International Journal of Engineering, Science and Mathematics
Vol. 7Issue 3, March 2018,
ISSN: 2320-0294 Impact Factor: 6.765
Journal Homepage: http://www.ijesm.co.in, Email: ijesmj@gmail.com Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

Antioxidant and Photocatalytic activity of Green Synthesized Zinc oxide Nanoparticles using Stem extract of *Rubia cordifolia*

Prachi* and Devendra Singh Negi**

Abstract:

Due to the potential applications in the expansion of nanotechnologies synthesis of zinc oxide nanoparticles (ZnO-NPs) became a expanding area of research. In the present research work, we described a low cost, eco friendly and simple method for the green synthesis of ZnO-NPs using stem extract of *Rubia cordifolia.* The structural and morphological properties have been characterized by XRD, SEM, EDX and TEM analysis. Synthesized NPs are hexagonal wurtzite structure with an average size 20.07 nm was obtained from XRD and they are spherical in shape. The applications of ZnO-NPs exhibit potential anti oxidant activity depend upon concentration of synthesized ZnO-NPs and photocatalytic activity towards degradation of methylene blue dye depend upon time exposure in the sunlight irradiation.

Key words: Zinc oxide nanoparticles (ZnO-NPs), *Rubia cordifolia,* anti oxidant and photocatalytic degradation.

Author correspondence

Ph.D scholar*, Professor**

Department of Chemistry, H.N.B. Garhwal (A Central) university

Srinagar, Uttarakhand, India, Pin-246174

1.Introduction:

Nanoparticles which having nanoscale dimension(1-100 nm) are nanomaterials and they are small sized and due to their large surface area to volume ratio they have improved catalytic activity, non linear optical performance, chemical steadiness and thermal conductivity. Nanoparticles because of their antimicrobial activities have been started consider as nano antibiotics. NPs have been incorporated into many industrial, food, space, health, chemical, feed and cosmetics industry so there is a need a green, non toxic and eco friendly approach to the synthesis of NPs. [1] In the past decades metal nanoparticles have been widely used for therapeutic purpose and as a catalyst for the reduction of toxic chemicals from the atmosphere like Fe_3O_4, CuO, ZnO and TiO_2. These metal NPs are also investigated for a range of biological activity. Among these metal NPs, ZnO NPs are utilized in the reduction of toxic chemicals from the water resources such as arsenic and sulfur due to its large surface area to volume ratio. They have significant application in diagnostic, drug delivery, bio-molecular detection, micro-electronics, antimicrobial and antioxidant activity etc.[2]

Rubia cordifolia belongs to *Rubiaceae* family, distributed throughout India also known as Manjishtha and Indian madder. It is found in the hilly areas from northwest Himalayas to Ceylon. It is a climbing herb upto 10 m long and grow healthy in sandy, medium and heavy soils. *Rubia cordifolia* is an essential plant in Ayurvedic system has a range of medicinal uses as blood filter, immunomodulator, antioxidant and anti-inflammatory. [3] It has a large number of phyto-chemicals such as anthraquinones, quinones, bicyclic hexapeptides, oleananes triterpinoid and iridoids [4], which helps the plant extract to act as a stabilizing and capping agent in the formation of nanoparticles.

In the field of nanotechnology Mariselvam et al. (2014), reported the green synthesis of copper quantum dots using *Rubia cordifolia* root extracts and its antibacterial properties [5], Mariselvam et al. (2013), reported the preparation of silver nanoparticles using root extract of *Rubia cordifolia* and their microbial properties [6], Prachi et al. (2017), reported the green synthesis of zinc oxide nanoparticles using root extract of *Rubia cordifolia* and their antibacterial properties. [7]

In this article we reported the green synthesis approach to the synthesis of zinc oxide nanoparticles using stem extract of *Rubia cordifolia* and their anti oxidant activity and photocatalytic activity by observing the degradation of methylene blue (MB)dye. To the best of our knowledge, we firstly reported the green synthesis of zinc oxide nanoparticles using stem extract of *R. cordifolia*.

