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GREEN SYNTHESIS OF ZINC OXIDE NANOPARTICLES FOR PHOTODEGRADATION USING METHYLENE BLUE DYE

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Abstract : Zinc Oxide nanoparticles were synthesized using Zinc nitrate as an precursor with orange juice extract at different temperatures (50˚C, 60˚C, 70˚C, 80˚C).X-Ray diffraction, UV-Visible and FTIR spectroscopy were used for characterization studies. The X-Ray diffraction analysis indicates that the synthesized Zinc oxide nanoparticles were Wurzite crystalline structure. The UV-Visible spectrometer was used to monitor the formation of green synthesized Zin oxide nanoparticles. In FTIR spectra analysis, there is a band present at 618cm-1 which is a characteristic signal of the Zn-O bond. The morphological structures are confirmed using Scanning electron microscopy (SEM). The Photocatalytic activities of green synthesized nanoparticles were investigated by the photodegradation of Methylene Blue under UV light radiation and the dye was completely degraded at 180mins.

Keywords **- Green Synthesis, Zinc Oxide Nanoparticles, Photodegradation, Methylene Blue Dye**

1. INTRODUCTION

Over the past few decades, environmental pollution became a life-threatening issue as one of which is due to the discharge of industrial effluents into water bodies, Dyes are one of the most prominent pollutants that shows an increasing ecological threat to living organisms. Dyes are non-biodegradable compounds that reduce the aquatic plants life by preventing the photosynthesis action into the water as well as contaminating the living organisms surroundings because of their toxity. For the above reason, it is necessary to keep the environment safe by removing dyes from contaminated effluents.[1]

Zinc oxide is a member of the group II- VI semiconductors family, whose covalence is on the boundary between ionic and covalent semiconductors [2]. At ambient conditions. The Wurzite structure is thermodynamically stable with every Zinc atom being tetrahedrally coordinated with four oxygen atoms. With the wide-band gap of 3.1-3.3eV. Zinc Oxide has great potential for application in many fields such as biosensors, cosmetics, drug carriers and antibacterial agents and Photocatalytic activity etc.,

Zinc oxide can be synthesized by many methods such as Sol-gel processing, homogeneous precipitation, Mechanical Milling, Organometallic synthesis, Spray Pyrolysis, thermal evaporation etc., However these kinds of methods usually use organic solvents and toxic reducing agents, the majority are harmful to the environment. Therefore, in order to minimize the impact on the environment, green synthesized process have been used to synthesize Zinc oxide nanoparticles[3].

In this work, Zinc Oxide nanoparticles were prepared by green approach by using Orange juice extract at different temperatures (50˚C, 60˚C, 70˚C, 80˚C). This type of synthesis makes less expensive, easily scaled up and environmentally benign. These orange extracts can act as both reducing and stabilizing agents for metal nanoparticles[4]. Zinc Oxide nanoparticles is used for the degradation process of Methylene blue dye. The green synthesized nanoparticles have been characterized in terms of crystalline, Morphological structure and Photocatalytic activities.

2. EXPERIMENTAL

2.1. Materials Used

Zinc Nitrate (Zn(NO3)2.6H2O) as the precursor, purchased from Sigma-Aldrich; Fresh Orange fruit has purchased from the market; de-ionized water as the synthesis medium, Methylene Blue dye were purchased from Sigma-Aldrich chemicals Co.Ltd.

2.2. Green Synthesis of ZnO Nanoparticles

The fresh orange fruit was collected and washed in water. Again, it was washed with deionized water to remove adhering particles. Using a squeezer, the juice is extracted from the lemon. This extracted juice was filtered with the help of Whatman No.1filter paper. 1ml of fruit extract with 50ml of deionized water has been taken and kept in a magnetic stirrer for 30 minutes. 2g of Zinc Nitrate has been added to 50ml of fruit extract. These mixtures are then stirred vigorously for 30 min to produce a white precipitate. After centrifugation, the supernatant was discarded, and the precipitates were collected. Residue in the obtained particles was removed by using DI water and ethanol. Finally, the resultant products were dried at different temperatures (500C, 600C, 700C,800C) in a hotplate for 30 minutes to obtain the resultant zinc oxide nanoparticles[7]. A schematic of the green synthesis process of the zinc oxide nanoparticles is shown in Fig.1.

