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Synthesis and Characterization of ZnO Nanoparticles - A Green Chemistry Approach

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ABSTRACT: Many green synthesis methods are used for synthesizing the nanoparticles in order not to harm the human kind which makes use of it. Sunscreen is one of the vital products that play a vital role in the human life now-a-days. Sunscreens are generally prepared with titanium dioxide and zinc oxide nanoparticles due to its higher bandgap which helps to protect the skin from UVB and UVA rays respectively. These nanoparticles are chemically prepared as far as now in the case of sunscreen products. Titanium dioxide nanoparticle does not give full protection over UV-A spectrum when compared to Zinc oxide nanoparticle. So sunscreen manufacturers opt for ZnO nanoparticle to give better results. Our motivation is to prepare green synthesized ZnO nanoparticle to use it in the preparation of transparent sunscreen. Here we use Aloe barbadensis leaf extract for the synthesis of ZnO nanoparticle.

Keywords: ZnO nanoparticles; green synthesis; Persea Amaericana; Sunscreen applications.

INTRODUCTION

Nanomaterials are being used in a wide variety of applications due to its varying properties on scaling down from bulk size to nanometer size (10^{-9}m). The surface area to volume ratio plays an important role in nanoparticles, due to which they become more reactive. Zinc oxide (ZnO) is a metal oxide semiconductor[1] which is non-toxic and bio-compatible[2] which has a bandgap of about 3.37eV. ZnO nanoparticles are being widely under use in a variety of fields due to its uniqueness and attractiveness in their properties like electrical, optical, dermatological and anti-bacterial[3 & 24]. This makes them to be a promising element the widely distributed fields like automobiles, electronics, optoelectronics, textiles, medicine, drug delivery and cosmetics.

Most commonly, ZnO nanoparticles are produced through chemical methods[2 & 3-6], like sol-gel processing[2 & 8], precipitation and electrodeposition method[9 & 10]. Since ZnO acts as a physical barrier to the Ultraviolet (UV) radiation, they are being used in transparent sunscreen applications[8]. Since they have wide bandgap and large excitation energy[7]. ZnO is considered as "generally recognized as safe" (GRAS)[11], but chemically prepared ZnO may be toxic as they involve use of toxic, hazardous chemicals. There is an increasing need to develop environmentally benign methods for nanoparticle synthesis which must be devoid of the use of toxic chemicals[12-14]. Biomimetics means applying biological principles in material formation which involves bio-reduction. Biological methods of nanoparticles synthesis using microorganisms[15 & 16], enzymes[17], fungus[19] and plants or plant extracts[18 & 20] have already shown to be possible.

In the present work, we investigated the synthesis of stable ZnO nanoparticles with the biological method using three kinds of extracts, one from mesocarp of fruit and another from mesocarp and seed of the fruit of avocado (Persea Americana Mill) which belongs to the family Lauraceae. Flavonoids in fruits of P. americana could be behind the anti-inflammatory, anti-cancer and anti-hypertensive properties of the plant. Flavonoids are potent water soluble super anti-oxidants and the fruit may also act as free radical scavengers. They prevent oxidative cell damage, have strong anti-cancer activity[21]. Another extract was

avocado oil made from endosperm of coconut (Cocos nucifera L.). It contains water, fat, protein and minerals which is the source of the coconut oil[22]. It also contains vitamins like B, C and E. Avocado fruit contains vitamins like B-6, C, E and K. The anti-oxidant property of vitamins makes it a vital molecule for skin health, so it might be used in cosmetic applications, especially in sunscreens.

MATERIAL AND METHODS

Biological Extracts: Avocado fruit of about 1kg and one coconut was collected from the local market to prepare the biological extract.

Aqueous Extract: Half of the mesocarp of one avocado fruit was taken and crushed to a fine paste using a blender. The paste is mixed with about 50 ml of distilled water. The mixture is then strained in muslin cloth to get about 40-45 ml of aqueous extract.

Oil Extract: The mesocarp of two avocado fruits are taken and crushed to a fine paste using a blender. The endosperm of one coconut is grated and grinded with 150 ml of distilled water in a blender which is then strained to obtain the coconut milk. The paste is mixed with coconut milk and cooked for about 2 hours and 15 minutes at about medium temperature. Initially the mixture was of pale green color and finally it was of dark brown color. As it gets cooked, it starts to ooze out oil. The final cooked product is then strained in a muslin cloth to get avocado oil of about 30 ml.

