Designing Zinc Oxide Nanoparticles (Hib/nZnO NPs) synthesizedusing 'Green' methods from Hibiscus rosa -sinensisflower extract as fluorescent probe for Dopamine

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Abstract:

In our work Zinc Oxide Nanoparticles (Hib/nZnO NPs) are prepared with the help of green methods from hibiscus rosa sinensis flower. SEM (Scanning Electron Microscope) analysis technique is used to characterize the morphology, microscopic structure and size of the Hib/nZnO NPs . The SEM clearly shows the distribution of ZnO nanoparticles prepared with natural surfactant. From SEM images it can be seen that the particles have sheet like structure with thickness which has the size below 100nm and no aggregation was seen. ZnO nanoparticles are analysed by UV-Visible Spectra and IR Spectra also. The interaction between dopamine and Hib/nZnO NPs solution was verified by fluorescence studies. Upon gradual addition of dopamine to the solution the intensity decreases i,e quenches and the λ_{max} moves towards higher wavelength, i.e., red shift takes place.

<u>Key Words:</u> Hibiscus rosa sinensis flower,Zinc Oxide Nanoparticles (Hib/nZnO NPs),UV-Visible Spectra, IR Spectra, SEM, Fluorescence spectroscopy

A. Introduction:

Particles of matter with the size in between 1 and 100 nanometer (nm) in size are known as nanoparticles. Green synthesis of metallic nanoparticles has gained an ultimate interest over the last decade due to their distinctive properties that make them applicable in various fields of science and technology. Green synthesis methods involving biological agents like bacteria,

fungi, plants and algae are a good alternative to the chemical and physical methods, as they are both environment friendly and economic[1-4]. Compared to other types of metal nanoparticles preparation, noble-metal based nanoparticle synthesis using various plants extracts has achieved an extensive interest because of its unique advancement of nanoscale activity, high selectivity and these are reusable in nature, also it is an eco friendly method to reduce the use of harmful chemical substances[5].

Metal nanoparticles which are synthesized by using plants have emerged as non-toxic, ecofriendly and of low cost. During this type of synthesis less energy is required.

ZnO nanostructures are gaining importance in research due to their unique properties and wide range of applications. ZnO nanoparticles are used because that they have antibacterial properties i,e they can strongly inhibit the action of pathogenic microbes when used in very small concentration. [6,7].

Dopamine (3,4-dihydroxyphenethylamine), an organic chemical belonging to catecholamine and phenethylamine families, acts as both hormone and neurotransmitter, playing a key role in the metabolism of brain and body. In the human body, role of dopamine is primarily in the cardiovascular, central nervous, renal, and hormonal systems, in addition dopamine monitor human metabolism too [8].

When ingested intravenously, Dopamine acts as sympathetic nervous system, which can produce effects such as increased heart rate and blood pressure [9]. Therefore, it is highly important to monitor the concentration of dopamine both in vivo and in vitro.

In our present study Zinc Oxide Nanoparticles (Hib/nZnO NPs) are synthesized using green methods from hibiscus rosa sinensis flower. The morphology, microscopic structure and size of the Hib/nZnO NPs were characterized by using SEM analysis which clearly shows the distribution of ZnO nanoparticles prepared with natural surfactant. From SEM images given below it can be seen that the particles have sheet like structure with thickness which has the size below 100nm and no aggregation was seen. ZnO nanoparticles are analysed by UV-Visible Spectra and IR Spectra also. The interaction between dopamine and Hib/nZnO NPs solution was verified by fluorescence studies. Upon gradual addition of dopamine to the solution the intensity decreases i,e quenches and the λ_{max} moves towards higher wavelength, i.e., red shift takes place.

B. Required materials:

- ZnSO₄.7H₂O
- Sodium Hydroxide (NaOH)
- Dopamine
- HCl
- Ethyl acetate
- Acetone
- Distilled water..etc.

C. Methods:

(i) Synthesis of a natural surfactant from *Hibiscus rosa-sinensis* flower:

Hibiscus petals are collected, cleaned, dried and crushed to powder. The fresh flower of *Hibiscus rosa-sinensis* are collected and the natural surfactant was extracted from it, under ambient conditions. During the process of synthesis, excess of an aqueous NaOH solution (pH-11) was added into the grind plant material of *Hibiscus rosa-sinensis* flower. After that the mixture was then heated on a water bath with continuous stirring for 1 hour and then it was allowed to stand for 12 to 18 hours. The alkaline extract was filtered, acidified with 10 ml aqueous HCl solution (pH-1), and allowed to stand for diserstion. Then by filtration, disersion was separated. The residue left was washed with distilled water and pre extracted with ethyl acetate by refluxing for about 5-6 hour. After that the pre- extractant were distilled off and the residue was extracted with acetone. The acetone which was extra obtained was mixture of natural surfactant. In this way, natural surfactant was finally separated and dried.

