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Zinc Oxide nanoparticles synthesis by use of aqueous extracts of *Muntingia calabura* L.

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ABSTRACT

Biological synthesis of metal nanoparticles gained worldwide and interest due to their rapid, non-toxic, economical, single-step technique and eco-friendly alternative. Green-chemical approach of production of Zinc Oxide (ZnO) nanoparticles (NPs) has been exploited in the field of medicine, food, packaging, nano-optical, and electrical devices. *Muntingia calabura* is a multipotent medicinal plant with astounded biological activities and phytoconstituents. The nanoparticles obtained using aqueous extracts of various parts of *M. calabura* were characterized with UV-VIS spectroscopy to obtain information concerning the optical properties of synthesized ZnO nanoparticles. The proposed green and economical method could be used for large scale production of nanostructures because of its advantages over other physical and chemical methods.

Keywords: Biosynthesis, Zinc oxide nanoparticles, *Muntingia calabura*, optical properties

1. INTRODUCTION

The green synthetic approach for nanoparticles put forward among other traditional methods of production of nanoparticles [1]. The biological methods of synthesis of nanoparticles have been acknowledged as an economical and alternative route, in which natural ingredients (phytochemicals) present in plant extracts are employed [2]. Zinc oxide nanoparticles (ZnO NPs) are a promising category of nanostructures with wide varieties of applications. Zinc oxide nanoparticles are reported to exhibit attractive antimicrobial properties against gram-positive, negative bacteria and fungi [3]. The applications of ZnO NPs are

synthesis (preparation method) specific, which includes antimicrobial nanoagents in food, medicine and textile [4].

Muntingia calabura L. belongs to the family Elaeocarpaceae and is a medium sized, evergreen tree native to the Southern Mexico and tropical America and distributed in the tropical regions. It is commonly known as Singapore Cherry and Jamaican Cherry, and cultivated in Southeast Asia, India, Malaysia, Philippines, and Indonesia [5]. It is a fast growing tree with a cluster of green foliage (**Fig. 1**). The stem is woody and brown with dark green, alternate and lanceolate pubescence hoary leaves. The flowers are white, single with prominent yellow stamens. The fruits are round, red, soft with musky juicy pulp and often consumed. The seeds are yellow, Tiny, and numerous [6].



Fig. 1. *Muntingia calabura* plant with flowers and fruits.

It has been reported that the traditional Columbian and Peruvian folklore used the bark and flowers of *M. calabura* as an antiseptic and to alleviate swellings. The decoction of the leaves is used as beverage reported to cure gastric ulcer, headache, cold and swelling in the prostate gland. Furthermore, the infusion of the flowers is used as a tonic and tranquillizer. In

Mexico, the plant is used against measles, mouth pimples, and stomach ache. The roots are also used as an emmenagogue and abortifacient. The fruits are eaten raw and used in preparation of jams and jellies [6, 7].

This plant is reported to possess various important bioactive compounds, viz., flavonoids, chalcones, flavonones, glycosides, tannins and volatile compounds like muntingone, calaburone, β -amyrenone, β -sitosterol, syringic acid, vanillic acid, etc. [8, 9]. The plant extracts of *M. calabura* are used vigorously in the synthesis of silver and gold nanoparticles [10-13] but the synthesis of Zinc oxide nanoparticles is largely deficit in the literature. Therefore, considering the unique properties and the applications of zinc oxide nanoparticles, the present study aims to utilize the medicinal plant *M. calabura* for the possible synthesis of ZnO nanoparticles. The study reveals the biogenic method of synthesis of zinc oxide nanoparticles using aqueous extracts of various parts of *M. calabura*.

2. MATERIALS AND METHODS

2. 1. Preparation of Zinc Nitrate solution

Zinc Nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] (Sigma-Aldrich, Saint Louis, MO, USA) was used as precursor in this study to synthesize nanoparticles. Freshly prepared aqueous solution of Zinc Nitrate (1 mM) was used throughout the experiments. All the glassware used were thoroughly washed and rinsed with single-distilled water and oven dried at 110 °C before preparation.