Liquid Extract: Half of the avocado mesocarp of one avocado fruit and one seed is crushed to paste using a blender. About 100 ml of distilled water is mixed with it and cooked at medium temperature for about 30 minutes. Then it is allowed to slightly cool down and strained in muslin cloth to obtain a thick liquid extract of about 55-60 ml.

Synthesis Procedure:

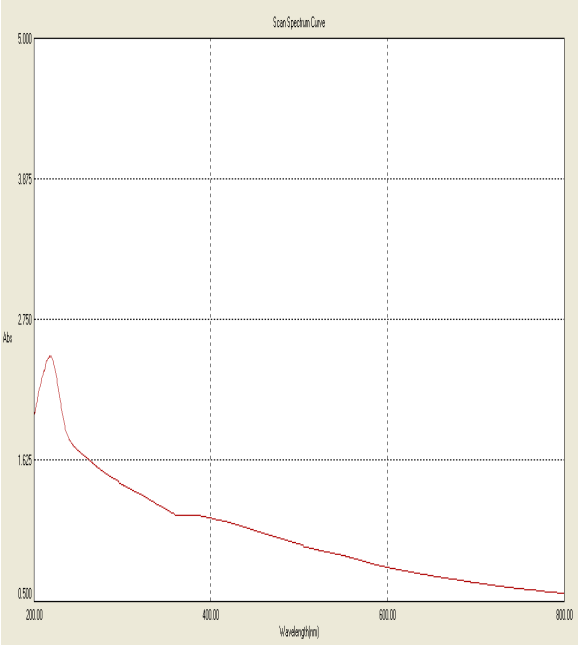
1. *Synthesis with 2ml aqueous extract:* 0.1 M of aqueous solution of Zinc nitrate dehydrate [$Zn(NO_3)_2.6H_2O$] and 0.5 gm of NaOH with 20 ml of distilled water has been used as starting materials to which 2 ml of aqueous extract has been added and kept under vigorous stirring. The pH value was noted to be 10 at the end of 1hour. After stirring for about 3hours, a light yellow precipitate was obtained finally.
2. *Synthesis with 5 ml aqueous extract:* 0.5 M of aqueous solution of Zinc nitrate dehydrate and 0.5 gm of NaOH with 20 ml of distilled water are mixed with 5 ml of aqueous extract and kept for vigorous stirring for about 1 hour and 30 minutes. At the end of 1hour the pH value was 10. Finally, a yellow precipitate was obtained.
3. *Synthesis with 5ml oil extract:* 0.5 M of aqueous solution of Zinc nitrate dehydrates and 0.5 gm of NaOH with 20 ml of distilled water was initially taken. 5ml of avocado oil is added to the initial mixture and kept for vigorous stirring. After 1 hour and 30 minutes the pH value was 12. After 1hour and 45 minutes, the liquid was at bottom and foam was formed at the top on stirring, slowly the foam and liquid gets mixed up to form a fine cream at the end of 2 hours and 30 minutes. After 3 hours a thick precipitate of light green color has been obtained.
4. *Synthesis with liquid extract:* 0.5 M of aqueous solution of Zinc nitrate dehydrate and 1.0 gm of NaOH with 40 ml of distilled water are mixed initially. 10 ml of liquid extract is added to them, which is then kept for vigorous stirring, for about 2 hours. Finally, a brown color precipitate was obtained.

All the samples are then transferred to the crucibles and calcined at 600 °C for about 2 hours. The calcined samples are crushed to fine powder and transferred to the micro centrifuge tubes.

