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Synthesis and Characterisation of Zirconium Nano Particles from Orange Juice and Orange Peel

Savita Patil, Sudha S. Hosapete, Sarita Irkal, Shivani Rajput.
Department of Chemistry, Jnanashakti Complex, Toravi, Karnataka State Akkamahadevi Universisty Vijayapur.

Abstract:
Metal nanoparticles are synthesis involves extraction of juice from Orange fruit and peal it is stored
Fig.1. citrus limetta *under controlled condition. Aqueous solution of 10ml, 0.1M metal nitrate solution is added to the 1ml juice extract reaction takes place colour change is observed within 5 minutes .Then filtered the precipitate and dried under controlled condition. Synthesized metal nano particles from orange juice and peal and characterize the target compound by FTIR, UV-Vissible, SEM and molar XRD. Synthesized nano particles subjected to different tests these nano particles shows antimicrobial, antifungal, antidiabetic, antioxidant and anticancer properties.*

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I. Introduction

The orange is the fruit of citrus species citrus sinensis In the family Rutaceae. It is also called sweet orange, to distinguish it from the related citrus aurantium refer to as bitter orange. The sweet orange reproduces asexually varieties of sweet orange arise through mutation

Sensory factors

acetyl acetate a volatile compound contributing to the fragrance of oranges
The taste of the oranges is determined mainly the relative ratio of sugars and acids where as orange aroma derives from volatile organic compounds, including alcohols, aldehydes, ketones terpens.
Taste quality tends to improve later in harvest when there is a higher sugar/acid ratio with less bitterness.
As a citrus fruit, the orange is acidic with PH level ranging from 2.9 to 4.0
Sensory qualities vary according to genetic background, environmental conditions during development, ripeness at harvest, postharvest conditions, and storage duration.

Nutrition value per 100g

Energy	197kJ (47 kcal)
Carbohydrates	11.75g
Fat	0.12g
Protein	0.94g
vitaminB6	0.06mg
Vitamin C	53.2mg
Vitamin E	0.18mg
Other constituent	Quantity
Water	86.75g

Nutritional value and phytochemicals:

- As with other citrus fruits, orange pulp is an excellent source of vitamin C, providing 64% of the daily value in 100g serving (right table).Numerous other essential nutrients are present in low amounts (right table).
- Oranges contain diverse phytochemicals including carotenoids (beta-carotene,lutein and bets cryptoxanthin), flavanoids (eg: naringenin) and numerous volatile organic compounds producing orange aroma,including aldehydes, esters, terpenes, alcohols and ketones.

- Orange juice contains only about one-fifth citric acid of lymour lemon juice (which contain about 47g per liter)

Production of oranges – 2016	
Country	**Production (millions oftonnes)**
Brazil	17.3
People's Republic of China	8.4
India	7.5
United States	5.2
Mexico	4.6
Egypt	3.4
World	**73.2**
Source: FAOSTAT of the United Nations[11]	

II. Materials And Methods

- The orange fruits were washed with sterile distilled water and the outer covering of the fruit was peeled off and fleshy part of orange was washed with sterile distilled water.
- The orange fruit was cut into small pieces and 10g of fruit was grind using mortar and pestle with distilled water.
- The extraction was filtered using muslin cloth and Whatmann No.1 filter paper .zirconium nitrate (0.1 M) was used as precursor for synthesis of zirconium nanoparticles .
- The mixture was incubated at 37 c.
- Then the mixture was filtered using whatmann filter paper .
- It was followed by redispersion of the precipitate in deionized water to get rid of any uncoordinated biological molecules .

Characterization of zirconium nanoparticles :
UV-Visible spectra analysis:
Ultraviolet visible spectrophotometer (UV-Visible) refers to absorption spectroscopy in the UV Visible spectral region .
This means it uses light in the visible and adjacent near UV and near-infrared (NIR).
Ranges the absorption in the visible range directly affects the perceived colour of the chemicals involved .
In this reagion of the electromagnetic spertrum , molecules under go electronic transitions .
Ultraviolet visible spectrophotometer (UV-Visible)is procured from cystronics .
A small aliquote of the sample was taken for UV –Visible spectral analysis (200-800nm).

UV visible spectra zirconium nanoparticles :

- The synthesis of green zirconium nanoparticles had been confirmed by measuring the UV visible spectrum of colloidal solution which has absorbance peak at 275.5 and 280nm,and the expanding of peak indicated that particles are mono dispersed as shown in figure 1
- UV visible spectroscopy is a simple and fast way to confirm the formation of zirconium nano particles.