2. 2. Collection of plant materials and preparation of broth solution

The plant materials were collected from the east-coast region of Puducherry (the south India) and identified with the help of flora of Tamil Nadu [14]. The plant parts like leaf, stem, root, flowers and fruits were collected from the healthy plants during 2014-2015. The plant parts were excised with sterilized scissors and immersed in 25% ethanol for one-two minutes to remove dust particles and other pathogenic spores. The plant parts were washed thoroughly with distilled water and finely sliced into small pieces. Five grams of finely chopped plant materials were boiled in with 50 mL of double distilled water in 200 mL Erlenmeyer flask for 15 min for the preparation of broth solutions. After boiling, the plant extracts were filtered through Whatman filter paper (90 mm). The extraction process was repeated for three times and the fresh extracts were used for further studies.

2. 3. Zinc oxide nanoparticles synthesis

The reduction of Zn^{2+} ions to ZnO was performed by combining the plant extracts with the precursor solution of Zinc nitrate. In a typical experiment, 1 mL of the plant extract was added to 9 mL of 1 mM aqueous Zinc nitrate solution. Reduction of Zinc nitrate was monitored by visual color change.

2. 4. Purification of ZnO NPs

After the completion of the reaction, ZnO NPs were spun at 10000 rpm (bench top, Eppendorf, Thermo Fisher Scientific, Darmstadt, Germany) for 15 min at ambient temperature

to eliminate any large aggregates; the supernatant was collected and used for further experiments.

2. 5. UV-visible Spectroscopy

The visual indication of the color exchange from colorless solution to yellow indicated the formation of the ZnO NPs. The formation of the ZnO NPs was further confirmed by monitoring the recordings/graphs of UV-Visible absorption spectra as a function of time. The absorption maxima of the ZnO NPs colloid were monitored between 200 nm and 700 nm by UV-Visible spectrophotometer (Systronics Double Beam Spectrophotometer, (Model 2202, Systronics Ltd. India).

The spectroscopic analyses were carried out on a freshly prepared sample at ambient room temperature (24–28 °C) using quartz cuvettes with an optical path length of 1 cm. The data were reported from the independent three experiments and each synthesis experiment holds a set of measurements with 10 replicates.

3. RESULTS AND DISCUSSION

3. 1. Synthesis of ZnO nanoparticles

The effective method of the synthesis of ZnO nanoparticles reported herein was achieved by the reduction of Zinc nitrate solution as reported by Shekhawat *et al.* [15]. Here, we report the single step and green method of synthesis of ZnO nanoparticles using the aqueous extracts of *M. calabura*. Furthermore, the color change was observed within 5 min after the mixing of the plant extract and the Zinc nitrate solution. The formation of nanoparticles was completed within 20 min of the initiation of reaction, which is a major advantage of this green synthesis approach.

Upon mixing the leaf extract with aqueous Zinc nitrate, the solution transmuted color rapidly from pale green to pale yellow within 0.5 min, indicating the formation of ZnO NPs. Stem and root extracts reaction mixtures changed from colorless to yellow upon heating the solution for 4 and 4.5 min, respectively. Flower extract solution changed its color within 3 min and the fruit reaction mixture changed the color from white precipitate to yellow precipitate by heating up to 5 min. It is reported that the changes in color of reaction mixtures were due to the localized surface Plasmon resonance (SPR) [16].

The hypothetical mechanism for nanoparticles synthesis was driven by the complex reducing molecules/free radical scavenging molecules present in the aqueous plant extracts like, antioxidants, enzymes, vitamins and phenolic compounds, which reduce metal cations into metal/metal oxide nanoparticles [17].

Earlier reports showed that the functional groups of phytochemicals in plant extracts, such as amines, alkanes, terpenoids, flavonoids, alkaloids induced ZnO nanoparticles synthesis in *Passiflora caerulea* [18]. *Aloe vera* and *Hibiscus subdariffa* leaves mediated ZnO NPs synthesis and their FT-IR spectra showed the presence of functional groups and protein as the stabilizing agent [19].

The functional groups, such as amine, alcohol, ketone, terpenoids, polyphenols, sugars, alkaloids, phenolic acids, and proteins present in plant extracts play crucial roles in the bio-reduction of metal ions and synthesis of corresponding nanoparticles [20].

