Green Synthesis and Relative Study of FTIR Spectra of MnO_2NPs by using Leaf Pulp Extract of Aloe vera

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Abstract
This work incorporates a comparison of Fourier transform infrared (FTIR) spectra with a wealth of studies to validate the production of nano MnO_2 powder. Using Aloe Vera leaf pulp as a reducing, stabilizing and capping agent, we succeeded to effectively synthesize MnO_2 nanoparticles using a green synthesis approach. The dried products were then analyzed using FTIR spectroscopy.

Because of their high surface area to volume ratio, nanoparticles are able to exhibit unique qualities that set them apart from larger particles including an infinite range of physico-chemical characteristics. Antimicrobial action against pathogenic microbes is one of the most widely used and relevant degradation qualities and a wealth of research on sanitation, hygiene, water treatment and health concerns at both the individual and commercial levels may be seen. This study is based on the comparative study of FTIR spectra for the formation of MnO_2 nanoparticles.

Keywords: Antimicrobial action, green synthesis, FTIR spectra, MnO_2 nanoparticles.

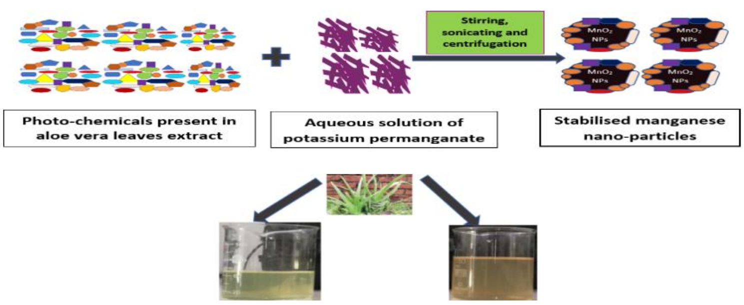
Introduction

Nanomaterials (NMs) are typically less than 100 nm in size. Worldwide interest in nanotechnology has grown due to its many possible uses in various fields of innovative research. Continuously promising and environmentally benign uses of metallic NMs are indicating a growing need. Some of the significant and in-demand domains where metallic nanoparticles are extensively researched, include separation, catalysis, medicine, thermal conductivity, water purification and electrical conductivity. Compared to the bulk, NMs have a comparatively larger surface area as one of their unique properties. A variety of biological, chemical and physical processes can be used to synthesize these.

Among these techniques, green synthesis is a respectable substitute because of its great efficiency, cheap cost and less harmful by products. Many sectors including the biological sciences, pharmaceutical, engineering, food and nutrition, environmental sciences and sensors, employ metal-based NMs. Plant extract contains numerous biomolecules and photo-chemicals that function as reducing or capping agents[19,21,23]. Graphene oxide(GO), copper oxide, calcium oxide, magnesium oxide, zinc oxide, titanium oxide, manganese oxide, silicon oxide, cerium oxide, cobalt-aluminium oxide and iron oxides are often utilized as NMs. Aloe vera (AV) leaf pulp (AVLP) (Botanical name; *Aloe Barbadenis Miller*) is typically utilized for skin care, cosmetics and health-related items.

Therefore, AVLP is highly recommended as a home therapy. Contrarily, manganese dioxide nanoparticles (MnO_2NPs) are extremely beneficial for antibacterial activity, photo-catalysis and catalysis, sensor production and sanitation[1,5,7-9,14-16,18,19,24,29]. Excellent catalytic qualities of MnO_2NPs have been used to enhance epoxy resin's fire safety, where TEM and TGIR analyses of the material's morphology and crystalline structure were conducted[7]. The biosynthesis of MnO_2NPs has been widely recognized in recent years by plant extraction methods[13].

More than 200 different biologically active phytochemicals are investigated in AV plant; however, aloe-emodin, aloin, aloesin, emodin and acemannan are the most investigated phytochemicals. Traditionally AV is applied for burns, cuts, insect bites, cure sores, antimicrobial, anti-inflammable, antihyperlipidemic, antidiabetic, anti-cancer, digestion protection, wound healing, skin health, blood sugar, dental plaque, canker sores (mouth ulcers/infections) applications[17,25].