- Synthesis of nano sized particles with antibacterial and antifungal properties is of great interest in the development of new pharmaceutical products.
- Among the deferent types of extracts prepared, citrus lemetta juice and fruit peel extract showed good antibacterial and antifungal activity.

juice extract

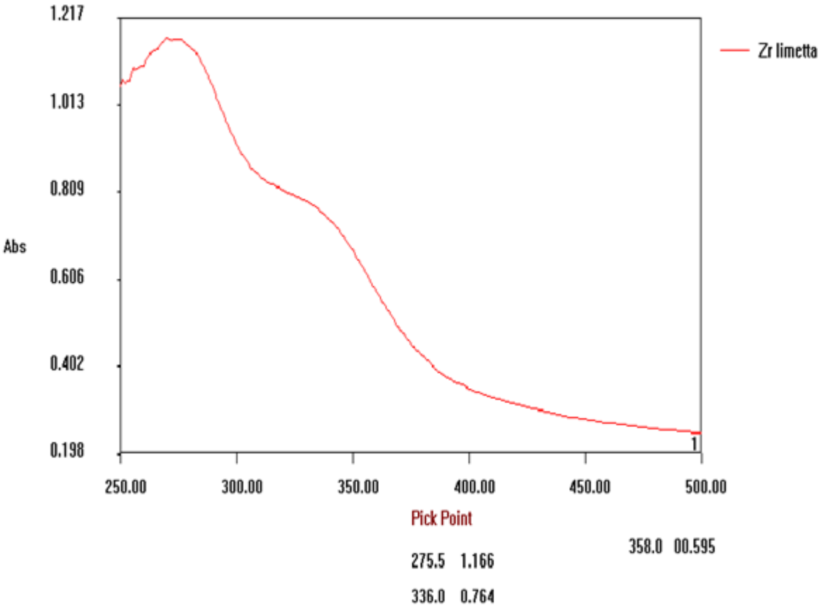
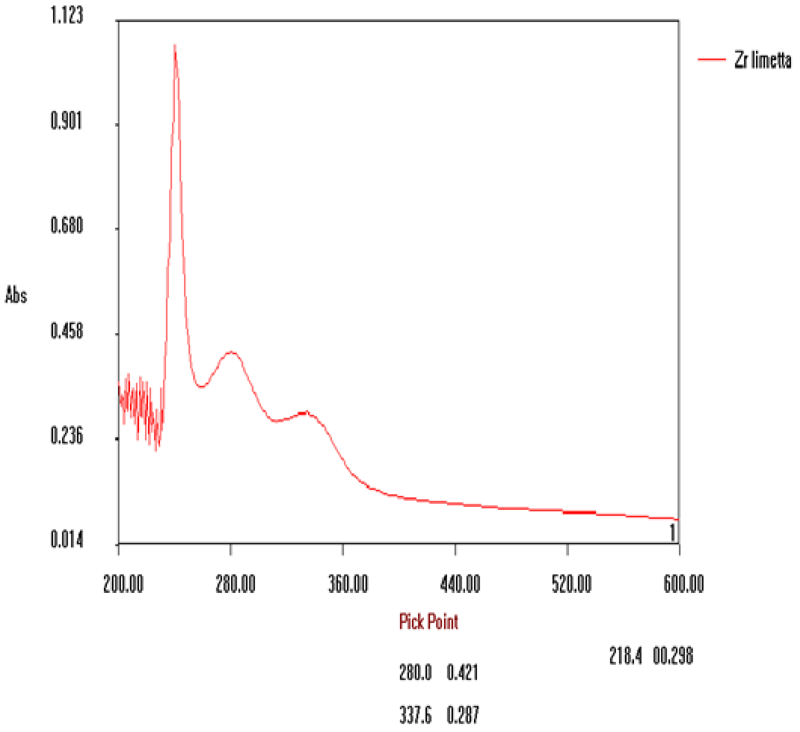