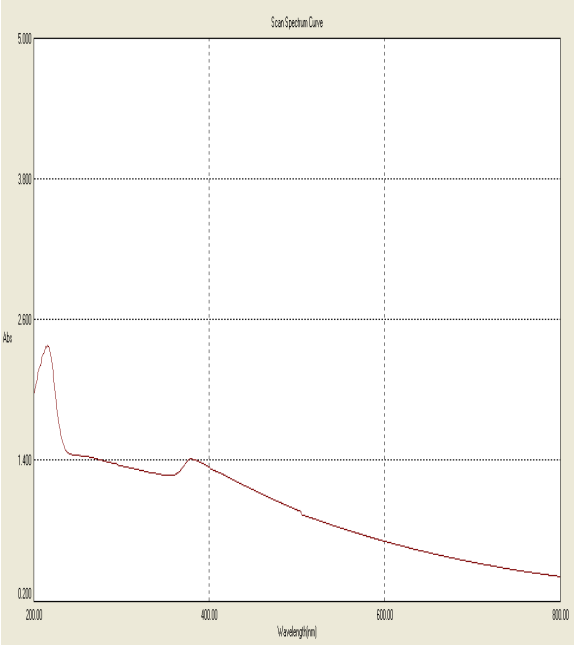
RESULTS AND DISCUSSION

UV–VIS spectroscopy: In sample A, there was a strong light absorption ($\pi \longrightarrow \pi^*$) at the wavelength of 220 nm and there is a weak light absorption ($n \longrightarrow \pi^*$) near 370 nm. The energetically most favorable ($\pi \longrightarrow \pi^*$) excitation has occurred from highest energy bonding pi-orbital (HOMO) to the lowest energy bonding pi-orbital (LUMO). When 2ml of aqueous extract is taken (Sample a) and when 5 ml of aqueous

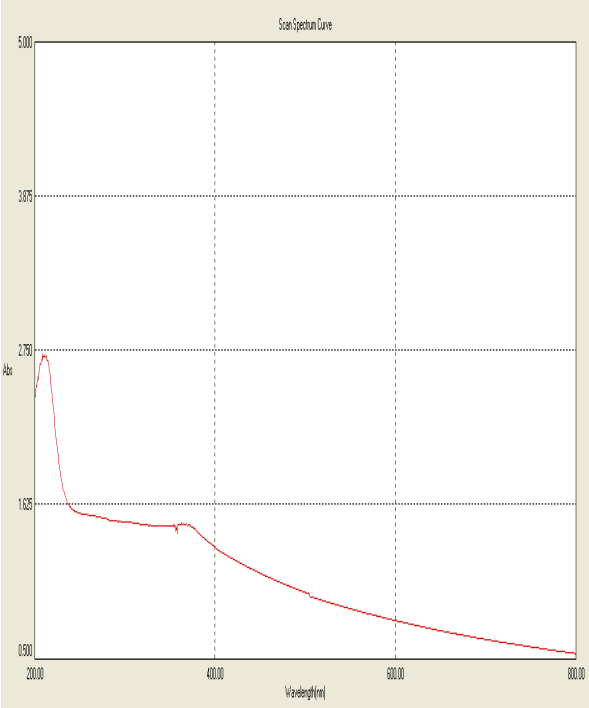
extract is taken (Sample b), the strong absorption was found to be of same range whereas the light absorption range has increased as there is an increase in concentration of extract. With 5 ml of oil (Sample c), strong absorption was at 212 nm and light absorption was at 371 nm and with 5 ml of liquid extract (Sample d), there was only a strong absorption at 213 nm. With the chemically synthesized sample (Sample e) strong absorption was at 379 nm. The intensity of absorption is comparatively high in biologically prepared samples to that of chemically prepared sample.