2.Experimental

2.1Materials :

The stem of R. cordifolia were collected from the Khirshu ($78^0$52'2'' and $30^0$10'15''), Uttarakhand. Then dry and washed carefully several times with distilled water and then cut into small pieces. 10 gm of stem added in 100 ml of distilled water and heated at 70-80^0C. Subsequently it was filtered through filter paper. Zinc nitrate hexahydrate with purity 99% is purchased from Sigma-Aldrich and NaOH is obtained from Fisher scientific.

2.2Preparation of ZnO-NPs

20 ml of plant extract is heated at 70^0C for 10 min under magnetic stirring and then 50 ml solution of Zn $(NO_3)_{2.}6H_2O$ (91 Mm) in double distilled water added dropwise to the plant extract. The mixture is heated under continuous stirring for 15 min and then few drops of NaOH is added for maintain the PH of solution. The reaction solution is centrifuged at 3000 rpm and then pale white precipitate is allowed to dry at room temperature . After drying the precipitate pale white NPs are washed with methanol to remove the unreacted material and used for further characterization.[8,9]

2.3Characterization:

X-Ray diffractometer(Shimadzu XRD-6000/6100 models) with CuK radians of wavelength(λ) 1.54 A^0 at 2 θ angle used for determined the purity and crystalline size of synthesized ZnO-NPs. Further, from Transmission electron microscopy (TEM, Tecnai, u-Twin 50-300 KV) analysis it has been confirmed the synthesized nanoparticles are in nano dimension range. The morphology of the ZnO-NPs were shown by scanning electron microscopy (SEM, ZEISS EVO 18) followed by EDX for the determination of elemental composition.

2.4Photocatalytic degradation of methylene blue dye:

Photocatalytic activity of green synthesized zinc oxide nanoparticles using stem extract of *R. cordifolia* was carried out by degradation of methylene blue under solar radiation. The MB dye solution prepared by adding 1 mg of MB in 100 ml distilled water and dissolve it with constant stirrer. Then 5 mg of ZnO-NPs was added in 25 ml of MB dye solution and then put this colloidal suspension in solar irradiation.[10] At every 60 min, 5 ml of colloidal suspension scanned at wavelength from 190-800 nm using Elico SL 218 UV-Vis spectroscope to study the degradation of MB dye in the presence of ZnO-NPs.

DPPH radical scavenging assay: DPPH (1,1- diphenyl-2-picrylhydrazyl) is a stable free radical and commonly used for the radical scavenging activity of anti-oxidant compound. DPPH scavenging activity was measured by the method described by Parimelazhagan Thangaraj in his book .[11] DPPH methanolic solution (0.1 mM) was prepared and incubated for 20 min at room temperature. We take different concentration of ZnONPs and make the volume to 100 µL with methanol solvent. Measure the absorbance at 517 nm. Mixture of methanol, DPPH and BHA (Butylated hydroxyanisole) was used as positive control and methanol with DPPH as negative control. The experiments performed in triplicate and calculate percentage inhibition from the absorbance of synthesized ZnONPs and negative control using this equation,

% inhibition = [control OD – Sample OD/ Control OD] × 100

Calculate IC_{50} from the concentration and % inhibition graph.

3.Results and Discussion:

3.1X-Ray diffraction analysis:

In fig-1 XRD pattern of ZnO-NPs from stem extract of *R. cordifolia* has been shown. The crystalline nature of zinc oxide nanoparticles are clearly indicated by diffraction peaks. The diffraction peaks appear at 2θ of 21.42, 28.78, 31.18, 33.8, 35.72, 47.24, 56, 62.34 and 67.48 (deg). The peak intensity profiles were confirmed the hexagonal wurtzite structure. The average crystallite size calculated by using Scherer's equation-(1)

$D = K\lambda / \beta\cos\theta \; A^0$ ------------------- (1)

Where D = average crystallite size, K= shape factor, λ= wavelength of X-Ray, θ= Bragg angle, β= Full width at half maxima in radian (FWHM)

The average powder particle size was found to be 20.07 nm.