Unboiled AVLP extracts **Boiled AVLP extracts**

Graphical abstract

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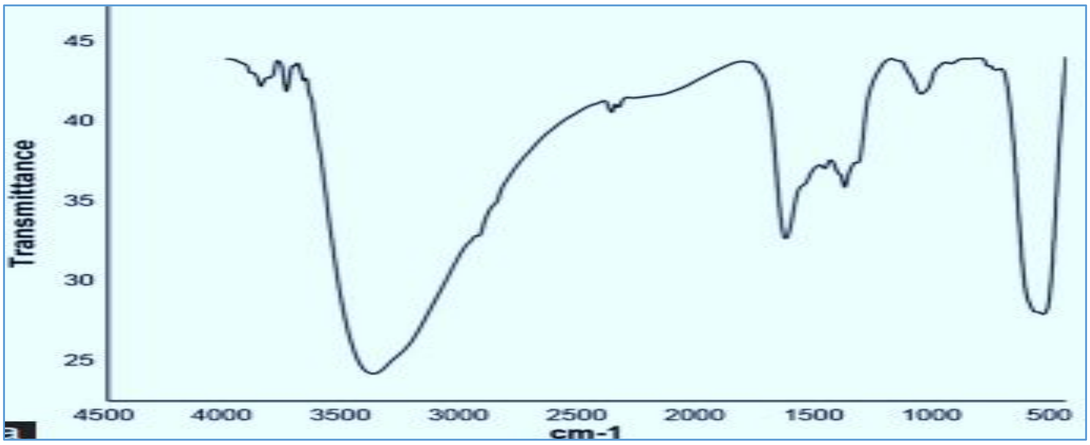


Figure 1: FTIR spectrum of MnO_2NPs[13]

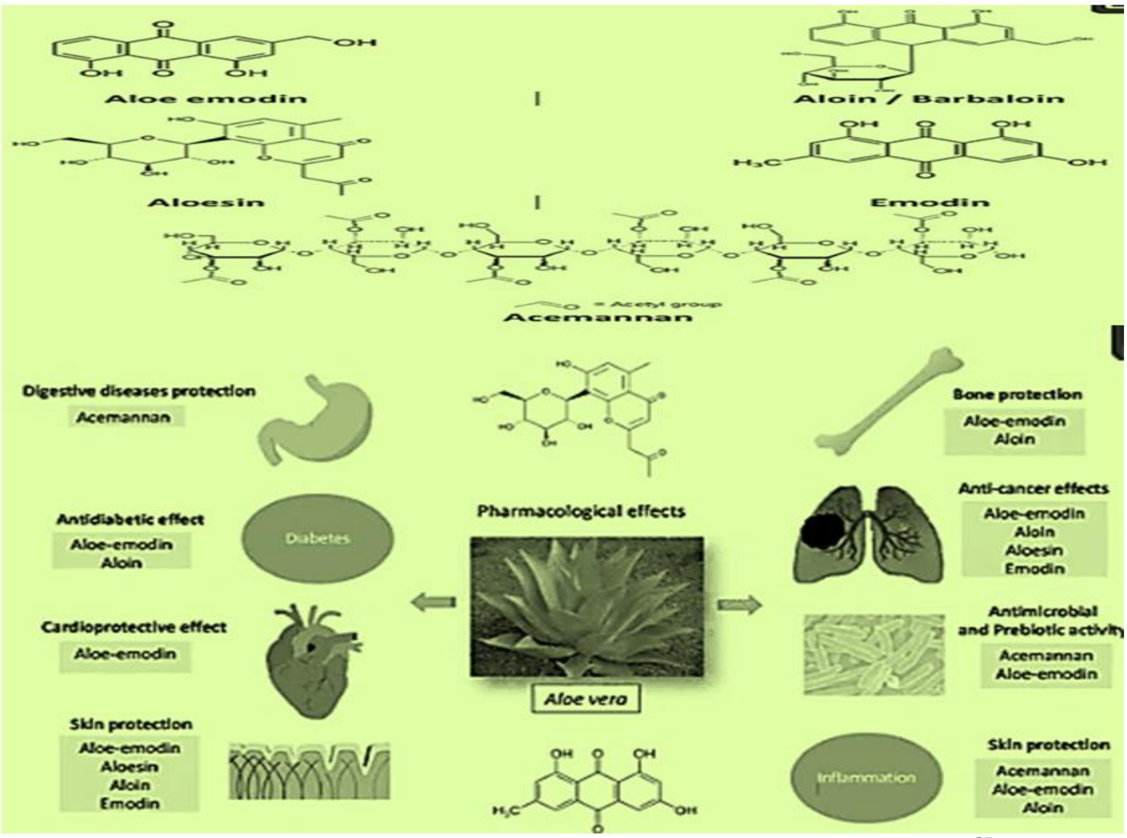


Figure 2: Pharmacologically active isolated components and their effect [25]

