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Research Article

Eco-Friendly Synthesis of WNPs, PbNPs and AlNPs Nanoparticles Mediated by Waste Peel Extracts of Watermelon (*Citrullus Lanatus*)

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Abstract
The present study demonstrates the bioreductive green synthesis of nanosized WO, PbO, and AlO nanoparticles using waste peel extract of watermelon (*Citrullus lanatus*). The peel extracts of *Citrullus lanatus* seem to be environmentally friendly, so this protocol could be used for rapid production of nanosized WO, PbO, and AlO. The formation of the plant protein-coated WO, PbO, and AlO nanoparticles were first monitored using UV–Vis absorption spectroscopy, FTIR Spectroscopy. The average particle size are measured by XRD SEM and EDX analysis A possible core–shell structure of the WO, PbO, and AlO nanoparticles have been proposed.

Keywords: Nanoparticles, *Citrullus lanatus* (watermelon), UV, FTIR, XRD, SEM and EDX

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1. Introduction

The field of nanotechnology is one of the most active areas of research in modern materials science. New applications of nanoparticles (NPs) and nanomaterials are emerging rapidly. Green synthesis provides advancement over chemical and physical method as it is cost effective, environment friendly, easily scaled up for large-scale synthesis and further there is no need to use high pressure, energy, temperature and toxic chemicals. Synthesis of NPs using biological entities has great interest due to their unusual optical, chemical, photoelectrochemical and electronic properties[1]. One of the most considered methods is the production of metal NPs using biological systems such as microbes, fungi and several plant extracts. NPs produced by plants are more stable and the rate of synthesis is faster in the case of micro-organisms. Moreover, the NPs are more various in shape and size in comparison with those produced by other organisms [2], The present study was designed to synthesize and characterize WNPs, PbNPs and AlNPs and to investigate the antibacterial activity

1.1 Plant description

Watermelon (*Citrullus lanatus*) is a flowering plant species of the Cucurbitaceae family. It is a highly cultivated fruit worldwide, with more than 1,000 varieties. Wild watermelon seeds have been found in the prehistoric Libyan site of Uan Muhuggiag. [3] There is also evidence from seeds in Pharaoh tombs of watermelon cultivation in Ancient Egypt. Watermelon is grown in favorable climates from tropical to

temperate regions worldwide for its large edible fruit, which is a berry with a hard rind and no internal divisions, and is botanically called a pepo. The sweet, juicy flesh is usually deep red to pink, with many black seeds, although seedless varieties exist. The fruit can be eaten raw or pickled, and the rind is edible after cooking. It may also be consumed as a juice or as an ingredient in mixed beverages Figure:4. Considerable breeding effort has developed disease-resistant varieties. Many cultivars are available that produce mature fruit within 100 days of planting. In 2017, China produced about two thirds of the world total of watermelons. The sweet watermelon was formally described by Carl Linnaeus in 1753 and given the name *Cucurbita citrullus*. It was reassigned to the genus *Citrullus* in 1836, under the replacement name *Citrullus vulgaris*, by the German botanist Heinrich Adolf Schrader. [4] (The International Code of Nomenclature for algae, fungi, and plants does not allow names like "*Citrullus citrullus*".) The bitter wooly melon is the sister species of *Citrullus ecirrhosus* Cogn. from South African arid regions, while the sweet watermelon is closer to *Citrullus mucosospermus* (Fursa) Fursa from West Africa and populations from Sudan.[5] The bitter wooly melon was formally described by Carl Peter Thunberg in 1794 and given the name Momordica lanata. [6] It was reassigned to the genus Citrullus in 1916 by Japanese botanists Jinzō Matsumura and Takenoshin Nakai. [7]



Figure:1 Images of *Citrullus lanatus* (Watermelon) fruit

2. Materials and methods

2.1 Sample collection

The peel of *citrullus lanatus* (watermelon) were collected from the watermelon road shop, Vridhachalam, Cuddalore district, Tamil Nadu, India

2.2 Reagents

All analytical grade chemical and solvents used in the sample preparation were purchased from local suppliers of Singma-Aldrich chemical company Pondicherry scientific company, Trichy.

2.3. Preparation of *citrullus lanatus* (watermelon) peel extract for synthesis of nanoparticles

The sliced *citrullus lanatus* (watermelon) peels were washed several times with de-ionized water and tried (Fig:1) five days in room conditions, then grained and powdered. A 20 g of powdered peel taken in 250 mL round bottomed flask and stirred with 100 mL de-ionized water, heated at 80°C for three min and filtered by using whatmann 1≠ filter paper to get the extract. The filtrate is used in the further synthesis process.