International Journal of Engineering, Science and Mathematics
Vol. 7Issue 3, March 2018,
ISSN: 2320-0294 Impact Factor: 6.765
Journal Homepage: http://www.ijesm.co.in, Email: ijesmj@gmail.com Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

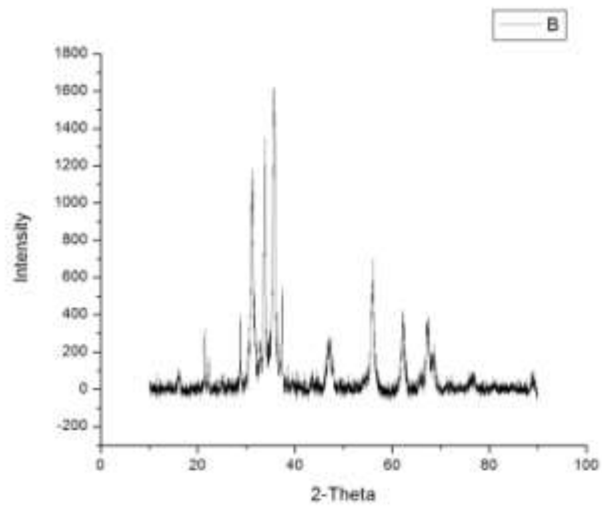
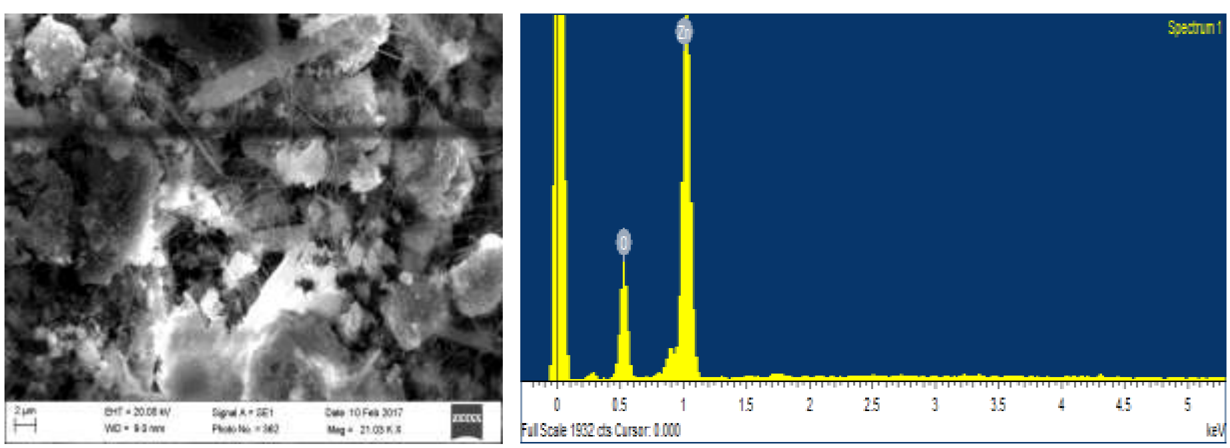


Figure-1: XRD pattern of ZnO-NPs

3.2SEM with EDX analysis:

The shape and morphology of synthesized ZnO-NPs are indicated by SEM image as showm in Fig-2 (a), the image prove that they have ZnO-NPs have nano sized range with spherical shape particles. Presence of elemental Zn and oxygen signals of ZnO-NPs is confirmed by Energy dispersive X-ray [Fig-2(b)].



(a) (b)

Figure-2: (a). SEM image of ZnO-NPs (b). EDX spectrum

3.3TEM analysis:

To the verification of results of XRD, ZnO-NPs was examined by TEM analysis. From TEM the calculated average diameter is 22.39, which is almost comparable to the particle size from XRD analysis. (Fig-3)