Fig.2.citrus limetta peel extract



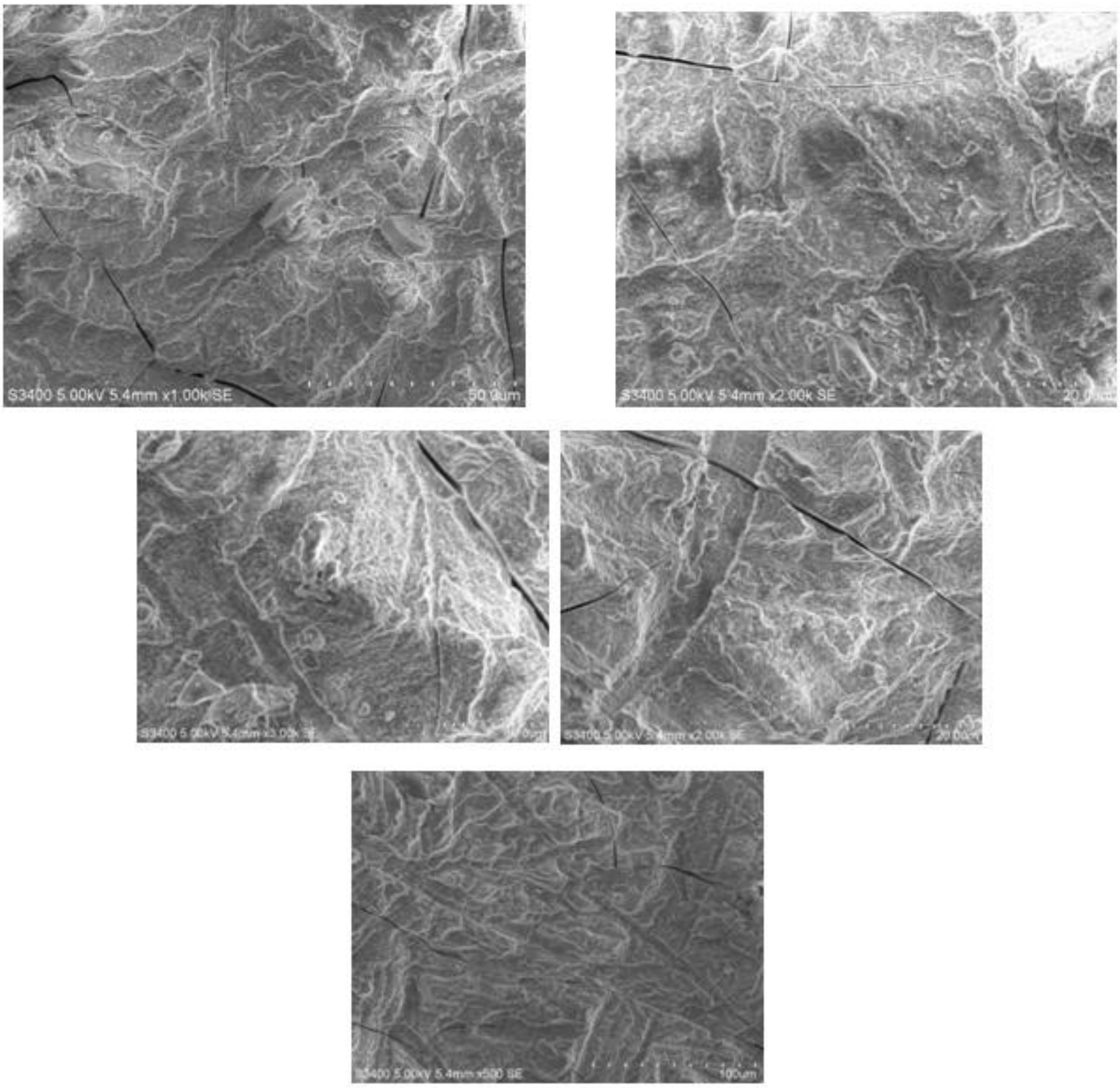
Characterization of zirconium nano particles:
Fourier Transform Infrared:

- Dried powder of zirconium nano particles was subjected to analyse the presence of possible functional group for resulting formation of zirconium nanoparticles using Forier Transform Infrared Spectroscopy.

FTIR spectra zirconium nanoparticles :

- The FTIR spectroscopy was done to study the functional groups and bonds present in the zirconium nano particles
- In fig 3 and 4, the peaks were observed at 487 per cm, 1129.0 per cm, 1364 per cm, 1636.3 per cm, 2355.5 per cm and 2920.4 per cm.
- The peak at 486 per cm is very broad and is the only significant peak below 1000 per cm.
- It is well known that in the FTIR spectrum the inorganic stretch peak is seen between 400 per cm and 1000 per cm so the peak at 487per cm is expected to be Zr-O stretch. The remaining peaks other than 486 per cm correspond to bonds(functional group), =C-H bend (alkenes),C-H rock (alkanes), C=O stretch(carboxylic acid), C=C- stretch(alkynes) and C-H stretch(alkanes) respectively.
- These stretches indicating the presence of organic compound were observed due to citric acid($C_6H_8O_7$) which is key constituent of citrus limetta.

