Safranin (S) in aqueous solutions (1mg/ 100mL). The Photocatalytic activities were revealed the reduction occurs in synthetic dyes using ZnO NPs under sunlight, which results to perform the dye degradation occurs only in Eosin (E) observed 520nm shown in graph (Fig. 4.1.).

The present study was compared with ZnO NPs after sunlight with ZnO treated with Leaf extract after sunlight were revealed that the reduction occurred in synthetic dyes using ZnO NPs under sunlight within 2 hrs (immediate response), which results to perform the dye degradation occurs in Methyl Red (MR), Methyl Violet (MV) and Safranin (S) observed 520 nm shown in graph (Fig. 4.2.).

Table 1: Photocatalytic Activities of ZnO NPs with Leaf Extract of *T. Subulata* using Synthetic Dyes

S. No	Synthetic Dyes	Wavelength of Dyes (520nm)	Wavelength of ZnO with Dye (520nm)		Wave Length of ZnO with Plant extract +Dye (520nm)	
			Before Sunlight	After Sunlight	Before Sunlight	After Sunlight
1	Methyl Red (MR)	0.106	0.116	0.274	0.213	0.102
2	Methyl Violet (MV)	0.046	0.226	0.172	0.232	0.108
3	Methylene Blue (MB)	0.006	0.423	0.051	0.293	0.378
4	Ethyl Eosin (E)	0.348	0.512	0.052	0.506	0.106
5	Safranin (S)	0.221	0.512	0.285	0.380	0.266

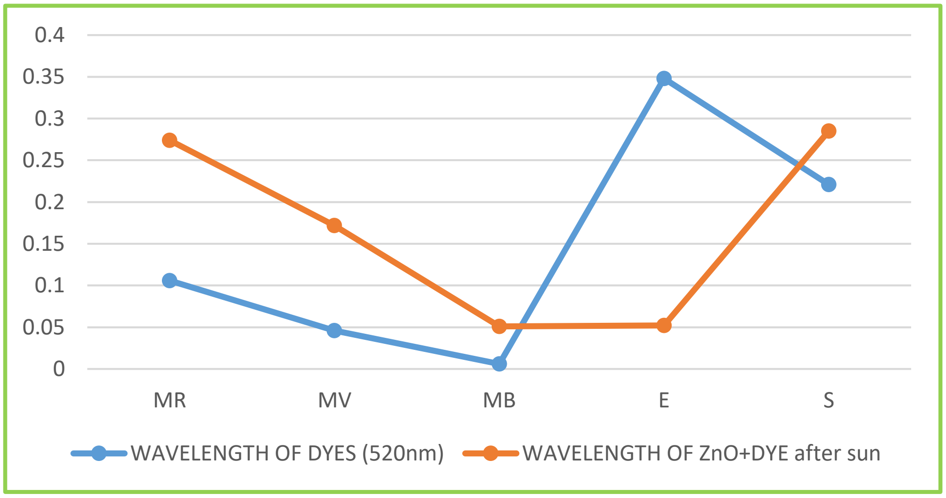

Figure 4.1: Reduction Occurs in Synthetic Dyes using ZnO NPs under Sunlight

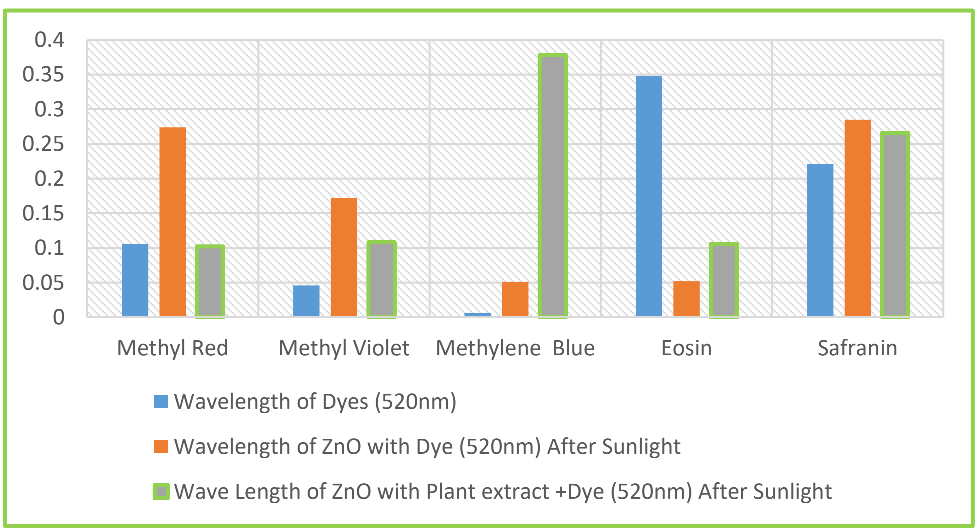

Figure 4.2: Dye Degradation occurs in ZnO NPs synthesized from *T. subulata* under Sunlight