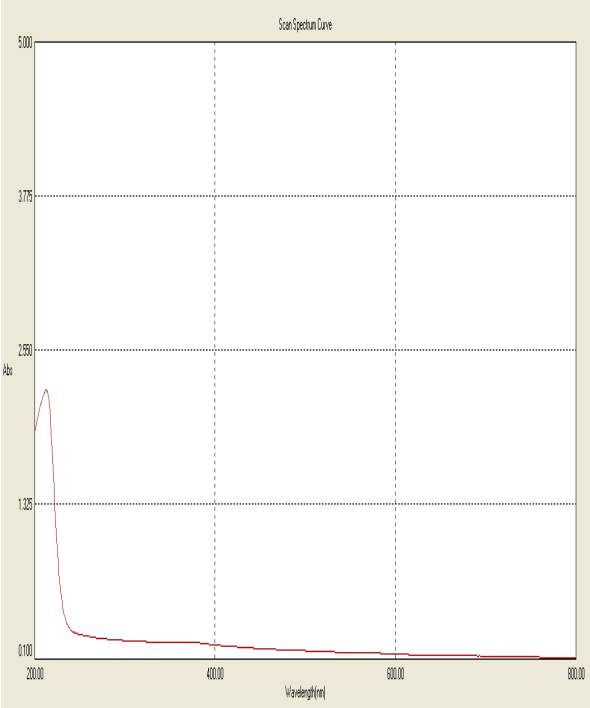
Sample a



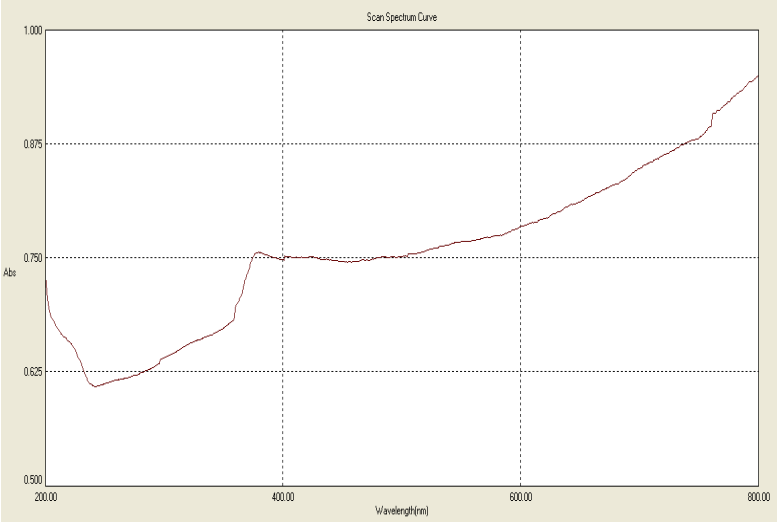
Sample b



Sample c

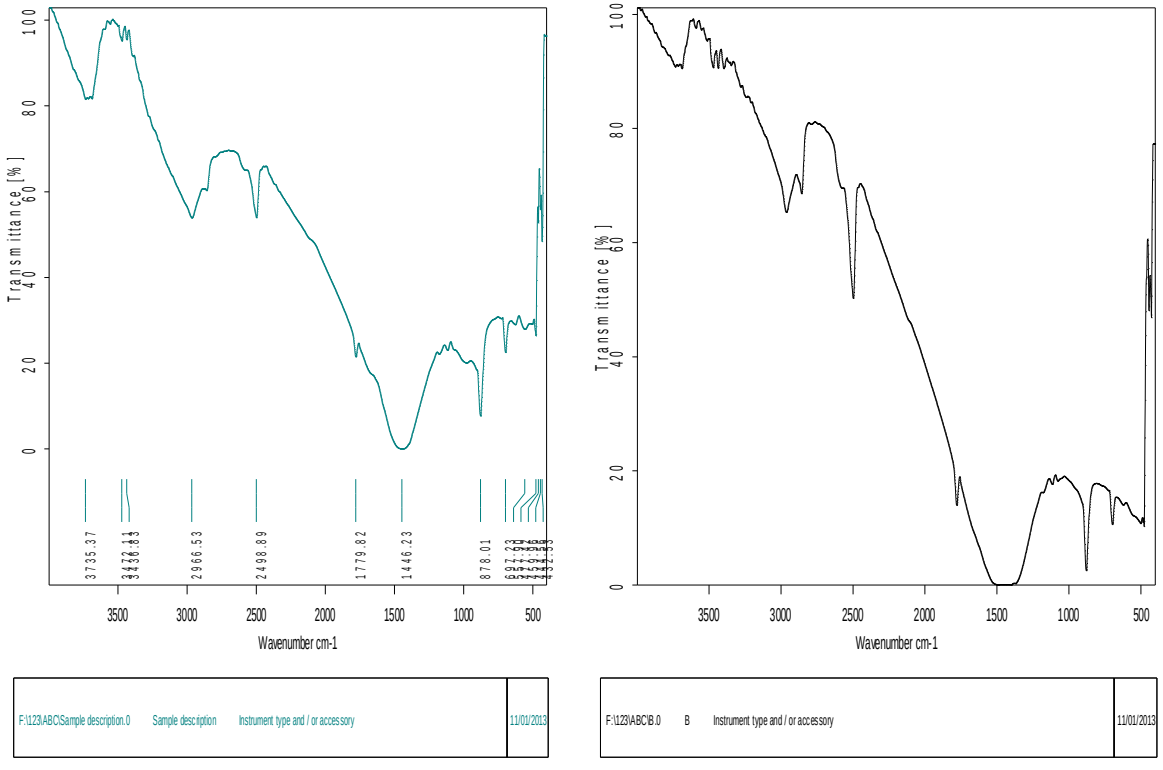


Sample d

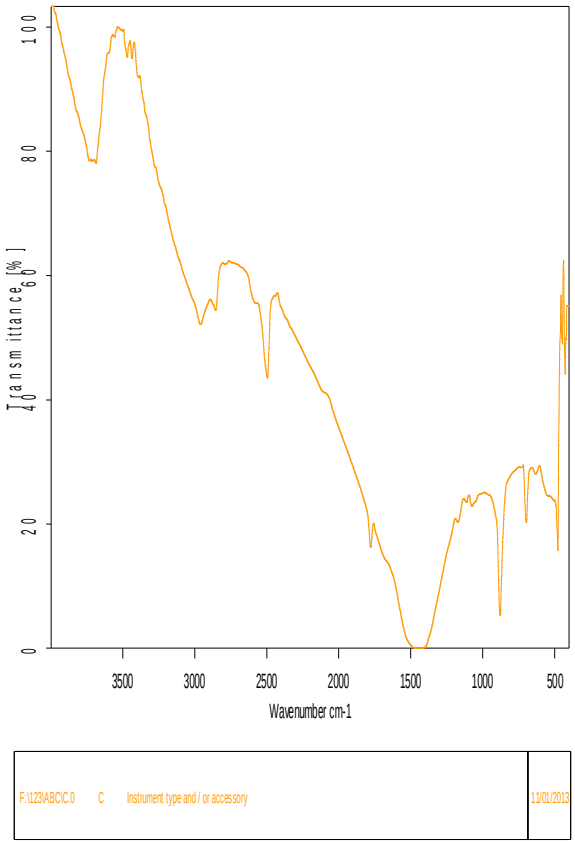


Sample e

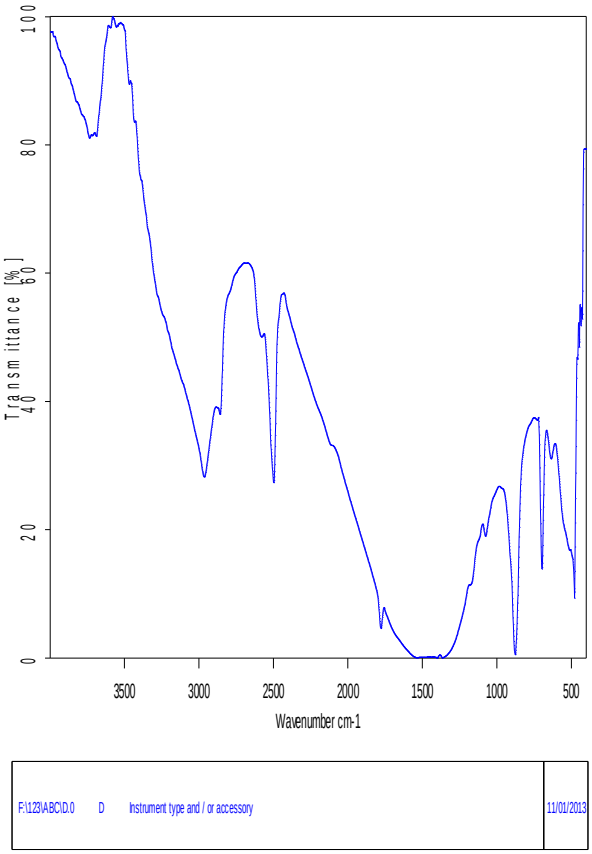
FTIR Spectrometry: The presence of functional groups in samples a, b, c and d are nearly same, with the change in transmittance percentage from one another. It shows that it has a C=X stretch region with multiple, sharp and medium peaks. There is a peak around 1600 cm^{-1} and several others at lower wave numbers. There are aromatic C-H peaks around 3000 cm^{-1}. In sample e, there is a change in spectrum pattern comparing to all other samples. In 1000-1300 cm^{-1}, C-O bonding occurs and a strong absorption is observed here. There was a multiple sharp and medium peaks in the region of 1400-1600 cm^{-1}, sharp and medium intensity peaks occur in the region of 2260-2210 cm^{-1}. There was also a very broad signal in the region of 2500-3300 cm^{-1}, centered near 3000 cm^{-1}.