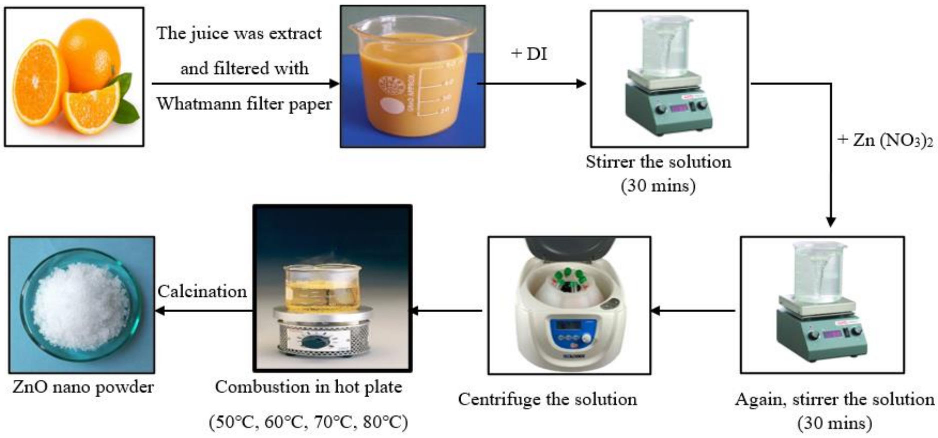


Fig.1. Schematic diagram of the green synthesis of ZnO nanoparticles

2.3. Characterization of Green Synthesized Zinc Oxide Nanoparticles

The Zinc oxide nanoparticles were characterized by UV-Visible Spectrometer (model UV-1800) and FTIR (model IR Affinity-1). The Crystal structures of the synthesized samples were studied using X-Ray diffractometer (Desktop X, model Miniflex-600). The surface morphology was examined by Carel Zeiss- EVO 18 Scanning Electron Microscope (SEM).

2.4. Photocatalytic Experiment

The photocatalytic activity of prepared samples was estimated by measuring the decomposition rate of Methylene Blue dye in aqueous solution under UV light irradiation. This photocatalytic experiment was carried out using HEBER multi lamp photo reactor.