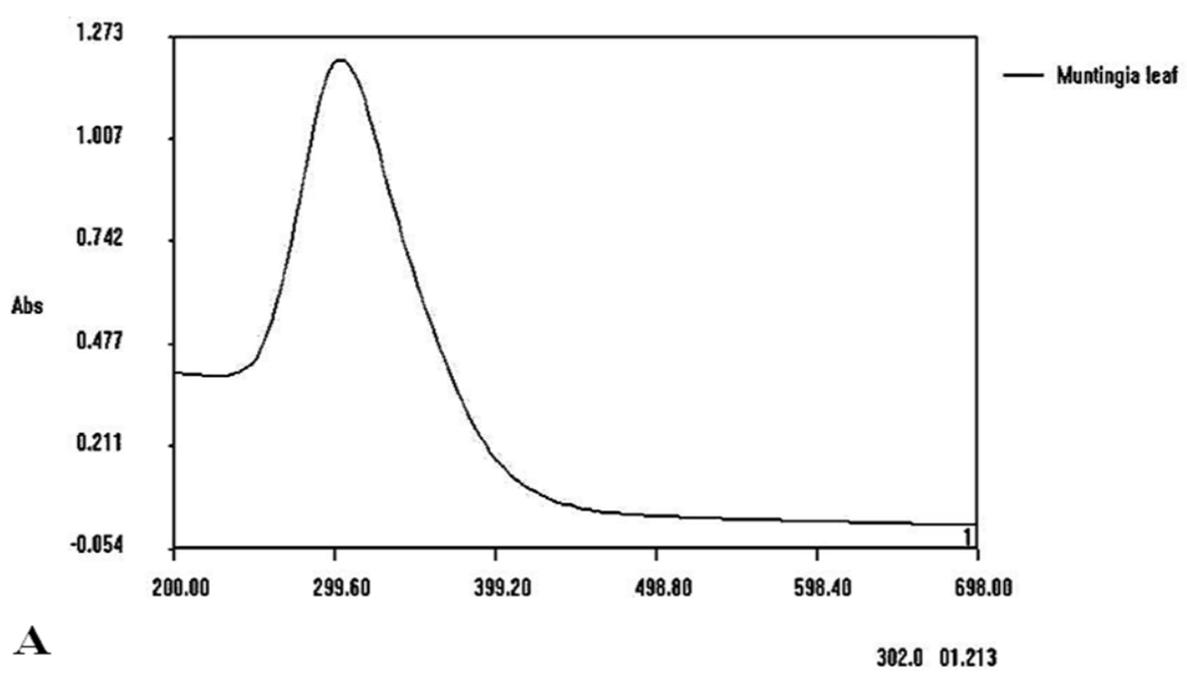
3. 2. UV-Visible spectroscopic characterization of Zinc oxide nanoparticles