Sample a **Sample b**



Sample c

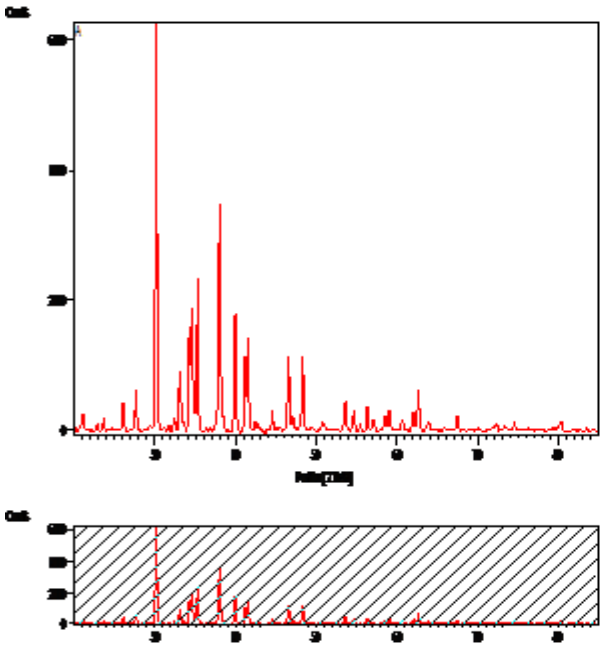


Sample d

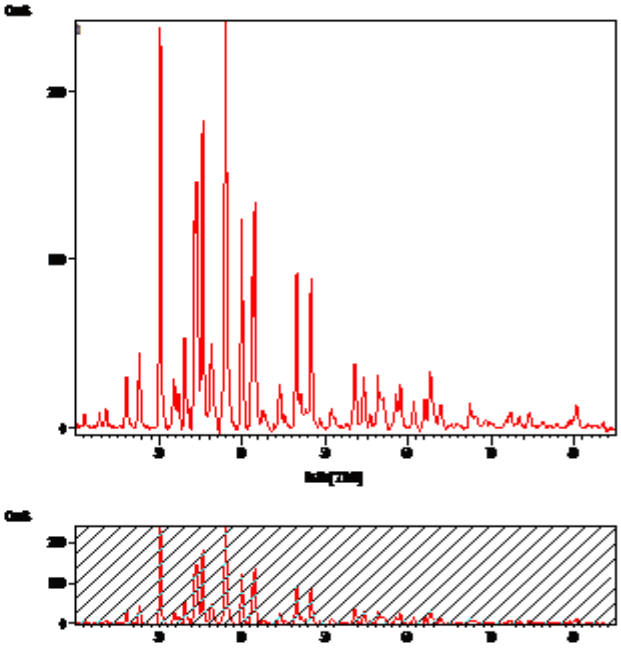
Sample e

XRD Analysis: In sample the intensity of the peak at maximum was around 30 in the 2-theta position. In sample b there are two successive maximum peaks one at the value of 2-theta as 30 and another around 37. In sample c, 2-theta values are nearly same as sample b, but there is a variation in the intensity height. In sample d, for the value of 2-theta at 30, intensity is little less than other samples, the maximum

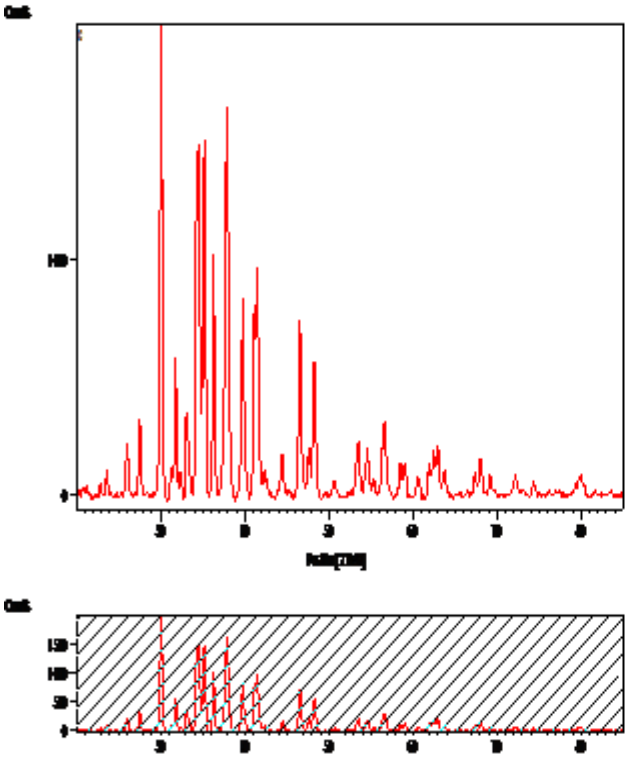
intensity peak was around 37 for the sample e. The maximum intensity peaks were above 6000, above 2000, above 1000, above 3000 and above 10000 for the samples a, b, c, d and e respectively.