Fig.3. FTIR spectra of Zirconium nano particles from citrus limetta peal extract



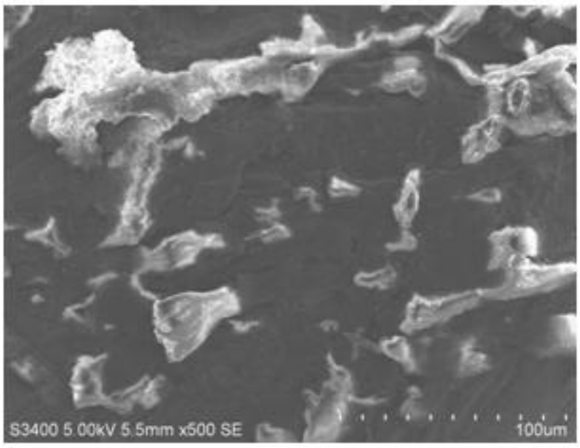
SEM Analysis of Zirconium nano particles:

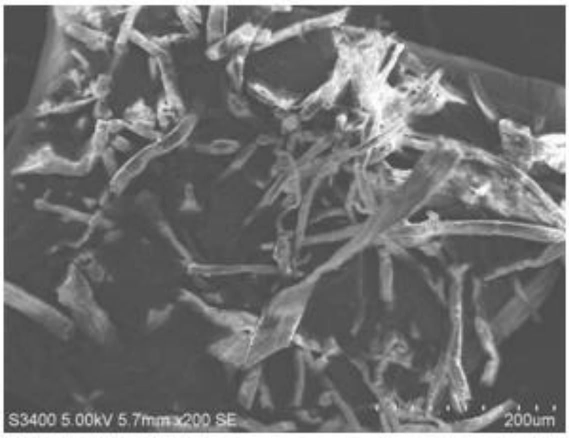
- Scanning electron microscope(SEM) analysis was done using (JEOL Model JSM-6390LV) SEM machine.
- The films of the sample were prepared on a carbon coated copper grid by just dropping a very small amount of the sample on the grid.

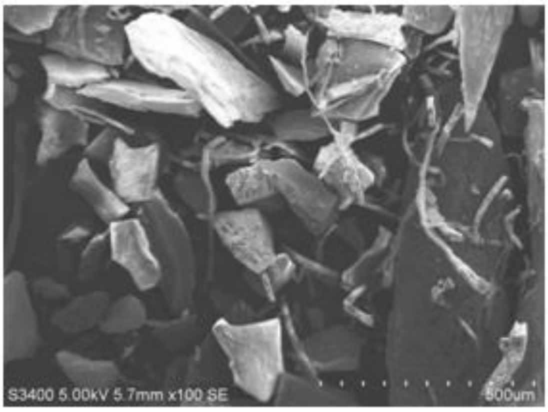
SEM of Zirconium nanoparticles:

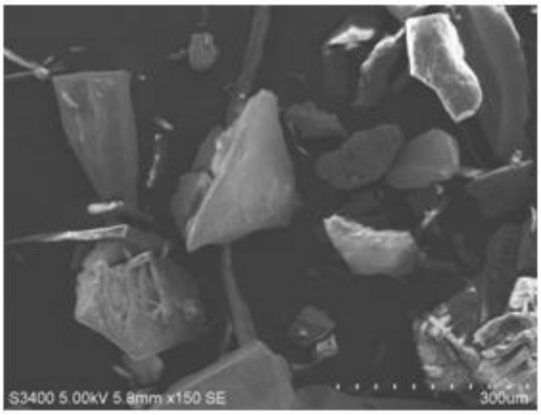
- The Zirconium nanoparticles synthesised by the help of citrus limetta extract were scanned by SEM as shown in the figure 4 and 5.
- The surface morphology of the Zirconium nanoparticles was observed at different magnification and it revealed that orange juice and peel extract mediated Zirconium nanoparticles were uniformly distributed on the surface of the cell with higy agglomeration.
- It reveals that Zirconium nanoparticles seen to be spherical in morphology and particles form cluster.
- It is easy to notice that the examined particles consist of smaller objects of few micrometer in size (10 to 100µm).
- However, we did not manage to examine the structure of the observed nanoparticles because of difficulties connected with getting higher *magnification.*