2.4 Synthesis of Nanoparticles

2.4.1 Green synthesis of Tungsten nanoparticles

Synthesis of WNPs was carried out by reducing tungstic acid (M.F:H_2WO_3, M.W: 249.85 g/mol) using *citrullus lanatus* (watermelon) peel extract. To achieve this purpose, 100 mL of saturated solution of tungstic acid is steadily mixed with 10mL of *citrullus lanatus* (watermelon) peel extract [8]. The colour of the solution was turning in pale yellow to chocolate brown in colour. Further, obtained suspension was transfer to 250mL separating funnel due to collect the suspended enriched part, the suspended enriched part is centrifuged at 4000 rpm/20 min. Supernatant was discarded and pellet containing WNPs was carefully washed 3 times with distilled water to remove awkward materials. The obtained powder assumed as WNPs was incubated at ~100 °C until the water evaporated completely. Finally, WNPs were systematically characterized.

2.4.2 Synthesis of Lead nanoparticles

Aqueous solution of lead nitrate was prepared by adding 1 mM of $Pb(NO_3)_2$ to 250 ml of distilled water at room temperature and stored in an amber colored bottle to evade auto oxidation of lead ions. Lead nitrate (2mL ; 1 mM) was added drop wise into Extract (0.6 mL) while stirring and heated (45 °C) in a water bath at pH 9. The resulting solution became brown after 30 min of heating, indicating the formation of lead nanoparticles [9], as showing in figure1. The colloidal suspension thus obtained was centrifuged at 4000 rpm for 30 min and the pellet obtained after discarding the supernatant was re dispersed in deionized water. The centrifugation process was repeated 2 to 3 times for the removal of any adsorbed substances on the surface of lead nanoparticles. The synthesized nanoparticles were lyophilized and recovered in powdered form.

2.4.3 Synthesis of Aluminum nanoparticles (AlNPs)

The synthesis of Aluminum nanoparticles carried out by, 100mL of 0.1M of Aluminum chloride (M.F: $AlCl_2.6H_2O$, M.W: 241.43 g/mol) solution is taken in a 250 ml clean conical flask. Then, 10 ml of OBL leaves extract was added drop by drop into Aluminum chloride solution under continuous stirring for 30 min at the room temperature [10]. Colourless solutions turn into pale bluish yellow in colour. The resultant residue was filtered by using whattman 1≠ filter paper, the precipitate is washed several in double distilled water, finally obtained the glittering crystalline product.. The obtained final product was dried, collects and stored the airtight clicklock tube. These AlNPs were thoroughly characterized.

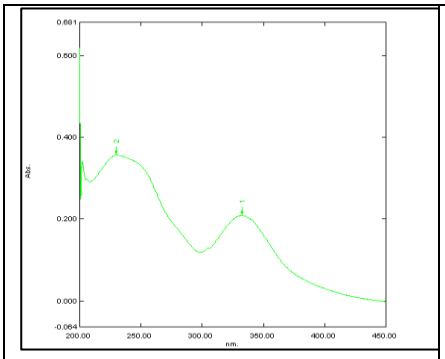
3. Result and discussion

3.1 UV Spectral analysis

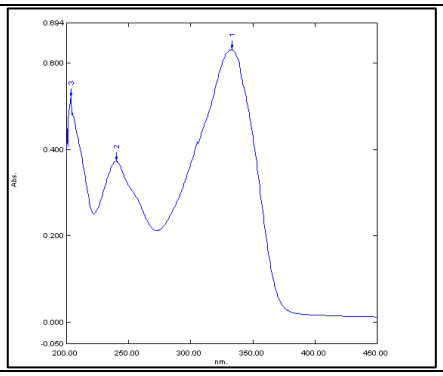
UV–vis absorption spectra were recorded in the range of 200–800 nm using an aqueous WONPs suspension. The samples displayed an optical absorption [11] peaks of absorption maximum value have been shown 228 nm for all the nanoparticle suspension but time increases absorption (a,u) only increases. The absorption maximum of lead oxide have shown in λmax=333nm have shown in (Fig:2 a,b,c). The dynamic absorption peaks are shown at 298 nm is evidence of the existence of various organic compounds that interact with Aluminum oxide ions in solution and implies a possible course for the reduction of the metal ions present in the solution the merged UV spectrum of aluminium nano particle suspensions.