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Table 2: Dye Degradation occurs in Different Time Intervals

Time interval \ Dyes	Methyl Red	Methyl Violet	Methylene Blue	Ethyl Eosin	Safranin
2	0.102	0.108	0.378	0.106	0.266
4	0.096	0.098	0.272	0.099	0.198
6	0.062	0.059	0.109	0.078	0.088

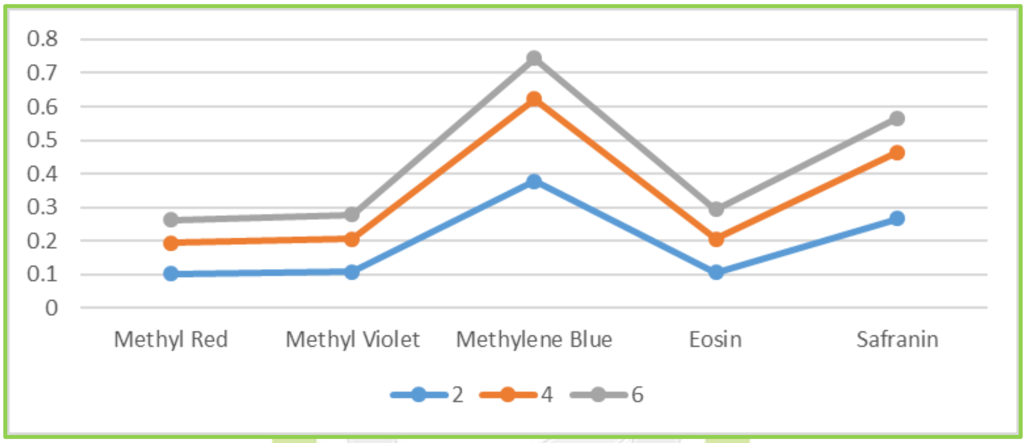

Figure 4.3a.: Dye Degradation Occurs in Different Time Intervals

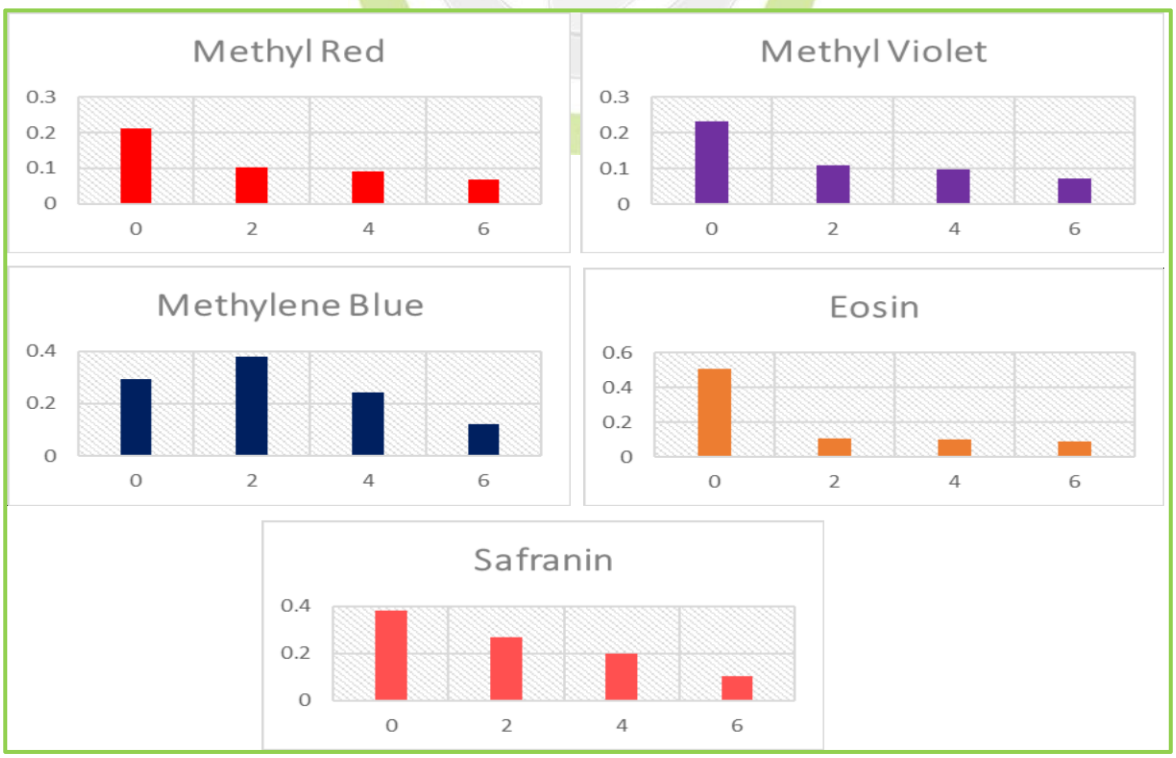

Figure 4.3b.: Dye Degradation Occurs Individuals Different Time Intervals

The present study, ZnO NPs after sunlight and ZnO with Leaf extract after sunlight was revealed that the degradation occurs in synthetic dyes under sunlight within 2 hrs, 4 hrs and 6 hrs differences, which results to perform the dye degradation occurs in all synthetic dyes disappears observed 520 nm shown in graph (Fig. 4.3. a and b).

The photocatalytic degradation efficiency was calculated as in equation.

$$\text{Dye degradation (\%)} = \frac{Co-Ct}{Co} \times 100\ \%$$

Where Co was the concentration of dye after 30 min of dark run and Ct was the concentration of dye at reaction time, t (min).

Table 5: Photocatalytic Degradation Efficiency

Dye	Dye degradation (%)
Methyl Red (MR)	70.8
Methyl Violet (MV)	74.5
Methylene Blue (MB)	62.7
Ethyl Eosin (E)	84.5
Safranin (S)	76.8

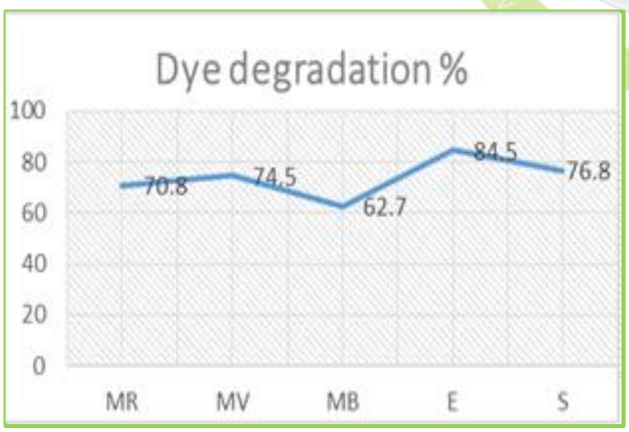

Figure 4.4: Photocatalytic Degradation Efficiency

The results obtained in the present study showed that the efficiency of reduction processes to enhance the removing dyes, which resists other conventional treatment processes. Dye degradation appears to be a promising technology that has many applications in environmental cleanup systems.