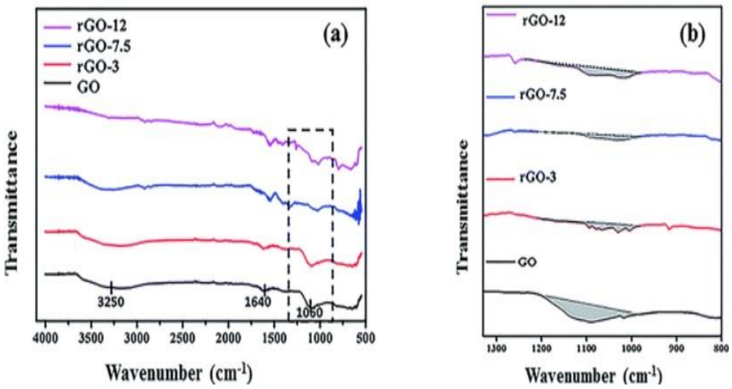


Figure 3: a) FTIR spectra of GO, rGO-3, rGO-7.5 and rGO-12 samples.
(b) Peak area analysis[3] of FTIR spectra at 1060 cm^{-1}

AV as a green reducing agent is applied for the reduction of GO. Maximum reduction was achieved with 7.5 g of AV with the efficiency of about 73% and marked by FTIR spectrum having notable dye removal ability with a maximum efficiency of ~98%. The methylene blue dye removal capability of rGO(7.5AV) was linked to enhanced surface area, π–π interaction and strong electrostatic attraction. Additionally, adsorption kinetics investigation proved pseudo second order adsorption phenomena. rGO recyclability confirmed an excellent desorption capability, enhanced current density and higher conductivity than GO sample.

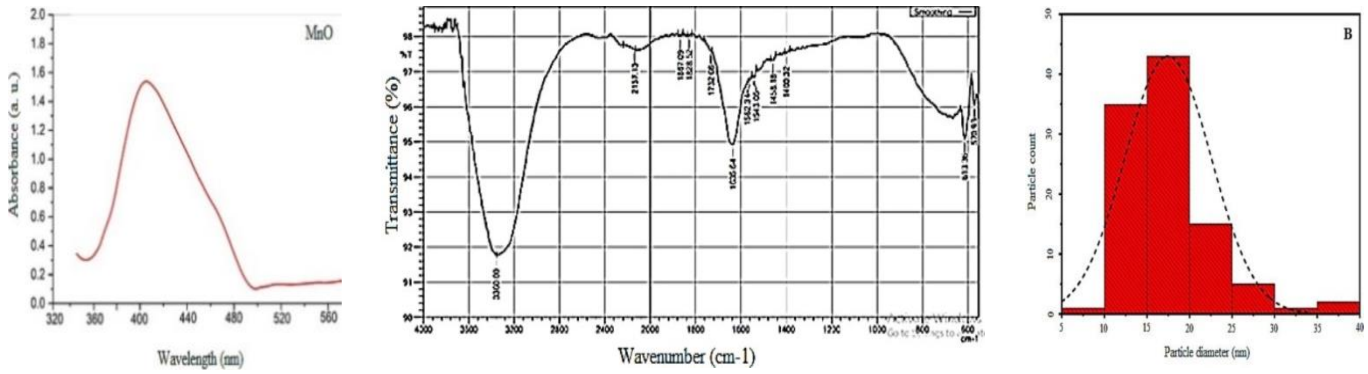
Proposed reduction mechanism demonstrates the role of sugars and anthaquinones as major components in the reduction of GO with electronics and sensing applications[3]. Amongst chemical and physical techniques, the biosynthesis method of metal nanoparticles has received the interest of many researchers owing to its environmental safety, simplicity and inexpensiveness. MnO_2NPs were successfully synthesised using green tea extract as the reducing agent and characterised by UV-Vis spectroscopy, X-ray diffractometry and FTIR spectroscopy. The shape and size of the MnO_2NPs were obtained by Scanning electron microscopy.

The size of MnO_2NPs was 20-30 nm. The MnO_2NPs exhibited strong antibacterial activity against pathogenic bacteria, namely, *Escherichia coli, Klebsiella pneumoniae* and *Pseudomonas aeruginosa*, with inhibition zones of 12mm, 14mm and 18 mm respectively. Moreover, the minimum inhibitory concentration (MIC) of the MnO NPs was 12.5 U/mL as determined by resazurin microtitre assay. The activities of some antibiotics remarkably increased when combined with MnO_2NPs (at MIC).