3.2 FTIR Spectral analysis

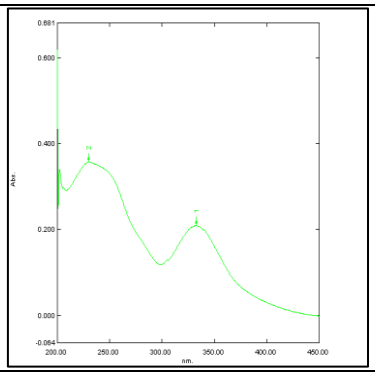
FT-IR spectrum of WNPs of *Citrullus lanatus* (Watermelon) peels extract shows different major peaks positioned at 3276, 2921, 2331, 2148, 2097, 1919, 1631, 1400, 1272 and 764 cm^{-1} which could be the esters, ethers, carbonyl (polyol's) or aromatic compounds. In particular, the 764cm^{-1} band arises most probably from the W–O stretching frequencies. The IR frequencies of broad peaks of 3276 and 2921cm^{-1} has shown hydroxyl group in various functional groups. FTIR studies were carried out for *citrullus lanatus* (watermelon) peel extract and synthesized Lead nanoparticles (Fig.3 a,b,c). The IR spectra peak shows the lead oxide nano particle showing a high intensity broad band at 2110.711 and 2092.668 cm^{-1} is due to the stretching mode of the lead and oxygen (Pb-O) bond. The absorption bands at 3440, 1596, 1459, 1420, 874 and 487 cm^{-1} were observed. The strong peaks at 3440 cm-1correspondes to Hydroxy group, H-bonded OH stretches. The band at 2498 cm-1 was attributed to methyl CH asym./sym stretches . 487 cm-1 have represented Al-O[12-13] stretching vibrations.