A detailed feasibility study has been carried out on photocatalytic degradation of Methyl Red (MR), Methyl Violet (MV), Ethyl Eosin (E) and Safranin (S) using ZnO NPs & ZnO with Leaf extract as a photo catalyst under sunlight. The Results of the study indicated that ZnO NPs with leaf extract is very effective & suitable alternative to ZnO NPs. The best reaction dosage of ZnO catalyst is about 1mg / 100mL. The maximum degradation efficiency of dye was achieved with the combination of Sunlight (UV) + Leaf extract of *T. subulata* + ZnO NPs.

CONCLUSION

Nanomaterials in different forms can be used for removal of other environmental pollutants. Nanoparticles (nano-scale particles = NSPs) obtained from plants, fungi and bacteria, have had actual application in removing some heavy metals from polluted sites. Nanoparticles from plants, fungi and bacteria are useful for detoxification and bioremediation of soil, water and other environments in highly polluted conditions. In future, modification and adaptation of nanotechnology will extend the quality and length of bioremediation. The results obtained from this work showed that ZnO with Leaf extract possessed impressive decolorization efficiency. It can be concluded that, various techniques have been suggested for remediation of waste water. Some of these are too expensive hence not viable. Those that are comparatively inexpensive are not very effective. The best option appears to be one involving several steps like biosorption using locally available agricultural waste followed by biological treatment using ZnO NPs with leaf extract of *T. subulata* which is very effective and suitable for use in the treatment of solution containing dye.

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