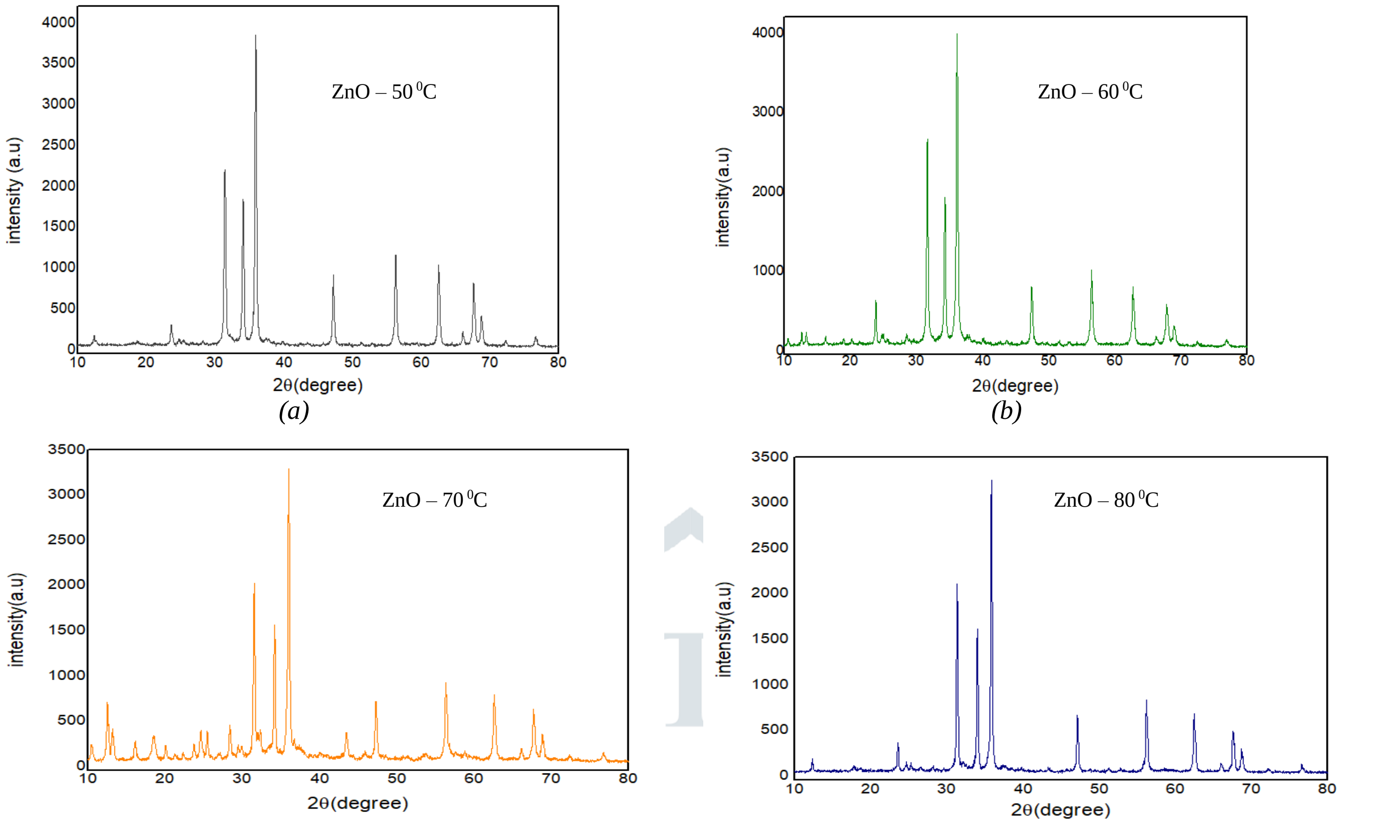
3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction Analysis

This is the powerful method for the investigation of the fine structure of the compound. Average grain size of the particle can be calculated by using Debye-Scherrer formula:

$D=K\lambda/\beta\cos\theta$.

For this synthesized zinc Oxide nanoparticles, it was found 27.52nm, 37.11nm, 47.52nm,50.22 nm for 50ºC,60ºC, 70ºC, 80ºC respectively. From the Fig.2, the sharp and narrow 2θ value diffraction peaks confirm the formation of a crystalline hexagonal Wurtzite structure of the zinc oxide nanoparticles.