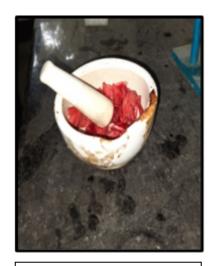


Fig 1A: Grinding Hibiscusrosa-



Fig 1B: Hibiscus solution



Fig 1C:Residue observed

(ii) <u>Surfactant assisted synthesis of Zinc Oxide Nanoparticles:</u>

88 ml of 1M aqueous solution containing ZnSO₄.7H₂O and natural surfactant was mixed with 12 ml aqueous NaOH solution(4M) in a reaction flasks. After that the mixture in the flask was stirred vigorously under room temperature and then respective reaction flask were exposed to reaction condition by placing them in microwave oven for 1 min. The white precipitate that obtained were filtered, washed with distilled water and then dried at room temperature.



Fig 2A: Refluxing



Fig 2B: Stirring



Fig 2C:Zinc Oxide Nanoparticles (Hib/nZnO NPs)

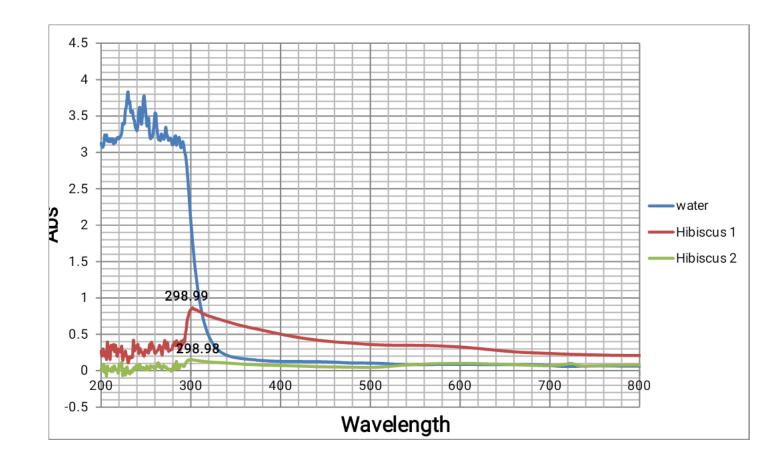
D. RESULTS AND DISCUSSION:

(i) Characterization of the prepared Zinc Oxide Nanoparticles (Hib/nZnO NPs):

The synthesized product thus obtained in our work has been characterized with various analytical techniques.

A. <u>UV-Visible Analysis:</u>

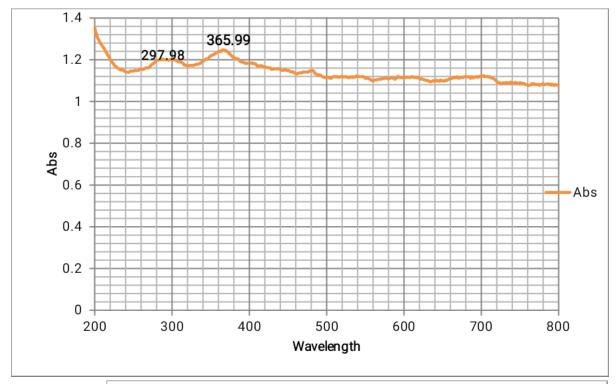
<u>Sample 1:</u> UV-Visible analysis of **aqueous** extract of *Hibiscus rosa-sinensis* flowersolution:

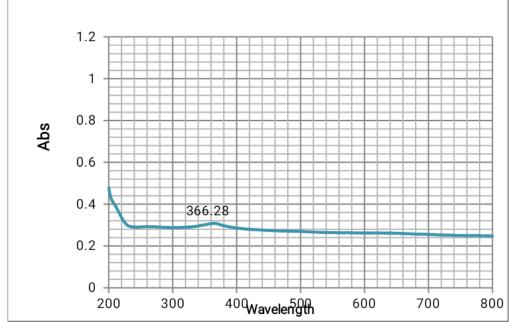


<u>Fig-3:</u> UV-Visible spectra analysis of aqueous extract of *Hibiscus rosa-sinensis* flower.