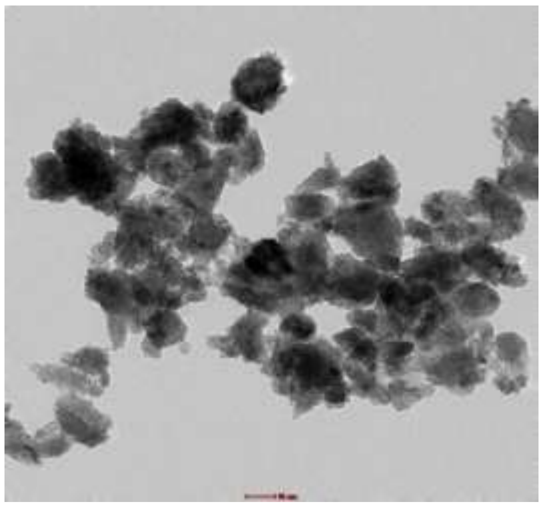
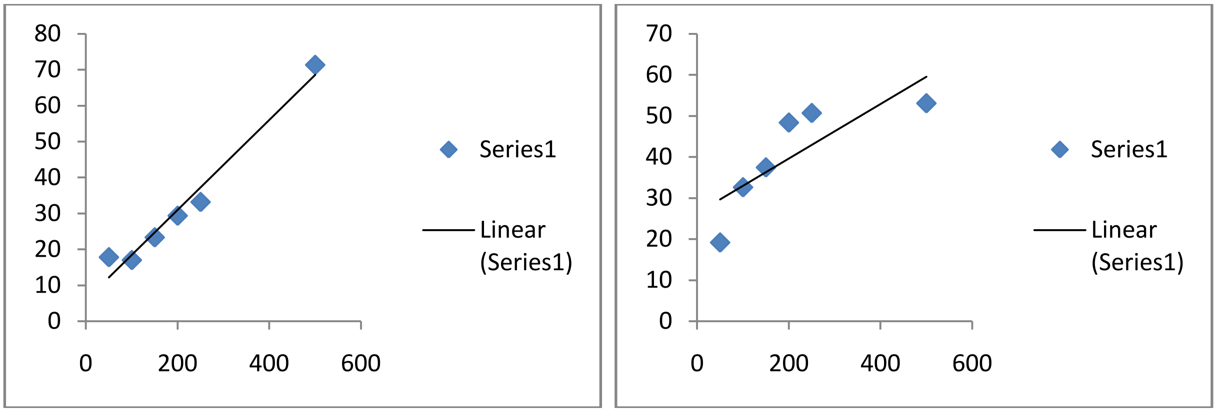


Figure-3: TEM image of synthesized ZnO-NPs

3.4DPPH radical scavenging assay:

Anti oxidant activity of synthesized zinc oxide nanoparticles using stem extract of *R. cordifolia* was studied by DPPH radical scavenging assay using different concentration of ZnO-NPs solution such as 50, 100, 150, 200, 250 and 500 µg/ml. BHA solution used as positive control of 50- 500 µg/ml concentration. The obtained results are shown in Fig- 4 (a) and Fig- 4 (b). We recorded that the activity increased with concentration of ZnO-NPs solution. We calculated the antioxidant activity of BHA with IC_{50}=354.22 and synthesized ZnO-NPs with IC_{50} = 358.18. synthesized ZnO-NPs using stem extract of *R. cordifolia* has good anti oxidant activity.



(a) (b)

Figure-4: (a). Antioxidant activity of BHA (b). Antioxidant activity of synthesized ZnO-NPs

3.5Photocatalytic Activity:

Photocatalytic activity was evaluated by methylene blue (MB) dye degradation on sun light irradiation. Degradation of dye by synthesized ZnO-NPs isually detected by change in color. Characteristic peak founded at 664 nm for pure MB solution. In the presence of green synthesized zinc oxide nanoparticles the degradation of dye was confirmed by the reduce the peak intensity at 664 nm during 120 min in solar light irradiation shown in Fig-5. The percentage (%) of dye degradation was calculated by using the equation – (2)

Dye degradation % = $[C_0 - C_t] \times 100$ ------------------ (2)

Where C_0 = initial concentration of MB solution, C_t = concentration of dye solution after 't' time in the sun light exposure. All concentration absorption peaks of dye measured at 664 nm by UV-Vis spectroscopy.

