Original Article

Synthesis of Zinc Oxide Nanoparticles from Physalis Angulata and its Effect in Reducing Calcium Oxalate

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Abstract

Physalis angulata, commonly called as angular winter cherry or balloon cherry is the most extensively used herbal plant as an antidiuretic. This study aims at synthesizing zinc oxide nanoparticles from the plant extract and testing it against kidney stones. The nanoparticles were synthesized from the aqueous extract of the plant, characterized using spectroscopic methods and were analyzed against calcium oxalate crystals. The rate of degradation of calcium oxalate was analyzed using FTIR technique. The results were encouraging which indicated the decrease in the concentration of calcium oxalate as the reaction time increased. This study can form a foundation for producing a new technique in treating kidney stones using nanoparticles without any side effects.

Keywords: Physalis angulata, Zinc oxide, Nanoparticles, Calcium oxalate, Kidney stones.

Introduction

Nanoparticle is an ultrafine unit with dimensions measured in nanometres (nm; 1 nm = 10^{-9} metre). Because of their sub microscopic size, they have unique material characteristics, and manufactured nanoparticles may find practical applications in a variety of areas, including medicine, engineering, catalysis, and environmental remediation.[6] Zinc oxide nanoparticles (ZnO NPs), as one of the most important metal oxide nanoparticles, are popularly employed in various fields due to their peculiar physical and chemical properties.[1]

Physalis angulata have been used for centuries as medicinal herbs in the treatment of urinary tract infection, skin diseases, gonnorhea, ulcers, sores and as vermicidal drug.[7] The purpose of this study is to synthesize of Zinc oxide nanoparticles using the plant extract and analyze the effect of synthesized ZnO NP on calcium oxalate crystals.

Materials and methods

Collection of sample

Physallis anguluta was collected from the Attappadi Reserved forest, Kerala and transported to the lab in which the work was carried out. The plant was washed thoroughly with running tap water and distilled water. Leaves and seeds collected from the plant were shade dried and ground into a fine powder.

Preparation of Plant Extract and Synthesis of Nanoparticles

The dried sample powder was extracted with deionized water using Soxhlet apparatus as per standard protocol [4, 8]. For the synthesis of nanoparticles, zinc acetate (0.02 mg) was mixed with 25 ml of distilled water and the mixture was added to 1ml of plant extract. This mixture was stirred at room temperature for 2 hours. About 0.02ml of NaOH solution was added drop by drop until the pH became 12. The mixture was again stirred for 1 hour to obtain a light yellow colour solution. Distilled water was added to the solution and centrifuged at 8000 rpm for 10 minutes. The pellet was collected in a petriplate, kept in a hot air oven in 600 C to obtain a white powder. The above mentioned procedure was repeated for Zinc nitrate (0.05 ml) [2, 9]. The resulting white powder was taken for characterization studies.

Characterization of zinc oxide nanoparticles

The synthesized particles were analyzed using UV-Visible spectrophotometry (ELICO SL195, India) at the wave length range of 200-800 nm. Similarly, the particles were also analyzed using X-Ray Diffractometer (Alpha-1, UK).[12]

Effect of ZnO nanoparticles on Calcium oxalate

Calcium oxalate (CaC_2O_4) crystals were prepared as per standard procedure.[11] Glass coverslips were first thoroughly cleaned by treatment with piranha solution for 1 hour in freshly prepared 3:1 of H_2SO4: H_2O_2. About 30 µl of CaC_2O_4 sub phase was prepared from stock solution of three salts: sodium chloride, calcium chloride and sodium oxalate in three different beakers. The solutions (pH = 5.5 - 6.5) were allowed to stand for 3 days at a temperature of about 25 ± 2°C. After 3 days, the CaC_2O_4 crystals grew in sub phase and deposited on the glass coverslips and air dried. Crystals of CaC_2O_4 which correspondingly grew in sub phase were called crystals. Beaker 1 was treated as standard. To beaker 2, NPs synthesized using zinc oxide was added at the concentration of 30 mmol/L. To beaker 3, NPs synthesized using zinc nitrate were added at the same concentration of 30 mmol/L. The mixture was allowed to stand for 3 days and the resulting crystals were analysed by Fourier transform infrared spectroscopy (Schimazdu IR prestige- 21, Japan).[3]

Results and discussion

Plant Extract Preparation and Nanoparticles Synthesis

The nanopaticles (ZNPs) were synthesized from the aqueous extract of the plant using zinc acetate and zinc nitrate. The resultant white powder formed is shown in Figure 1.