<u>Sample 2</u>: UV-Visible analysis of ZnOnanoparticles :

To study the UV spectroscopy of synthesized ZnO nanoparticles, they are first sonicated in distilled water for about 15 minute and after that UV spectra were recorded. Supplementary data Fig-2(A) and Fig-2(B) shows the UV-Visible





absorption spectra of ZnO nanoparticles.

Fig-4 (A): UV-Visisble spectra of ZnO nanoparticles at comparatively higher concentration.

Fig-4 (B): UV-Visible spectra of ZnO nanoparticles at comparatively lower

concentration.

The UV-Visible absorption characteristic of the aqueous extract of *Hibiscus rosa-sinensis* flowers were investigated, and a prominent peak was observed in the wave length range of 295-300 nm as shown in the **Fig-3**.

Subsequently, UV-Visible spectroscopy was employed to analyze the prepared ZnO nanoparticles, using both higher and lower concentration of the prepared solution. The spectra of ZnOnanoparticles is shown in the Fig -4(A) and Fig-4(B).

In Fig-4(A), the UV-Visible spectrum of the higher concentration demonstrated the characteristic peak of pure ZnO nanoparticles within the range of 360nm -370nm. Notably, this peak coincided with the presence of *Hibiscus rosa-sinensis* peak observed in the 295-300 nm range. The concurrent appearance of these peaks indicated the successful synthesis of ZnO nanoparticles, while also suggesting the retention of *Hibiscus rosa-sinensis* components in the solution.

Conversely, **Fig-4(B)** exhibited the UV-Visible spectrum of the **lower concentration**, revealing only the distinctive peak of ZnOnanoparticvles at 360nm – 370 nm. Interestingly, the peak corresponding to *Hibiscus rosa-sinensis* was absent, implying that its concentration in the solution was negligibly low due to dilution.

This finding clearly shows the successful synthesis of ZnO nano particles (Hib/nZnO NPs).

FT-IR analysis of *Hibiscus rosa- sinensis* flower:

Fig-5A shows the FT-IR spectrum of *Hibiscusrosa-sinensis* extract. FT-IR spectra of *HibiscusRosa Sinensis* flower exhibited the characteristic bands at 3280 cm⁻¹. This clearly indicates the presence of alcohol and phenol (O-H) groups. The peak observed at 2916 cm⁻¹ and 2845 cm⁻¹ are ascribed to the stretching vibration of C-H bond of the Methyl or Methylene group. The FT-IR spectrum at 1630 cm⁻¹ indicates the presence of Carbonyl(C=O) group. The peak at 1010 cm⁻¹ is ascribed to the stretching vibration of C-N bond of aliphatic amines.

Then synthesized Zinc Oxide nanoparticle were put to FT-IR analysis to detect the various characteristic functional group associated with the synthesized nanoparticle. The observed peaks indicate the characteristic functional group present in the synthesized Zinc Oxide Nanoparticle. It can be inferred that the samples have absorption peaks in the range of 3370 cm⁻¹, 1520 cm⁻¹, 1395 cm⁻¹, 1095 cm⁻¹, 735 cm⁻¹, and 500 cm⁻¹ – 697 cm⁻¹. The absorption peak at 500-697 cm⁻¹ and 735 cm⁻¹ corresponds to Metal-Oxygen means ZnO stretching vibration mode. The peak at 1095 cm⁻¹ is ascribed to the stretching vibration of C-N bond of the primary amine or to the stretching vibration of the C-O bond of the secondary alcohol. The peak at 1395 cm⁻¹ is ascribed to primary or secondary or phenol or tertiary alcohol in-plane bend or vibration. The peak at 1520 cm⁻¹ is ascribed to the

vibration modes of aromatic nitro compound and alkyl. The peaks at 3370 cm⁻¹ are ascribed to the stretching vibration of hydroxyl compound.

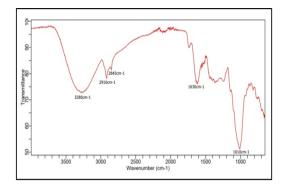


Fig-5A: FT-IR Spectra analysis of *Hibiscusrosa* -

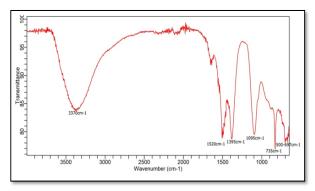


Fig-5B: FT-IR Spectra analysis of ZnO nanoparticles.