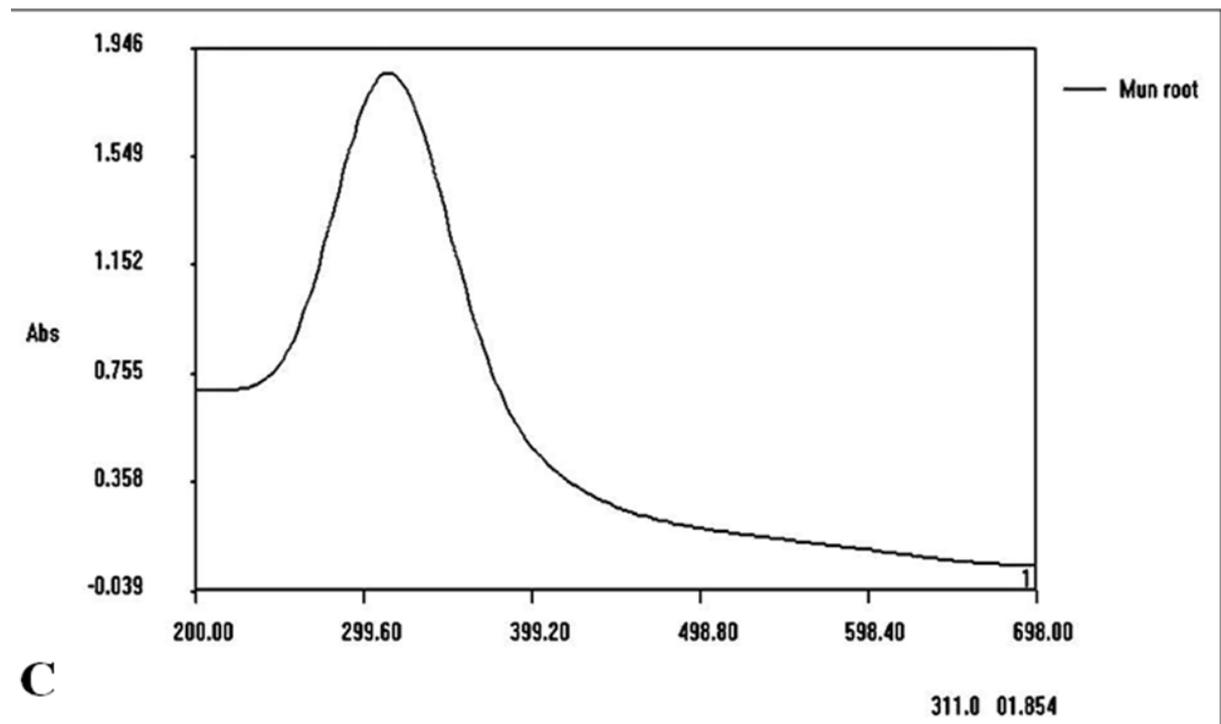
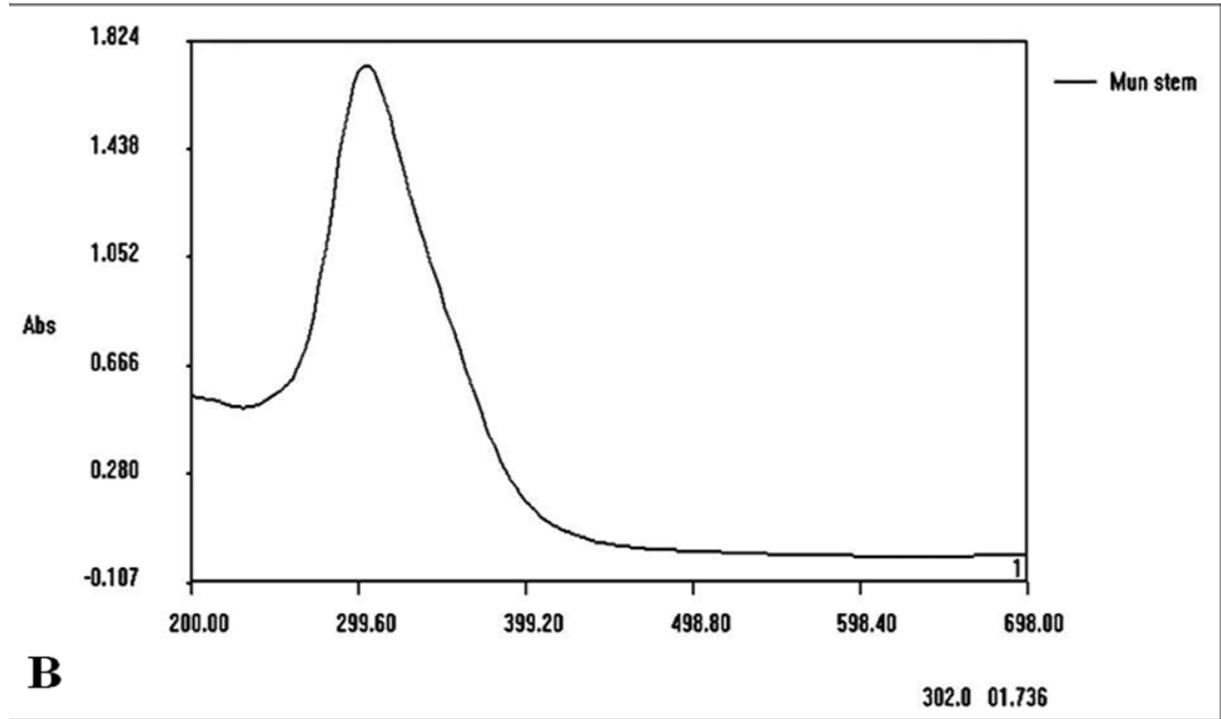
The formation of ZnO nanoparticles was evident from the color change of the solutions from colorless, pale green to yellow. The presence of the characteristic plasmon absorbance spectra in the range of 302-317 nm with distinct peaks again confirmed the synthesis of ZnO nanoparticles with different time intervals.