2(a) UV Spectrum of WNPs



2(b)UV Spectrum of PbNPs



2(c)UV Spectrum of AlNPs

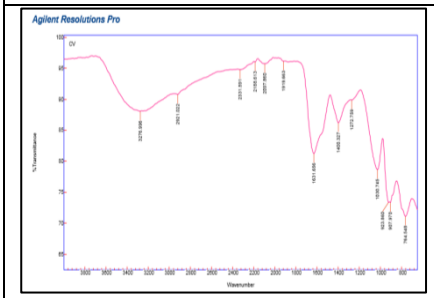


Fig:3 a, FTIR Spectrum of WNPs

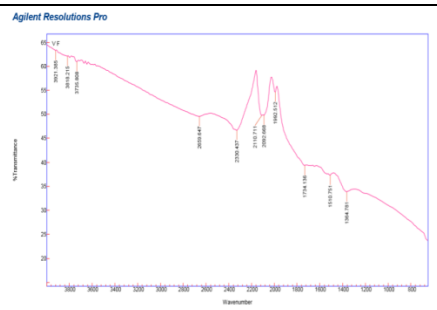


Fig:3 b, FTIR Spectrum of PbNPs

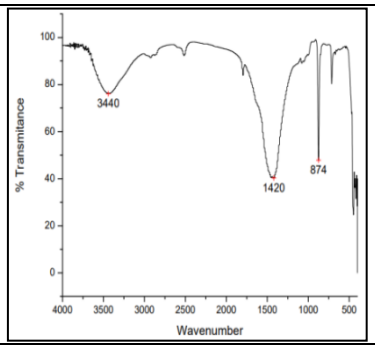


Fig:3c, FTIR Spectrum of AlNPs

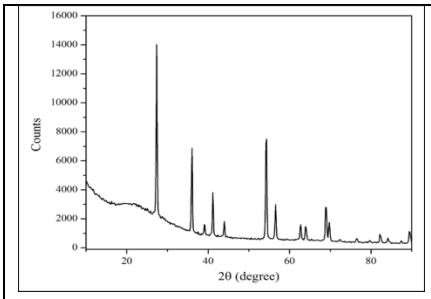


Fig:4a XRD pattern of WNPs

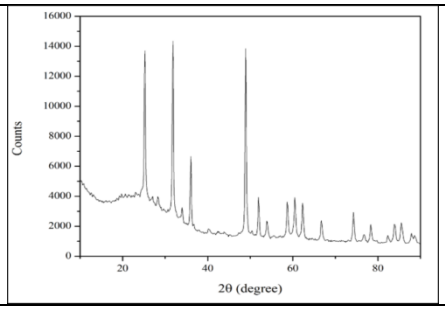


Fig:4b XRD pattern of PbNPs

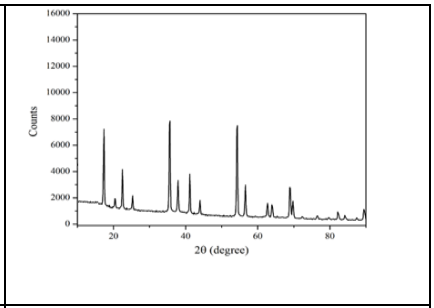


Fig:4c XRD pattern of AlNPs

3.3 XRD Analysis

X-ray diffractions(Fig:4a,b,c) is a versatile, non-destructive analytical method for identification and quantitative determination of various crystalline forms, known as "phases" of compound present in powder and solid samples. The size of metal oxide nanoparticles was obtained by Debye–Scherrer's formula given by the equation: $d_{hkl} = K\lambda/\beta\cos 2\Theta$. Analysis showed four distinct diffraction peaks at 26.24°, 32.26°, 38.53° and 49.04° and can be indexed 2θ values of (101), (110), (121) and (111) crystalline planes of cubic W. The average grain size of the tungsten nanoparticles formed in the bio reduction process is determined using scherr s formula d=(0.9 * 180)/ Cos and is estimated to be 7.2 nm.. Analysis showed four distinct diffraction peaks at 26.24°, 32.26°, 38.53° and 49.04° and can be indexed 2θ values of (111), (211), (222), (301) crystalline planes of cubic Ag. The average grain size of the lead nanoparticles formed in the bio reduction process is determined using scherr s formula d=(0.9 * 180)/ Cos and is estimated to be 5.2 nm.. Analysis showed four distinct diffraction peaks at 26.24°, 32.26°, 38.53° and 49.04° and can be indexed 2θ values of (101), (110), (121) and (111) crystalline planes of cubic W. The average grain size of the aluminum nanoparticles formed in the bio reduction process is determined using scherr s formula d=(0.9 * 180)/ Cos and is estimated to be 7.2 nm. Joint Committee on Powder Diffraction Standards (JCPDS) was used as a reference to assign the lattice planes according to the peaks obtained by the three nanoparticles.