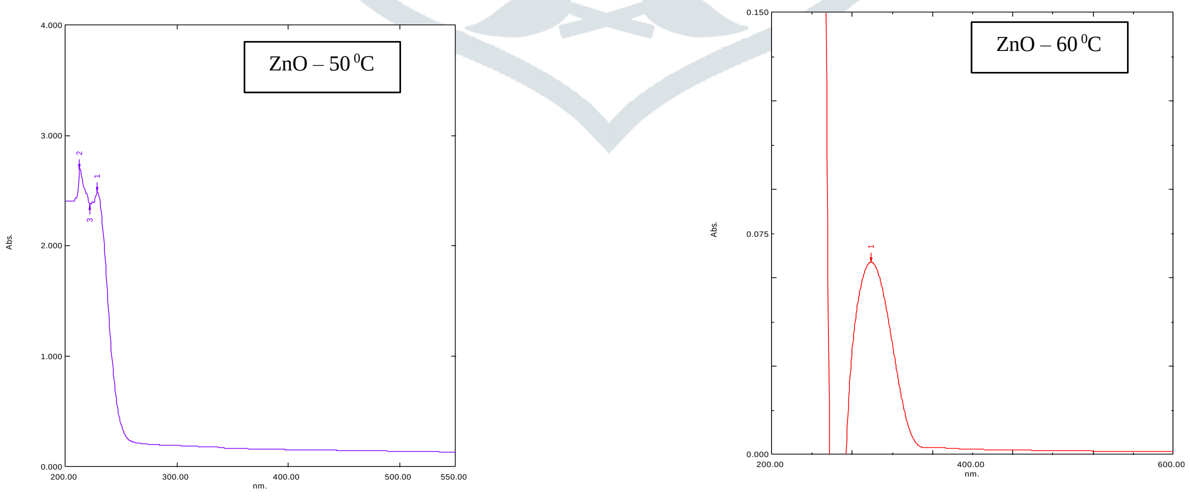
(a) *(b)*

(c) *(d)*

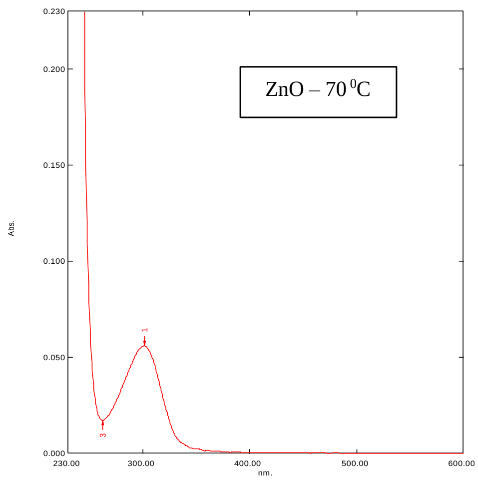
Fig. 2. XRD pattern of ZnO nanoparticles at different temperature ((a)50⁰C, (b) 60⁰C, (c)70⁰C, (d) 80⁰C)

3.2. UV-Visible Spectrometer

The UV-Visible spectrometer was used to find out the formation of green synthesized Zinc oxide nanoparticles. Orange fruit extract exhibit white colour in aqueous solution. On mixing the extract with zinc nitrate solution, the colour changes from pure white colour, which is an indication of the reduction process. From the Fig.3, It is to be confirm the synthesized ZnO nanoparticles observed by the highly shifted absorption maximum occurring around the wavelengths were 50ºC- 228nm,60ºC- 299nm, 70ºC-301nm, 80ºC- 301.5nm. It reveals the formation of nanoparticles by showing surface Plasmon resonance at corresponding nanometer level.



(a) *(b)*



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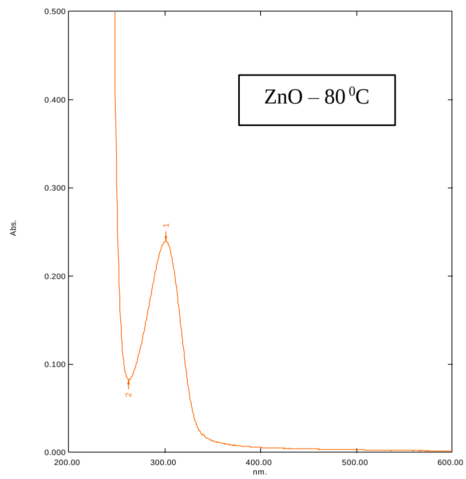


(d)

Fig.3. UV Spectroscopy analysis of ZnO nanoparticles at different temperature ((a)50^{0}C, (b) 60^{0}C, (c)70^{0}C, (d) 80^{0}C)

3.3. FTIR Spectroscopy

The FTIR spectra of green synthesized Zinc oxide nanoparticle is represented in Fig.4. There is a band present at 618cm-1, which is a characteristic signal of the Zn-O bond, confirming that the prepared sample is Zinc oxide nanoparticle. And also, the bands at 1644 cm-1, 843 cm-1 and 1378 cm-1 are attributed to the aromatic rings and their functional groups present in the organic compounds at different temperature.