Fig.4.*SEM images of Zirconium nanoparticles with citrus limetta juice extract*









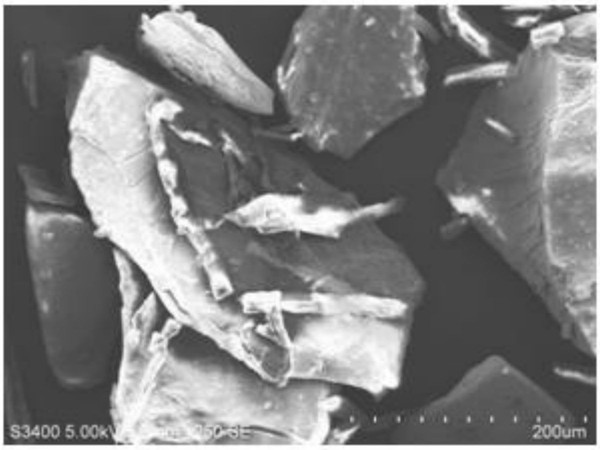


Fig.5.SEM images of Zirconium nanoparticle with citrus limetta peal extract

X-Ray Diffraction Analysis:

- To determine the nature and the size of the synthesized Zirconium nanoparticles, X-Ray diffraction (XRD) was performed using on an Bruker, D-8 advance technology in Germany, which was operated at a voltage of 40KV and current of 40mA

Result of XRD Analysis:

- X-ray diffraction spectrum of citrus limetta fruit juice and peel mediated zirconium nanoparticles showed the Braggs reflections in the XRD pattern at 2θ =29.66, 35.63, 36.53, 38.78, 42.39, 43.40, 48.97, 50.54, 61.43, 66.23, 68.15, 73.53, 74.16, 89.96, and 95.19 for citrus limetta juice and XRD pattern at 2θ=32.55, 35.54, 36.46, 38.72, 42.37, 48.81, 53.45, 58.27, 61.52, 66.40, 68.17, 72.39, 75.06, and 82.78 for citrus limetta peel extract respectively .
- These Braggs reflection clearly indicated the presence of (202), (111), (200), (220) and (311) sets of lattice planes and further on basis that they can be indexed as face-centred-cubic(FCC) structure of zirconium
- A comparison of obtained XRD spectrum with the standard, confirmed that the zirconium particles formed in present experiments were in the form of nano crystals .
- X-ray diffraction results clearly showed that the zirconium nano particles formed by the reduction of zr^+ ions by citrus limetta juice and peel extract are crystalline in nature (fig.5&6) .
- The average crystallite size of green route synthesized zirconium nanoparticles was estimated from the full width half maximum (FWHM) of (111) reflection by using scherrer formula ,$D=0.9\lambda/\beta \cos\theta$ .where D is the average crystallite domain size perpendicular to the reflecting planes ,λ is the X-ray wavelength source (0.1541nm), β is the full width at half maximum and θ is the diffraction angle .
- It was observed that the average diameter of the zirconium nanoparticles crystal was about 24nm .
- Some unassigned intense diffraction peaks ,might be related to the crystallization of bioorganic phases that attached on the surface of the nanoparticles .
- The average particle size of zirconium nanoparticles synthesized by the present green method can be calculated using the Debye –Scherrer equation.