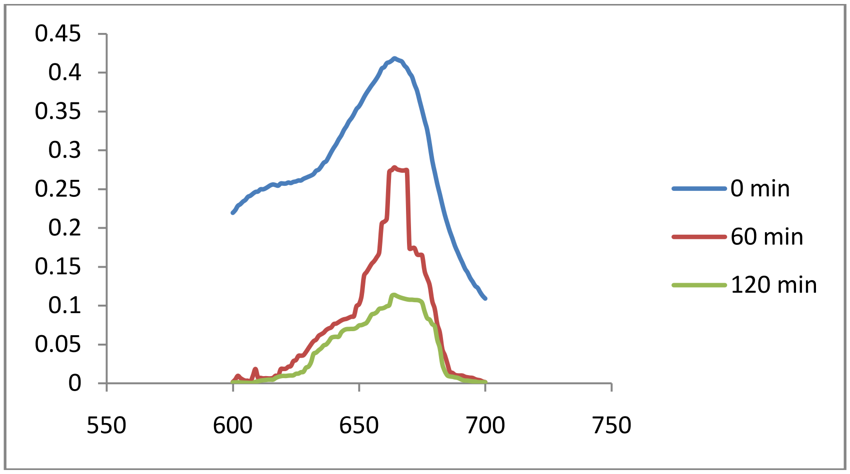


Figure-5: Photocatalytic degradation of MB dye using ZnO-NPs using stem extract of *R. cordifolia*

4.Conclusion:

The green method used for the synthesis of zinc oxide nanoparticles are eco-friendly, cost effective, more stable and the rate of reaction is fast as compare to chemical and physical method. The size of the synthesized ZnO-NPs was found around 20.07 nm and spherical in shape. They have good anti oxidant activity. The photocatalytic activity concludes that the synthesized ZnO-NPs has good efficiency to degrade MB dye solution under sun light. So they have application in water treatment plant and textile industries.

References:

1. Happy Agarwal, S. Venkat Kumar, S. Rajeshkumar, "A review on green synthesis of zinc oxide nanoparticles – An eco-friendly approach", *Resource-Efficient Technologies* 1-10, 2017.
2. J. Santhoshkumar, S.Venkat Kumar, S. Rajeshkumar, "Synthesis of zinc oxide nanoparticles using plant leaf extract against urinary tract infection pathogen", *Resource-Efficient Technologies* 0 0 0, pp. 1–7, 2017.
3. Karodi R, Jadhav M, Rub R, Bafna A, **"**Evaluation of the wound healing activity of a crude extract of *Rubia cordifolia* L. (Indianmadder) in mice", *International Journal of Applied Research in Natural Products*, Vol. 2(2), pp. 12-18, June-July 2009.
4. Rupali Patil, Mahalaxmi Mohan, Veena Kasture and Sanjay Kasture, "Rubia cordifolia: a review", *Oriental Pharmacy and Experimental Medicine*, vol. 9(1), pp. 1-13,2009.

5. Mariselvam et al. , **"**Green Synthesis of Copper Quantum Dots using *Rubia cardifolia* Plant Root Extracts and its Antibacterial Properties", *Journal of Academia and Industrial Research (JAIR*),Vol. 3(4), pp.191-194, 2014.
6. Mariselvam et al. , **"**Preparation and characterization of silver nanoparticles using *Rubia cordifolia* plant root extract and their microbial properties", *International Journal of Advanced Research* , Vol. 1(8) ,pp. 56-61, 2013.
7. Prachi et al., "Green synthesis of zinc oxide nanoparticles using *rubia cordifolia* root extract against different bacterial pathogens", *Indo american journal of pharmaceutical research*, vol.7 (9),pp.759-765, 2017.
8. Niranjan Bala, S. Saha, M. Chakraborty, M. Maiti, S. Das, R. Basub and P. Nandy , "Green synthesis of zinc oxide nanoparticles using Hibiscus subdariffa leaf extract: effect oftemperature on synthesis, anti-bacterial activity and anti-diabetic activity",*The royal society of chemistry* , vol. 5, pp. 4993-5003, 2015.
9. Ghorbani, "Synthesis of ZnO by precipitation method", *Orient. J. Chem.,* vol. 31(2), pp. 1219-1221, 2015.
10. C.Parthibana, N.Sundaramurthy, "Biosynthesis,Characterization of ZnO Nanoparticles by Using *Pyrus Pyrifolia* Leaf Extract and Their Photocatalytic Activity", *International Journal of Innovative Research in Science,Engineering and Technology*, Vol. 4,(10) ,pp-9710-9718, 2015.
11. Parimelazhagan Thangaraj, "Pharmacological assays of plant based natural products, progress in drug research", *springer*, 71:58, 2016.