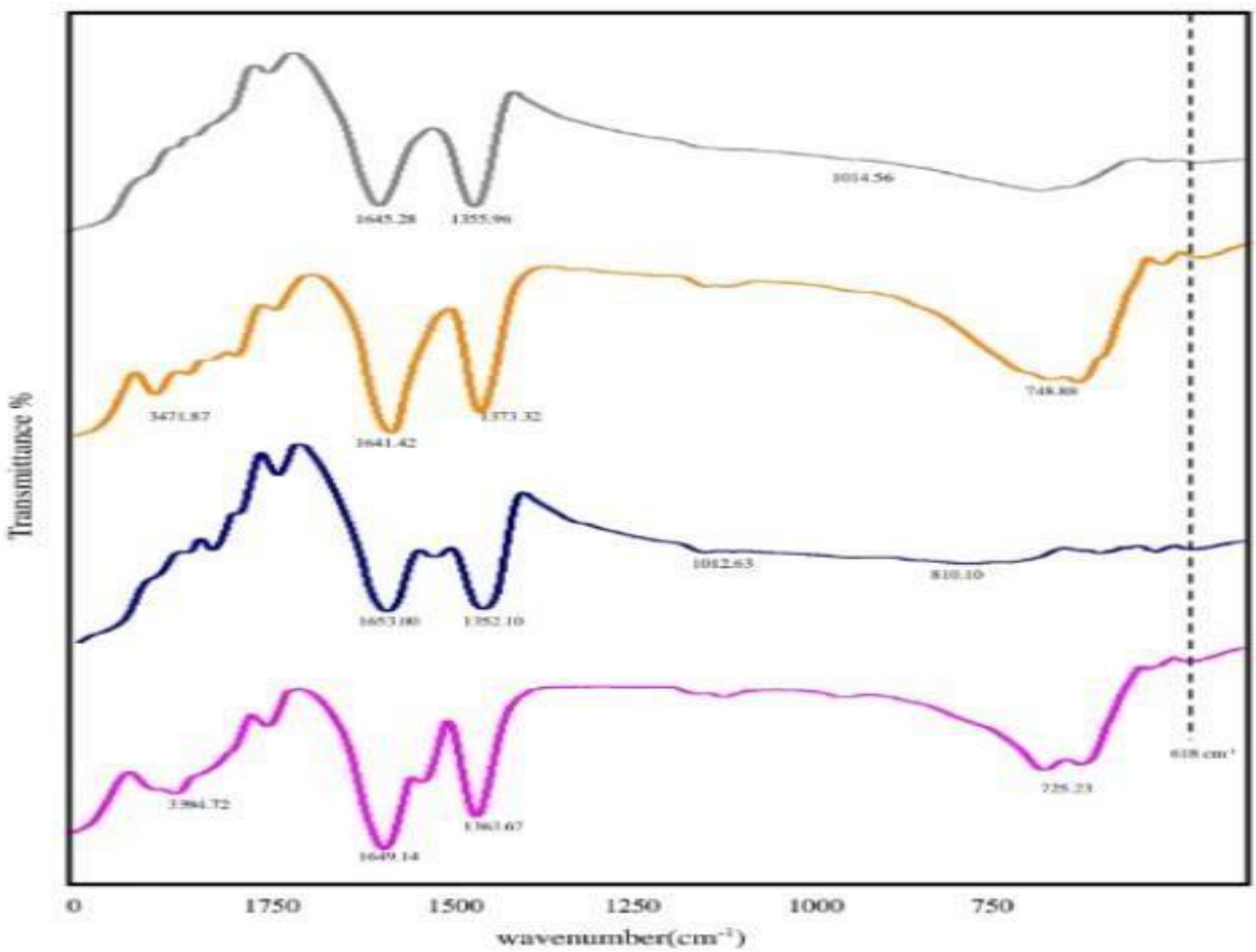
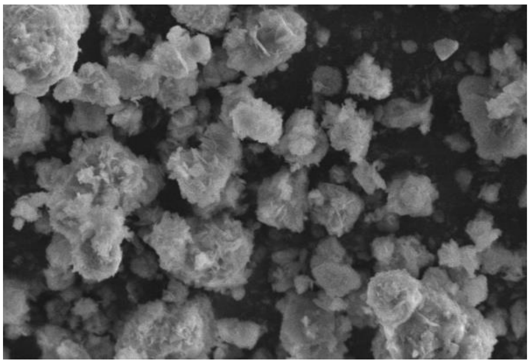