3.4 SEM And EDS Analysis

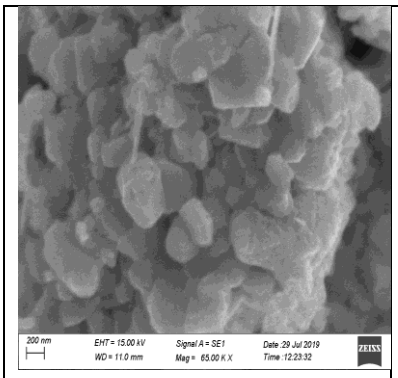


Fig:5a SEM Images of WNPs

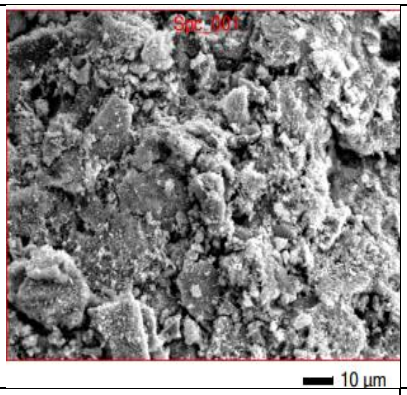


Fig:5b,EDS image of WNPs

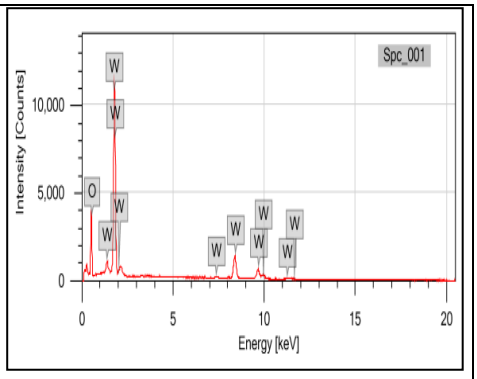


Fig: 5c. EDS spectrum of WNPs

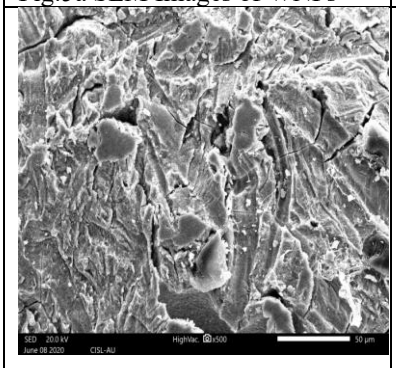


Fig:6a, SEM image of PbNPs

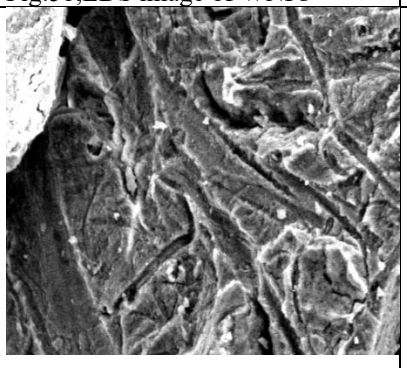


Fig:6b,EDS image of PbNPs

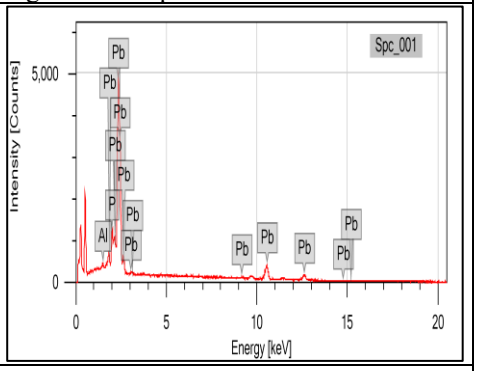


Fig: 6c. EDS spectrum of PbNPs

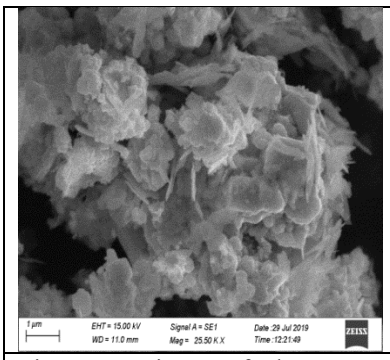


Fig:7a SEM image of AlNPs

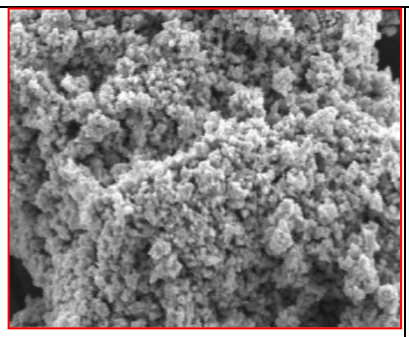


Fig:7b EDS image of AlNPs

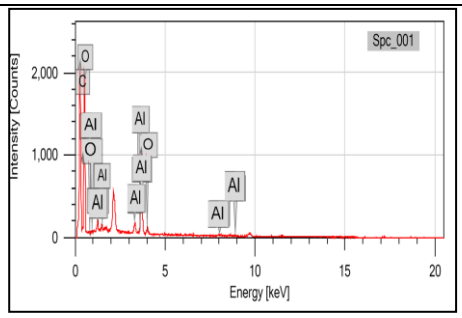


Fig: 7c. EDS spectrum of AlNPs

The SEM analysis was used to determine the structure of the reaction products that were formed. Thin films of the sample were prepared on a gold coated copper grid by just dropping a very small amount[14] of the sample on the grid, extra solution was removed using a blotting paper and then the film on the SEM grid were allowed to dry by putting it under a mercury lamp for 5 min . SEM image has showed individual zinc particles as well as a number of aggregates. SEM analysis is done to visualize shape and size of nanoparticle. The SEM image of synthesized Tungsten nanoparticles is shown in **(**Fig.5a, 6a, 7a**).** From the SEM images were seen in different magnification ranges like 1µm–20µm which clearly demonstrated the presence of spherical and mountain rock shaped nanoparticles. 10µm–50µm which clearly demonstrated the presence of spherical and mountain rock shaped nanoparticles for PbNPs, 1µm–20µm which clearly demonstrated the presence of spherical and mountain rock shaped nanoparticles for AlNPs. The elemental information of biosynthesized WNPs was analyzed by EDX [15-16]. As shown in the (Fig: 5b&5c, 6b & 6c and 7b &7c) evident that particle size 10µm, PbNPs has shown 11 µm and AlNPs have shown in 10 µm.

4. Conclusion

The green synthesis of tungsten nanoparticles, lead nanoparticles and aluminum nanoparticles from *Citrullus lanatus* (Watermelon) peel extract was studied. The reduction of the metal ions led to the formation of metal nanoparticles of fairly well-defined dimensions using the extract. Further, characterization studies of *Citrullus lanatus* (Watermelon) peel extract has been enhanced on synthesizing WNPs, PbNPs and AlNPs nanoparticles from it. This green chemistry approach towards the synthesis of metal nanoparticles has many advantages such as environmental friendly, cost effective and easily scaled up to large scale synthesis.

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