Figure 2 shows that FTIR spectrum of MnO_2. The bands at 515 and 480cm^{-1} correspond to the Mn-O bond. The absorption peak at 1313.96 cm^{-1} corresponds to O-C bending. 1118.53 cm^{-1} and 1021.32 cm^{-1} correspond to C-N stretching. The peaks at 908.59, 815.66 and 764.85 cm^{-1} corresponds to O-H bending and 627.55 cm^{-1} corresponds to C-H bending. MnO_2 nanoparticles of simple cubic structure were synthesized by co-precipitation method. The FTIR spectral analysis reveals the characteristic peaks of Mn-O stretching[28].

Material and Methods

Preparation of leaves pulp: The collected leaves of AV were washed with distilled water, dried in air and peeled. The obtained AVLP was crushed in a mortar and filtered with Whatmann filter paper. A required amount of distilled water was also added in the filtrate pulp and then divided into two parts. One part was kept un-boiled and the other one was boiled for 20 min. These two filtrates have been used as AVLP extract and preserved at below 4°C for the synthesis of MnO_2-NPs



(a) (b) (c)

Figure 4: a. UV spectrum, b. FTIR spectrum and c. Size distributions of green tea extract and MnONPs[20]

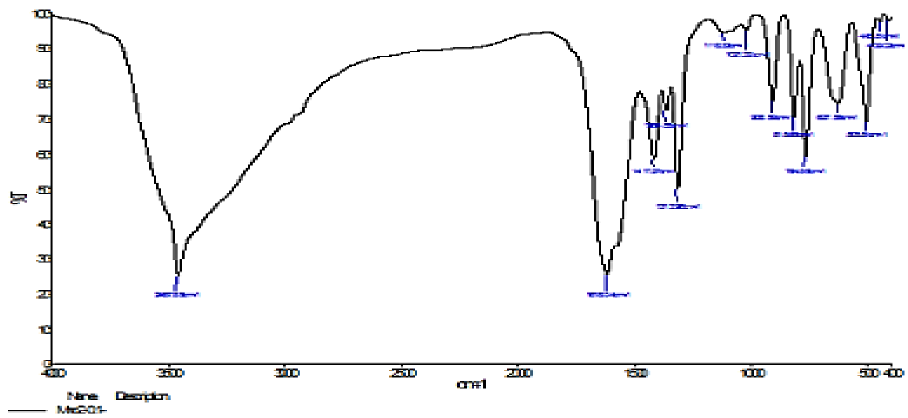
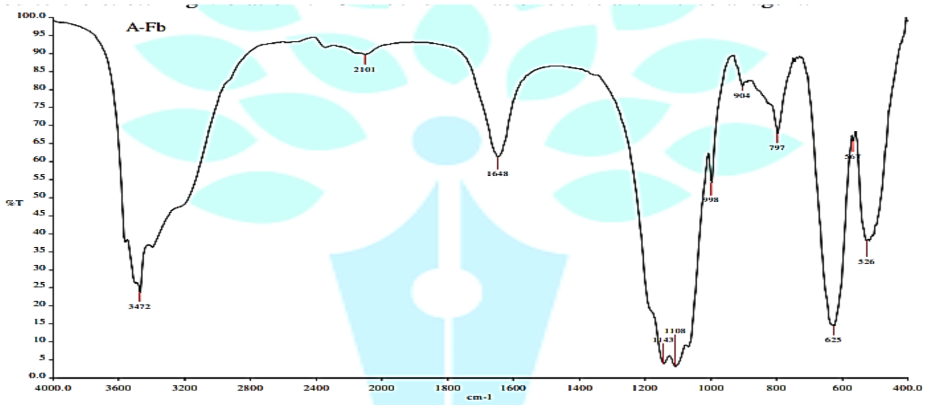
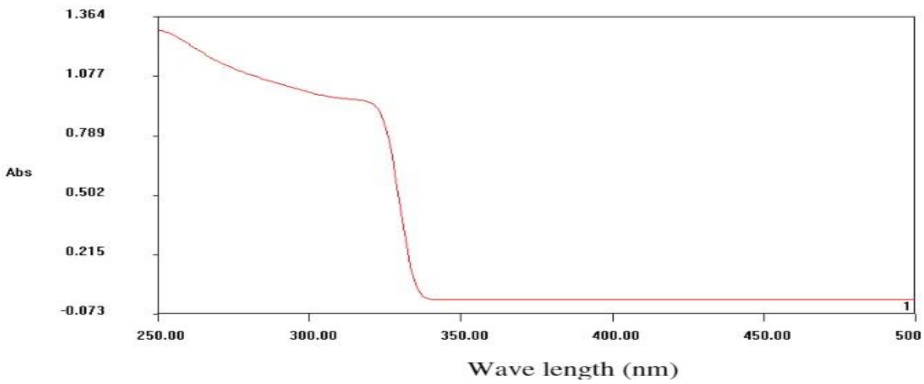