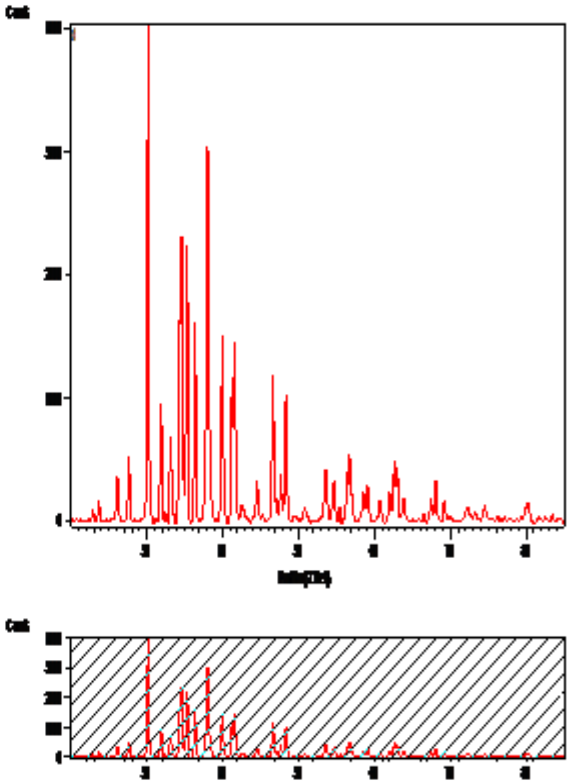
Sample a



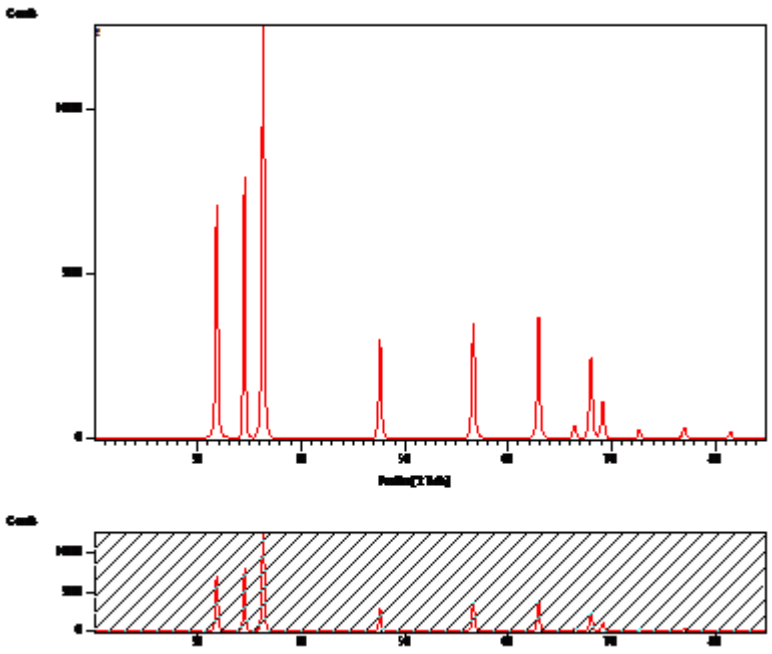
Sample b



Sample c



Sample d



Sample e

CONCLUSION

The biological ZnO nanoparticle is prepared by sol-gel synthesis method using avocado Fruit extract (Persea Americana). The obtained powder is characterized under UV visible spectroscopy, FTIR spectroscopy and X-Ray diffractometer to analyze it. This ZnO nanoparticle can be used to prepare transparent sunscreen. Comparison of chemical and biologically synthesized ZnO nanoparticle.

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