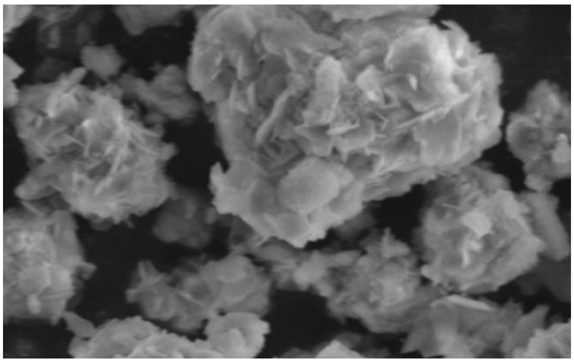
Fig. 4. FTIR analysis of ZnO nanoparticles at different temperature (50^{0}C, 60^{0}C, 70^{0}C, 80^{0}C)

3.4. SEM Analysis

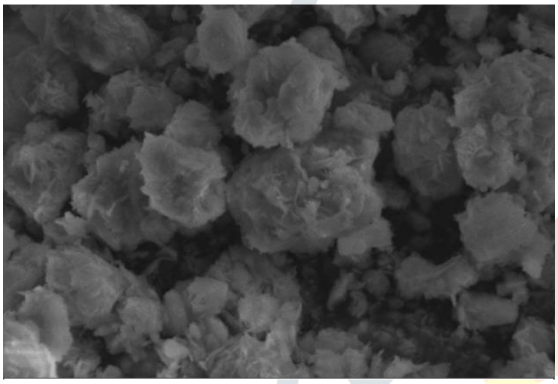
The structure and morphological study of Zinc Oxide nanoparticle were predicted using Scanning Electron Microscopy and the corresponding images are shown in the Fig.5. The SEM image of Zinc oxide nanoparticles synthesized from orange extract shows in higher magnification nano flake like structure which is in a random arrangement [8].



(a)



(b)



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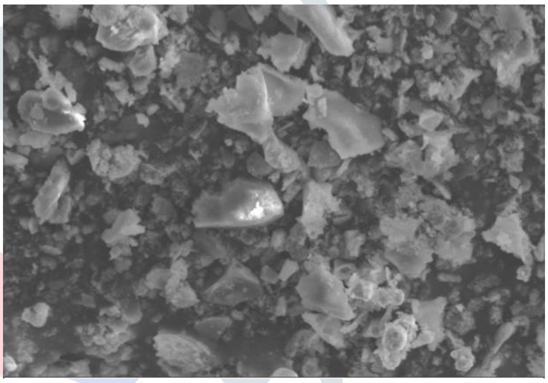

(d)

Fig. 5. SEM image of ZnO nanoparticles at different temperature ((a)50^0C, (b) 60^0C, (c)70^0C, (d) 80^0C)

3.5. Photocatalytic Degradation of Dye

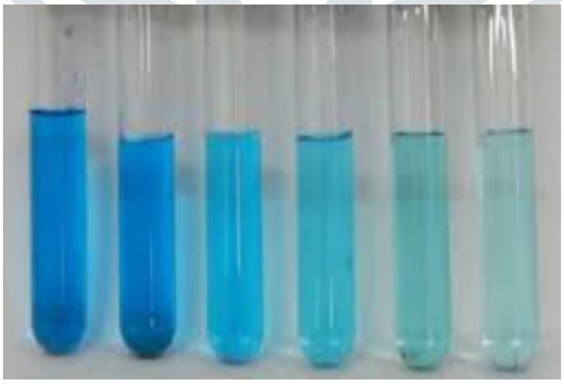

Fig.6. Degradation of Methylene Blue dye

The dye degradation of Methylene Blue under UV light irradiation evaluates the photocatalytic activities of green synthesized zinc oxide nanoparticles. The dye degradation was observed visually from the Fig.6. The result shows that the gradual change in solution colour from deep blue to colourless. The characteristic absorption peak at 662nm was observed for pure Methylene Blue dye solution which was utilized to trace the photocatalytic degradation process and verified by the decrease of the peak intensity after 180 mins exposure in UV light.