TABLE NO.1

S.NO	2θ	Sin^2 θ	1x Sin^2 θ/ Sin^2 θmin	2x Sin^2 θ/ Sin^2 θmin	3x Sin^2 θ/ Sin^2 θmin	4x Sin^2 θ/ Sin^2 θmin	5x Sin^2 θ/ Sin^2 θmin	6x Sin^2 θ/ Sin^2 θmin	7x Sin^2 θ/ Sin^2 θmin	h k l values
1	29.66509	0.0655	1	2	3	4	5	6	7	
2	35.63223	0.0935	1.42	2.84	4.26	5.68	7.1	8.52	9.94	3 0 0
3	36.53168	0.0982	1.49	2.98	4.47	5.96	7.45	8.94	10.43	3 1 0
4	38.78259	0.1102	1.62	3.36	5.04	6.72	8.4	10.08	1.76	3 1 1
5	42.39297	0.1307	1.99	3.98	5.97	7.96	9.95	11.94	13.93	3 2 0
6	43.40651	0.1367	2.08	4.16	6.24	8.32	10.4	12.48	14.56	3 2 1
7	48.97498	0.1718	2.62	5.24	7.86	10.48	13.1	15.72	18.34	4 1 1
8	50.5405	0.1822	2.78	5.56	8.34	11.12	13.9	16.68	19.46	3 1 1
9	61.43973	0.2609	3.98	7.96	11.94	15.92	19.9	23.88	27.86	5 1 1
10	66.23704	0.2985	4.55	9.1	13.65	18.2	22.75	27.3	31.85	
11	68.15315	0.3139	4.79	9.58	14.37	19.16	23.95	28.74	33.53	4 4 1
12	73.53445	0.3582	5.46	10.92	16.38	21.84	27.3	32.76	38.22	6 1 1
13	74.16123	0.3635	5.55	11.1	16.65	22.2	27.7	33.3	38.85	6 1 1
14	89.96798	0.4997	7.62	15.24	22.86	30.48	38.1	45.72	53.34	7 2 0
15	95.19189	0.5452	8.32	16.64	24.96	33.29	48.61	49.92	58.26	7 3 0

TABLE NO.2

S.NO	2θ	Sin^2 θ	1x Sin^2 θ/ Sin^2 θmin	2x Sin^2 θ/ Sin^2 θmin	3x Sin^2 θ/ Sin^2 θmin	4x Sin^2 θ/ Sin^2 θmin	5x Sin^2 θ/ Sin^2 θmin	6x Sin^2 θ/ Sin^2 θmin	7x Sin^2 θ/ Sin^2 θmin	8x Sin^2 θ/ Sin^2 θmin	h k l values
1	32.55849	0.07857	1	2	3	4	5	6	7	8	2 2 0
2	35.54592	0.09317	1.185	2.37	3.55	4.74	5.92	7.11	8.29	9.48	3 0 0
3	36.46147	0.09787	1.235	2.47	3.70	4.94	6.17	7.41	8.64	9.88	3 0 0
4	38.72753	0.10993	1.399	2.79	4.19	5.59	6.99	8.39	9.79	11.19	3 1 1
5	42.37188	0.13060	1.662	3.32	4.98	6.64	8.31	9.97	11.63	13.29	3 2 0
6	48.81324	0.17074	2.173	4.34	6.51	8.69	10.86	13.03	15.21	17.38	4 1 0
7	53.45328	0.20225	2.574	5.14	7.72	10.29	12.87	15.44	18.01	20.59	4 2 0
8	58.27296	0.23706	3.017	6.03	9.05	11.06	15.08	18.10	21.11	24.13	4 2 2
9	61.523	0.26159	3.329	6.65	9.98	13.31	16.64	19.97	23.30	26.63	5 1 0
10	66.40465	0.29986	3.816	7.63	11.44	15.26	19.08	22.89	26.71	30.52	5 2 1
11	68.1748	0.31411	3.997	7.99	11..99	15.98	19.98	23.98	27.97	31.97	
12	72.39711	0.34879	4.439	8.87	13.31	17.75	22.19	26.63	31.07	35.59	5 3 1
13	75.0613	0.37110	4.723	9.44	14.16	18.89	23.61	28.33	33.06	37.78	