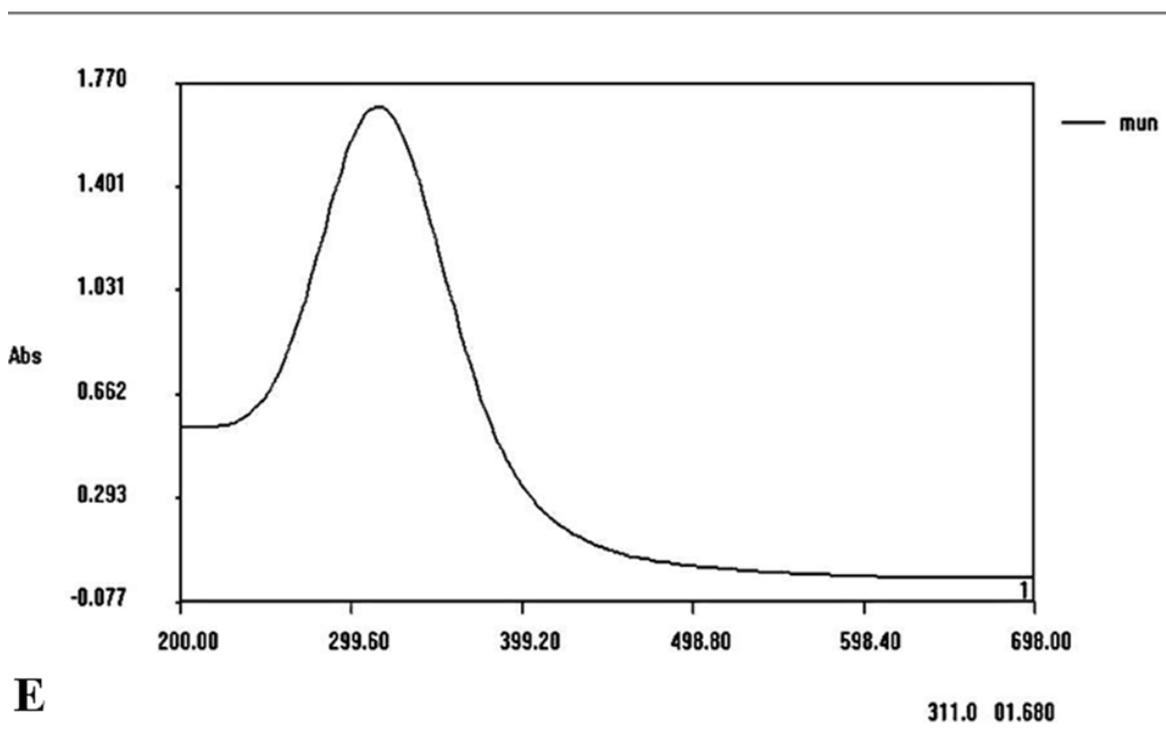
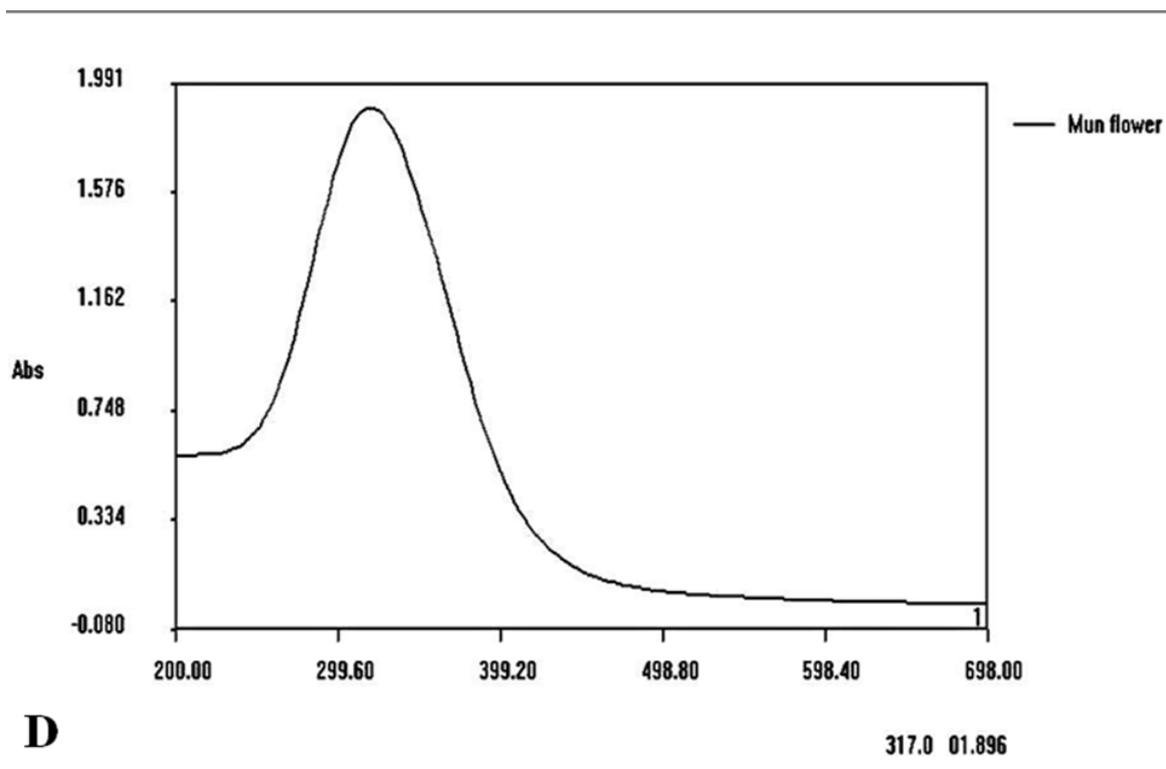
The repeated synthesis and UV-Vis spectroscopy analysis confirmed the completion of the reaction within 30 min after mixing of the solutions and incubation at room temperature as stable peaks were obtained without any further change. The aqueous reaction mixture of leaf and stem showed distinct peaks at 302 nm with 10 and 13 min of incubation periods, respectively. The root and fruit reaction mixtures showed peaks at 311 nm after 22 and 17 min of incubation. The flower reaction mixture presented strong absorbance peak at the wavelength 317 nm after 29 min of incubation (**Fig. 2A to 2F**).