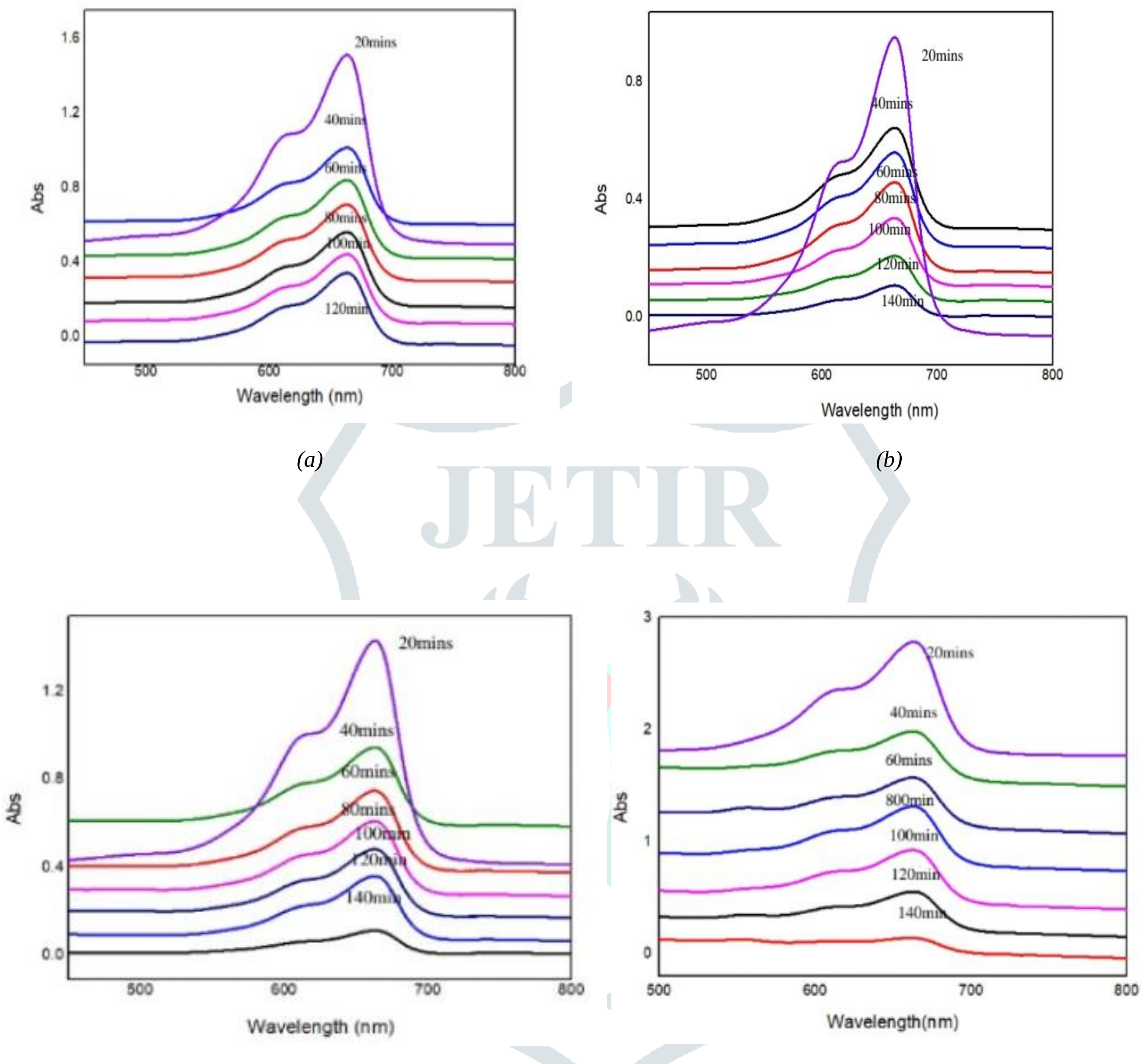

Fig.7. Photocatalytic activity of ZnO nanoparticles at different temperature ((a)50^0C, (b) 60^0C, (c)70^0C, (d) 80^0C)