14	82.78269	0.43718	5.564	11.12	16.69	22.25	27.82	33.38	38.94	44.51	6 2 2

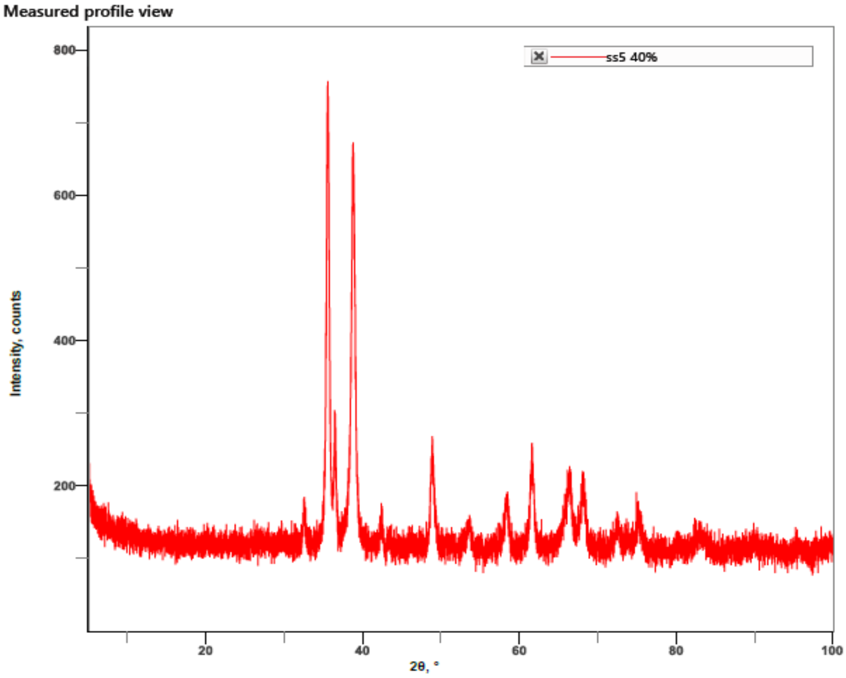


Fig.5.*XRD of zirconium nano particles from citrus limetta peel extract*

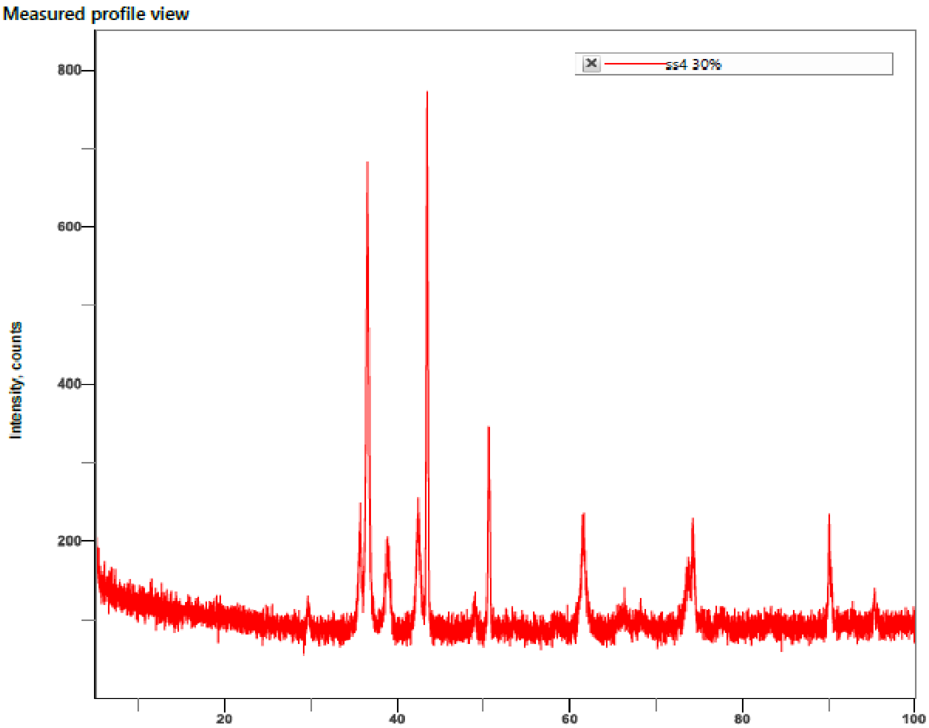


Fig.6.XRD of zirconium nano particles from citrus limetta juice extract

Antibacterial and Antifungal Activity

- The antifungal potential of the biosynthesised zirconium nanoparticles was investigated according to a modified method described
- Else where Five millilitre of the zirconium nanoparticles at various concentration (50,100,200,and 400 µg/ml in sterile distilled water)was added into 5ml of the autoclaved media before it solidified.

- The mixture was poured into the sterile 8-cm petri dishes .negative controls containing media only were also considered .
- The petri dish were then incubated in the dark at 25°c for 48 hours, after which the petri dishes were inoculated with agar plugs of the growing fungal mycelia (5mm in diameter).
- The plates were incubated in the dark at 25°c for further five days .
- The radial growth of fungal mycelia was calculated using the of two fungal colony diameters at right angles.
- The inhibition potency of zirconium nanoparticles towards each fungal strain was calculated using the following equation inhibition rate (per cent)=R-r/R×100;
- Where R is the radial growth of fungal mycelia in the negative control (cm) and r is the radial growth of fungal mycelia challenged with the zirconium nanoparticles .