4: SEM Analysis:

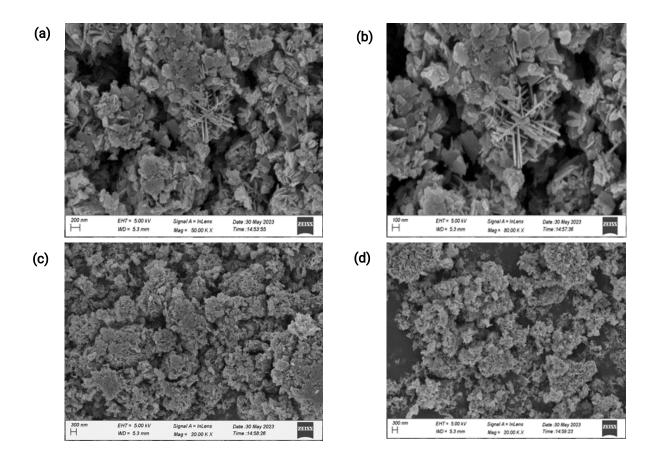


Fig 6A: SEM analysis of the prepared Hib/nZnO NPs

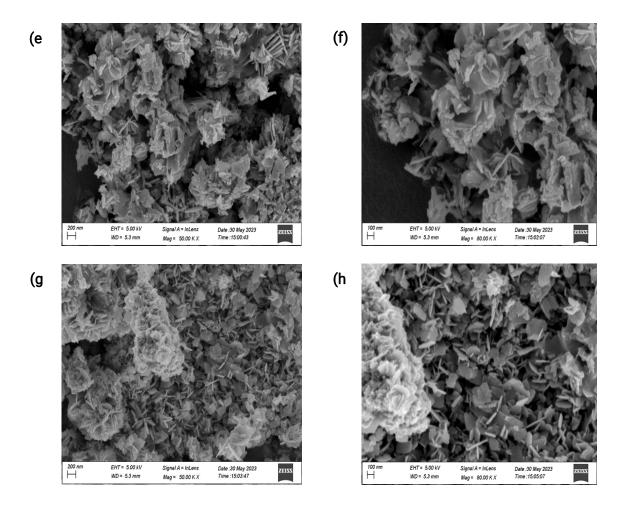


Fig 6B: SEM analysis of prepared Hib/nZnO NPs

The morphology, microscopic structure and size of the Hib/nZnO NPs were characterized by SEM analysis and that clearly shows the distribution of ZnO nanoparticles prepared with natural surfactant. From the SEM images it can be seen that the particles have sheet like structure with thickness which has the size below 100nm. It can clearly seen that no aggregation is formed. 3-D structure of prepared ZnO nanoparticle is shown in the Fig-6A and Fig-6B.

(ii). Flurescence study

The interaction between dopamine and Hib/nZnO NPs solution was verified by fluorescence studies. Upon gradual addition of dopamine to the solution the intensity decreasesi,e quenches and the λ_{max} moves towards higher wavelength, i.e., red shift takes place.

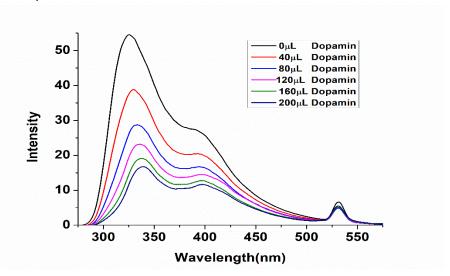


Figure 7: Fluorescence emission spectrum of Hib/nZnO NPs solution (black), Hib/nZnO NPs solution and 200 µL dopamine-aqueous solution (dark blue). Red shift occurs on addition of dopamine-aqueous solution

E. CONCLUSIONS:

- 1. In our present work, ZnO nanoparticles were synthesized using green and ecofriendly method with the help of surfactant which was isolated from the flower of *Hibiscusrosa-sinensis* which is act as a reducing agent.
- The synthesized ZnO nanoparticle have been characterized using FT-IR, UV
 -Visible Spectroscopy and SEM.. All these studiesconfirms the successful
 formation of ZnO nanoparticles.
- 3. The interaction between dopamine and Hib/nZnO NPs solution was verified by fluorescence studies. Upon gradual addition of dopamine to the solution the intensity decreases i,e quenches and the λ_{max} moves towards higher wavelength, i.e., red shift takes place.

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Conflict of Interest

We hereby declare no competing conflict of interest

F. REFERENCES:

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