In Fig.7. The degradation of Methylene Blue dye has been determined. The degradation of Methylene Blue dye under UV irradiation in the presence of Zinc oxide nanoparticles were studied from 0min to 180min at an interval of 20min. The characteristic absorption peak decreases rapidly with increase in temperature. From the Fig.8. It is inferring that Methylene Blue dye has been more efficiently degrade in Zinc oxide nanoparticles at 80ºC.

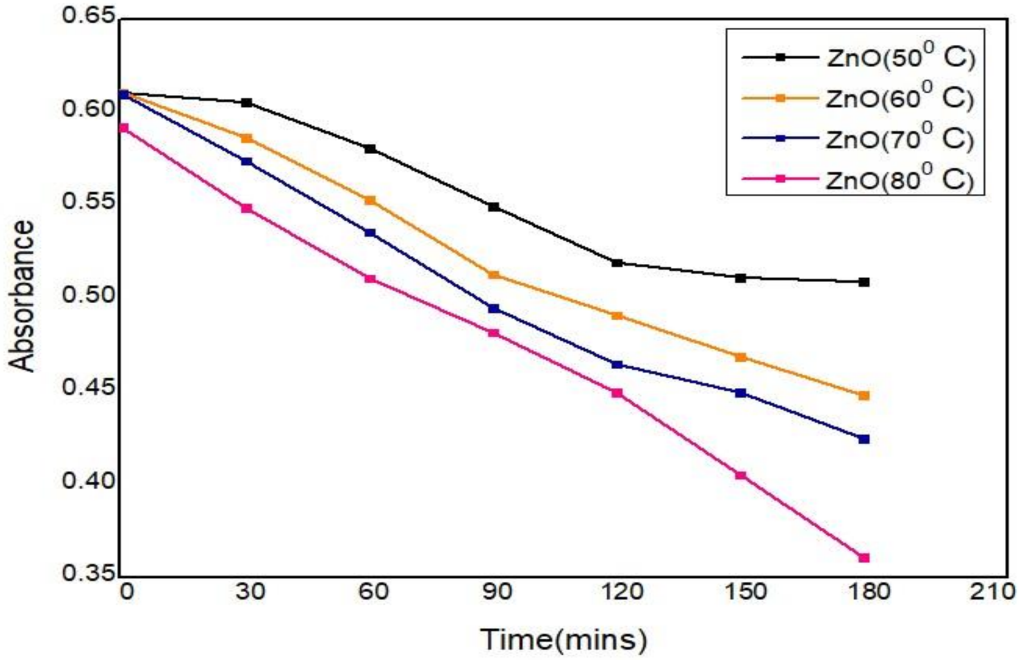

Fig.8. Degradation of ZnO nanoparticles at different temperature with regular time interval under UV irradiation

4. CONCLUSION

The green synthesized zinc oxide nanoparticles have been characterized and its photocatalytic activity was studied. From X-Ray diffraction, the average size of zinc oxide nanoparticles was found to be 27.52nm,37.11nm,47.52nm,50.22nm at 50ºC,60ºC, 70ºC, 80ºC respectively. From UV-Vis spectroscopy, the synthesized Zinc oxide nanoparticles were confirmed by the highly shifted absorption maximum occurring around the wavelength 50ºC - 228nm,60ºC - 299nm, 70ºC - 301nm, 80ºC – 301.5nm. In FTIR, the band present at 618 cm-1 is responsible for stabilizing and capping of Zinc oxide nanoparticles. In Photocatalytic activity, the characteristic absorption peak revealed that Methylene Blue dye has been more efficiently degrade in Zinc oxide nanoparticles at 80ºC.Thus, the green synthesized nanoparticles are highly proficient for recycling and removal of heavy metal from waste water without any loss in their stability and degradation of a variety of organic pollutants and could solve various waste water quality issues worldwide.

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