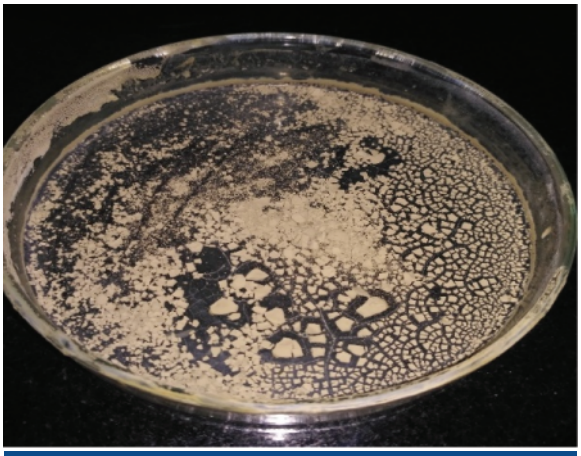


Figure 1: Synthesized Nanoparticles

UV-Visible spectroscopy

In order to analyze the nature of the sample synthesized, the powder was subjected to UV- visible spectroscopy. The absorption spectrum of synthesized nanoparticles is shown in Figure 2 & 3. The distinct peak centred around 350 nm is specific for ZNPs which is due to their large excitation binding energy at room temperature. It is well known from absorption spectroscopy that the band gap increases on decreasing particle size. There is also an opposite ratio between band gap and the wavelength of absorption as we know about the absorption for bulk ZnO occurs around 385nm. The high blue shift absorption for the synthesized ZNPs in comparison with the bulk ZnO can be due to a high decrease in particle size.

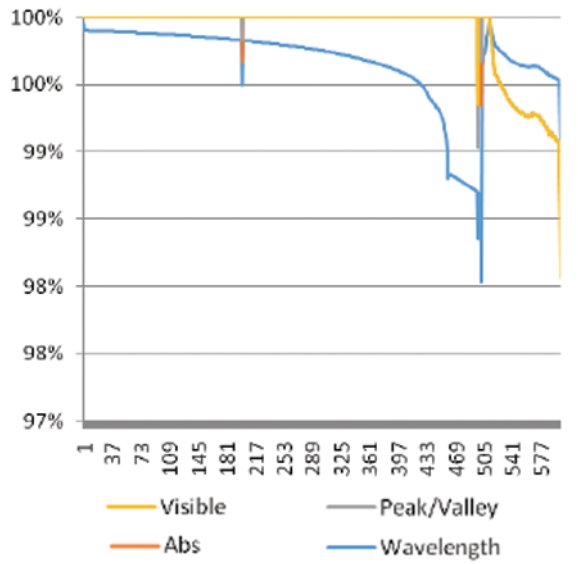


Figure 2: UV-VIS analysis of Zinc acetate mediated nanoparticles

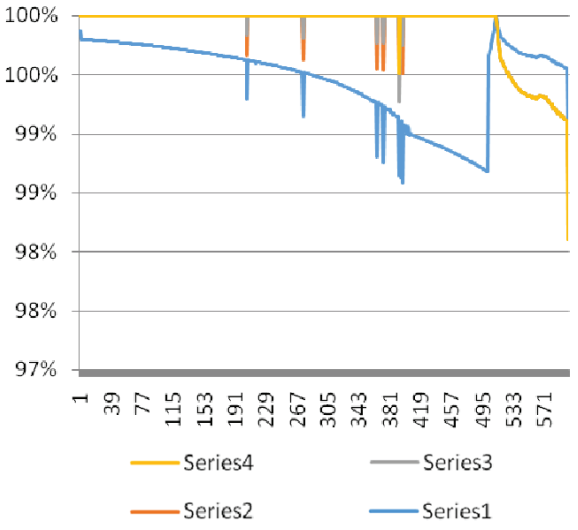


Figure 3: UV-VIS analysis of Zinc nitrate mediated nanoparticles

From the above results, it is clear that a peak is observed at 513 nm which indicates the possibility of formation of zinc nanoparticles.[5] This result can be further confirmed by XRD.

X-ray diffraction analysis

The following figures (Figure 4 (A) & (B)) show the results of XRD analysis.