Antibacterial or antimicrobial activity

- The figure 8 shows the nanoparticles synthesized from zirconium are capable of showing antimicrobial or antibacterial activity against E-coli ,streptococcus and pseudomonas bacteria .
- The zone of inhibition for these organisms found to be 2.1 mm, 1.8mm, and 1.5mm, 1.8mm, for juice and peel respectively .
- The synthesized zirconium nanoparticles prepared from citrus limetta juice and peel extract showed antibacterial activity.
- However the antibacterial or antimicrobial activity of zirconium nanoparticles depends on the type of bacteria along with the size of the zirconium nanoparticles and also the formation of pits in the cell wall of micro-organism .
- The zirconium nanoparticles affects fungus cell by attacking their membrane distrusting the membrane potential .
- The biological synthesized zirconium nanoparticle prepared by direct reduction method showed antibacterial or antimicrobial activity against E-coli, spectrococcous pseudomonas.The highest antibacterial or antimicrobial activity was observed against juice and peel.

HEALTH BENEFITS OF ORANGE JUICE

- Include preventing cancer
- Fighting free radicals
- Boosting immunity
- Detoxifying the body
- Fighting inflammation
- Supporting liver health
- Supporting blood circulation
- Reducing high blood pressure
- Preventing ulcers
- Support weight loss
- Relieving kidney stones and treating
- Rickets in children
- Rich in several importance nutrients including vitamin C and potassium
- High in antioxidant

III. Results And Discussion

Nanotechnology mainly deals with the fabrication of nanoparticles having various shapes, sizes and managing their chemical and physical parameters for further use in human benefits with their growing applications in various fields. Preparation of metal nano-sized, usually ranging in size from 1 to 100 nanometers (nm), is amongst the most emerging areas in the field of nanotechnology. Currently the application of nano materials is becoming increasingly important in order to solve the problems associated with material sciences, including solar energy conversion, photonics , catalysis microelectronics, antimicrobial functionalities, and water treatment.

Nanoparticles usually have better or different properties than the bulk material of the same elements. The antibacterial effect of silver nanoparticles (AgNPs) is greatly enhanced because of tiny size. Nanoparticles have immense surface area relative to volume. Therefore, minuscule amounts of AgNPs can lend antimicrobial effects to hundreds of square meters of its host material. Nanomaterials are the leading requirement of the rapidly developing field of nanomedicine, and bionanotechnology. Nanoparticles are being utilized as therapeutic materials tools in infections against microbes thus, the properties of nanoparticles and their effect on microbes are essential to clinical applications. Among noble metal nanoparticles, AgNPs have received considerable attention owing to their attractive physicochemical properties. The AgNPs have various and important applications. Historically, silver has been known having a disinfecting effect and has been found in applications ranging from traditional medicines to culinary items. It has been reported that AgNPs are non-toxic to human and most effective against bacteria, virus and other eukaryotic micro-organism at low concentrations and without any side effects. Moreover, several salts of silver and their derivatives are commercially manufactured as antimicrobial agents. A small concentration of silver is safe for human cells, but lethal for micro organisms. Antimicrobial capability of AgNPs allows them to be suitably employed in numerous household applications such as textiles disinfection in water treatment, food storage containers, home appliances and in medical devices. The most important application of silver and AgNPs is in medical industry such as tropical ointments to prevent infection against burn and open wounds .

Biological synthesis of nanoparticles by plant extracts is at present under exploitation as some researchers worked on it and testing for antimicrobial activities. For the last two decades, extensive work has been done to develop new drugs from natural products because of the resistance of micro-organisms to the existing drugs. Nature has been an important source of a products currently being used in medical practice.

A number of synthetic methods have been employed for the synthesis of silver-based nanoparticles involving physical, chemical and biochemical techniques. Chemical reduction method is widely used to synthesize AgNPs because of its readiness to generate AgNPs under gentle conditions and its ability to synthesize AgNPs on a large scale . However, these chemical synthesis methods employ toxic chemicals in the synthesis route which may have adverse effect in the medical applications and hazard to environment. Therefore, preparation of AgNPs by green synthesis approach has advantages over physical and chemical approaches as it is environmental friendly, cost effective and the most significant advantage is that the conditions of high temperature, pressure, energy and no toxic chemicals are required in this synthesis protocol .

In this present work, we report the synthesis of ZrNPs by using orange juice and orange peel extract, which was used as green reducing agent and stabilizer. The efficacy of the synthesized ZrNPs as anti-inflammatory, antioxidant, antibacterial and antifungal agent was studied.

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