The typical absorption peak of ZnO in respective reaction mixtures were reported as the intrinsic band gap absorption of ZnO due to the electron transitions from the valence band to the conduction band ($O_{2p}-Zn_{3d}$) [21, 19].

The presence of phytochemicals in different plant parts is varying. The stability and the reaction completion time also varied with different plant parts of various species as the constituent phytochemicals act as reducing and stabilization agent [22]. Dobrucka and Długaszewska [23] reported that the stability in nanoparticles is observed after 120 hours in *Trifolium pratense* flower extracts using UV-Vis spectrophotometer. Incubation of plant extracts with aqueous zinc ions at room temperature resulted in the formation of ZnO nanoparticles, suggesting that the free molecules in the plant extracts acted as a strong reducing agent.







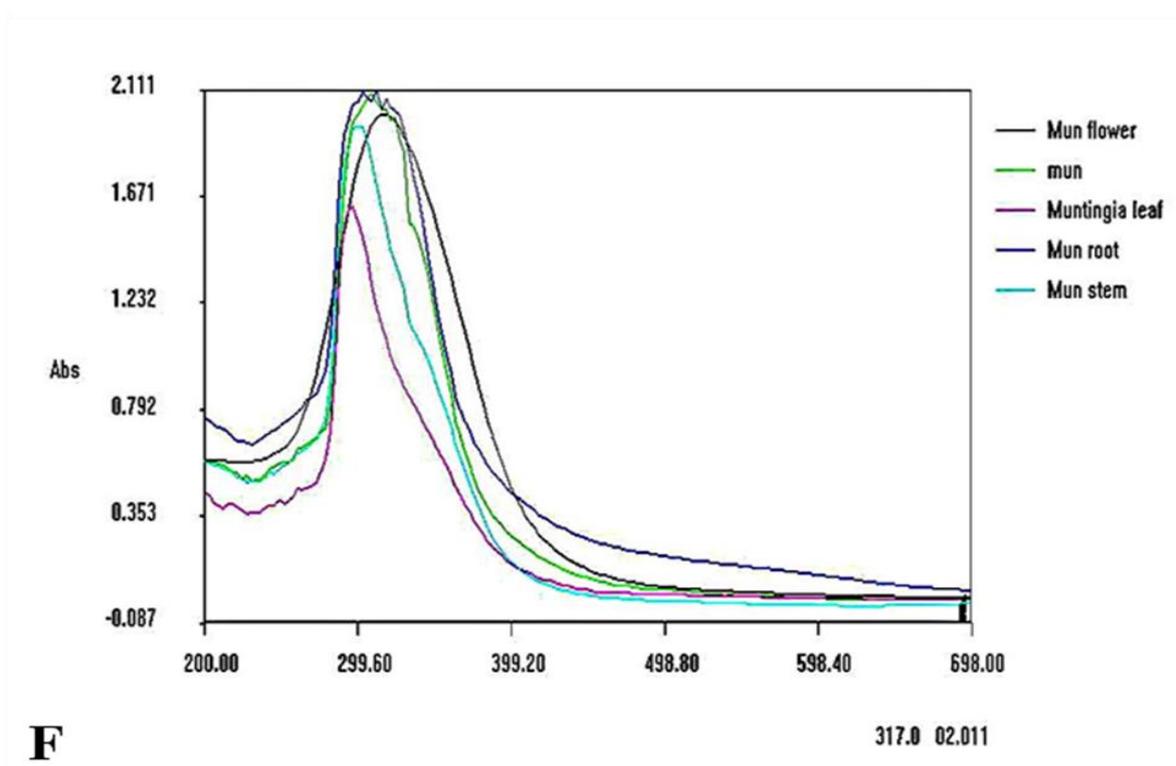


Fig. 2. UV-Vis spectral absorbance peaks of different reaction mixtures. **A.** Leaf, **B.** Stem, **C.** Roots, **D.** Fruits, **E.** Flowers and **F.** Combined peaks of all the reaction mixtures.

The extracts of *M. calabura* reported to contained amines or cysteines, carbonyl group and other aromatic compounds which stabilized the Silver NPs. Peddoju *et al.* [10] synthesized Ag nanoparticles from the aqueous extracts of *M. calabura* leaves. Patra *et al.* [11] reported heterobimetallic cubical nanoparticles from the flower extracts of *M. calabura*. Udhaya [12] synthesized 28-43 nm sized silver nanoparticles using the aqueous leaf extracts of *M. calabura*. Recently, Wahab *et al.* [13] reported the synthesis of gold nanoparticles using the leaves of *M. calabura*. The phytochemicals present in the leaves (tannins, saponins, and flavonoids) were acting as a bioreductor to produce gold nanoparticles, which were characterized by UV-visible spectra, Scanning Electron Microscopy (SEM) and X-Ray diffraction (XRD).

4. CONCLUSIONS

The present biosynthetic way of production of ZnO NPs by the use plant extracts of *M. calabura* is a simple, eco-friendly “green” alternative and contrast to the traditional reduction of metallic ion solutions with hazardous (chemical) reducing and capping agents. It would satisfy the increasing need for the development of new methods for the synthesis of nanoparticles. The formation of ZnO nanoparticles was evident from the color change in solution (from colorless to yellow). The UV-Vis characterization results revealed the presence of the typical plasmon peaks in the range of 302-317 nm. These biosynthesized ZnO NPs could

be further explored for their biocompatibility and applications in various fields assisting in health and human welfare.

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