XRD pattern of synthesized ZNPs clearly indicates crystalline structure for the synthesized nanoparticles (Figure 4). The sharp diffraction peaks were observed at 2θ values 31.46, 34.29, 36.33, 47.51,

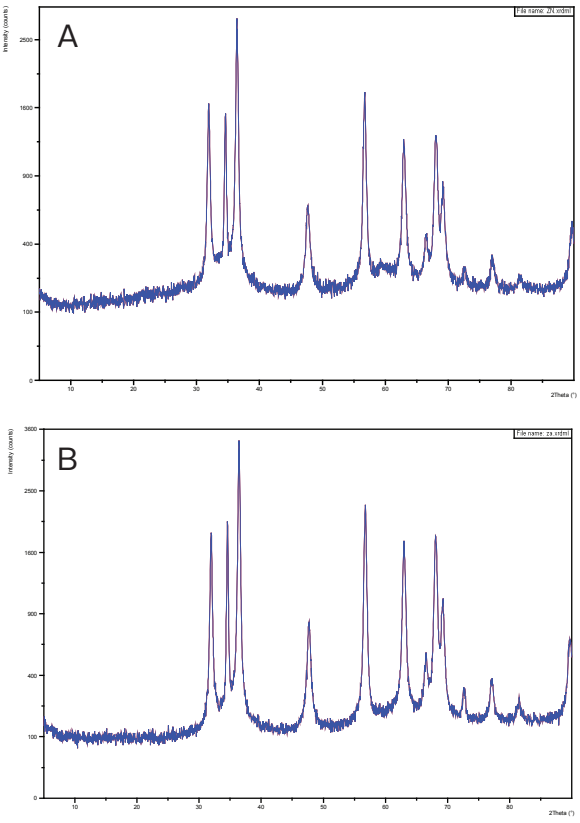


Figure 4: XRD results for the synthesized ZNPs by (A) zinc acetate mediated nanoparticles; (B) zinc nitrate mediated nanoparticles

56.50, 62.84, 67.79 and 76.83 degrees. These peaks are indexed as (100), (002), (101), (102), (110), (103), (112), and (202) diffraction lattice planes respectively which confirm the hexagonal quartzite structure for the synthesized nanoparticles. This pattern is in accordance with the standard peaks displayed by the International Centre for Diffraction Data [12]. The average size of ZNPs was calculated from the highest intense peak (101) using the Debye–Scherer equation,

$$D=K\omega\beta\cos\theta$$

where ω is the X-ray wavelength coming from Cu-K_α (1.540560 Å), β is the full width at half maxima of the diffraction peak in radians, θ is the Braggs' angle in degrees, and K is the shape factor and its value is equal to 0.9.

Effect of ZnO nanoparticles on Calcium Oxalate Crystals

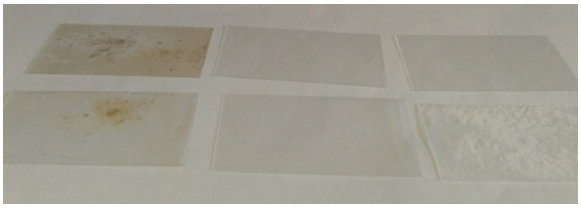
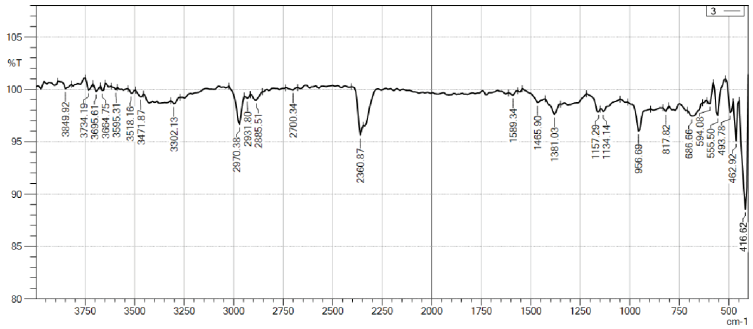


Figure 5: Synthesized Calcium oxalate crystals

A



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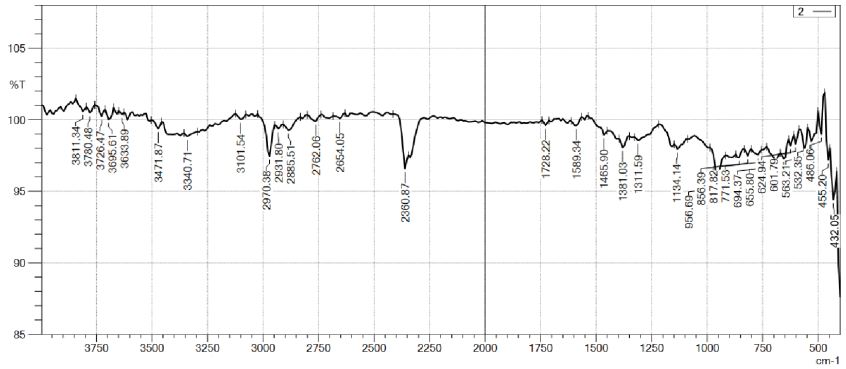
6	Apodization	Happ-Genzel
9	No. of Scans	45

B



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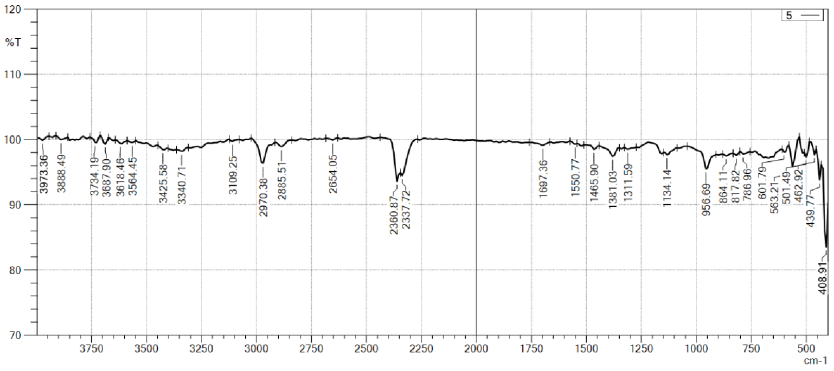
C



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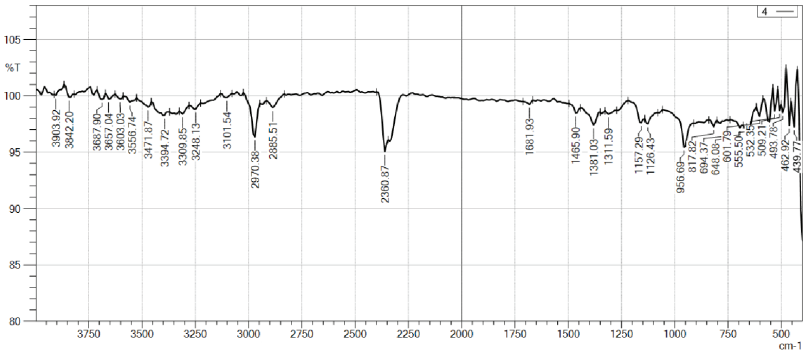
D



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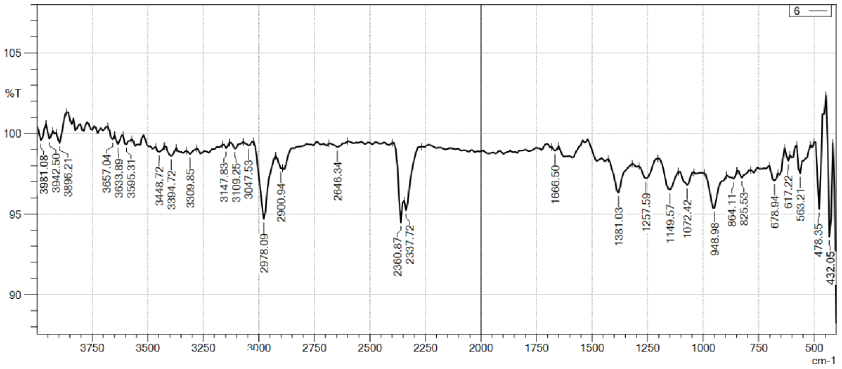
E



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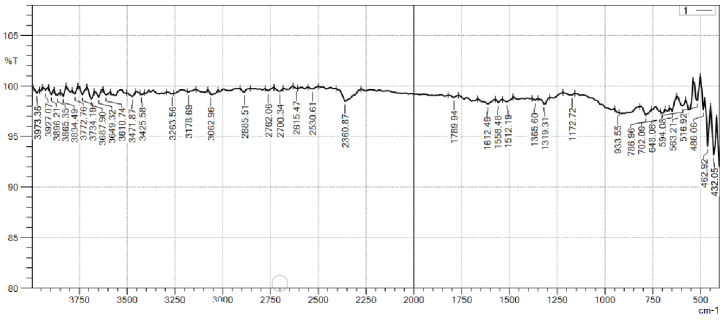
F



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6	Apodization	Happ-Genzel
9	No. of Scans	45

Figure 6: FTIR analysis of calcium oxalate crystals

System	Vs (-OH) (cm^{-1})	Vas (C=O) (cm^{-1})	Vs (C=O) (cm^{-1})	Vs (O-Zn-O) (cm^{-1})	(O-C-O) (cm^{-1})	(C-O-Zn) (cm^{-1})
$Na_2C_2O_4$ powder in the presence of nanoZnO				1036		583
Crystal (I) (COM)	3061-3488	1613	1323		784, 662	
Crystal (IV) (COD)	3386	1639	1319	1039		569

Table 1: Frequencies of bands in Na2C2O4 powder in the presence of nanoZno sol, crystal (I) and crystal (IV).

Calcium oxalate crystals (COM – Calcium Oxalate monohydrate; COD – Calcium Oxalate dihydrate) were synthesized using the principle of supersaturation and deposited on a glass slide.[10] They were mixed with the synthesized ZnO nanoparticles, incubated for 3 days. The crystals were subjected to FTIR to check the effect of nanoparticles on calcium oxalate. Fig. 6 (A – F) indicates the FTIR spectra of the fate of calcium oxalate crystals.

FTIR spectra of Na2C2O4 powder in the presence of nanoZnO sol, crystal (I) and crystal (IV) were shown in Fig. 6 (A-C) for Zinc acetate mediated nanoparticles and D-F for Zinc nitrate mediated nanoparticles). The frequencies of bands were listed in Table 1. It was observed from spectra that the main characteristic bands of crystals (I) were confirmed to the characteristic peaks of COM crystals. In Fig.6b, the characteristic absorptions of COM crystals were at 2360.87 and 2970.38cm–1 and C=O valence oscillation band was at 1323 and 1613cm^{-1}; the hydration valence oscillation band of COM crystals split into five single bands from 3061 to 3488cm–1. In the FTIR spectra of $Na_2C_2O_4$-nanoZnO sol system (Fig. 6a), the band at 583cm–1 was the characteristic absorption of C-O-Zn valence and the band at 1036cm–1 was the character absorption of O-Zn-O valence. The same pattern can be observed in all the spectra.

Vs – Symmetric stretching vibration; Vas – Asymmetric stretching vibration

In the CaC_2O_4-nanoZnO sol system (Fig. 6e), the FTIR spectra showed that the wide but not split band at 3386cm^{-1} was the water of hydration band, and the band at 1639cm^{-1} was the C=O valence oscillation. These were the characteristic absorptions of COD crystals. The band at 1319cm^{-1} indicated an admixture of COM and COD crystals. The band at 569cm–1 was the characteristic absorption of C-O-Zn valence and the band at 1039cm–1 was the characteristic absorption of O-Zn-O. In comparison with Fig. 6a and c, the absorptions of C-O-Zn and O-Zn-O in CaC_2O_4-nanoZnO sol system were stronger than in $Na_2C_2O_4$-nanoZnO sol system. These indicated that nanoZnO could coordinate with $C_2O_4^{2-}$ as C-O-Zn and O-Zn-O valences in CaC2O4-nanoZnO sol system. It could be concluded that the coordination between nanoZnO and $C_2O_4^{2-}$ induced to form the spherical COD crystals containing Zinc. From this result, it is clear that the ZnO nanoparticles are capable of destructing calcium oxalate which means it can be used to treat kidney stones.

Conclusion

The zinc oxide nanoparticles are widely used for the various medicinal purposes. The extraction of zinc oxide nanoparticles from the plant Phyasalis angulata which is widely used for the several medicinal purposes made possible. Characterisation of nanoparticles is done through UV-visible spectroscopy, UV visible spectroscopy. The reaction of zinc acetate, zinc nitrate and Phyasalis angulata displayed vivid colours confirming the synthesis of zinc oxide nanoparticles.[2,5] UV- Vis spectra showing a maximum absorption in room temperature at 200 to 800 nm characteristic of the zinc oxide nanoparticles further affirmed the formation of the nanoparticles. The confirmation on the crystal structure was carried out by using vibrational frequencies at different wavenumbers exerted by FTIR. The X-ray Crystallography data was used to determine the orientation of crystal and the average spacing between the layers of the atoms. The synthesized zinc oxide nanoparticles are capable to use for the medicinal application of urinary tract infection and kidney stones.

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