Figure 5: FTIR spectrum of MnO_2[28].



(a)



(b)

Figure 6: a. FTIR spectrum and b. UV-Vis spectrum of MnO_2NPs [4].

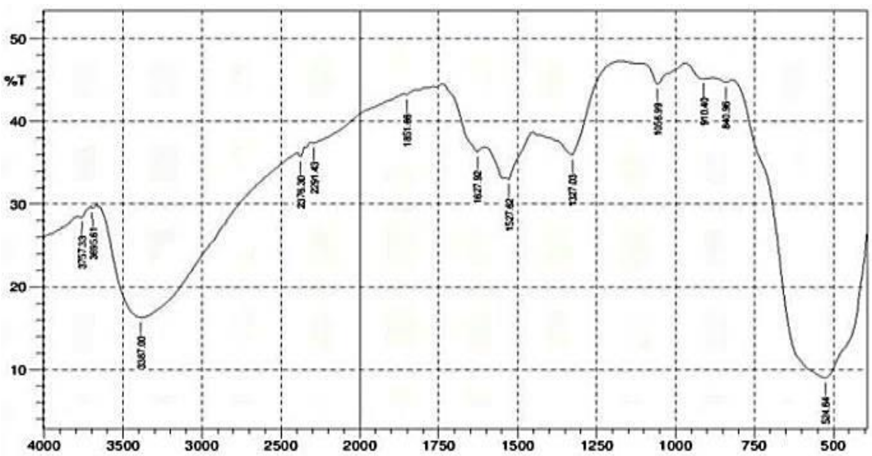


Figure 7: FTIR spectrum of MnO_2[26]

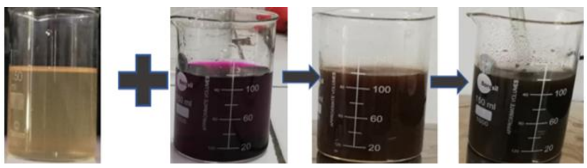


Figure 8: Boiled AVLP added with aqueous solution of $KMnO_4$ and showing change in colour

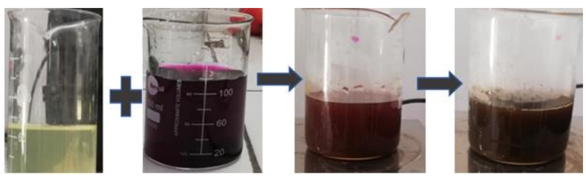


Figure 9: Un-boiled AVLP added with aqueous solution of KMnO4 and showing change in colour

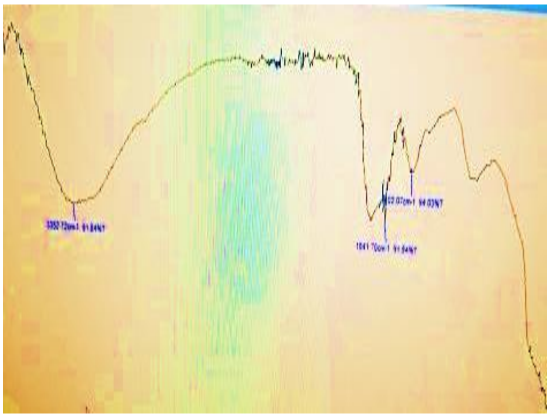


Figure 10: FTIR spectrum of MnO_2 by un-boiled AVLP.

Figure 11: FTIR spectrum of MnO_2 by boiled AVLP.

$KMnO_4$ used was of AR grade. The aqueous solution of $KMnO_4$ was prepared by dissolving 0.05 g $KMnO_4$ in 100ml of distilled water. 15 ml un-boiled and boiled AVLP extracts were dissolved in 50 ml of $KMnO_4$ solution separately. Changed colours of the both extracts are shown by the figure 10 and 11. These solutions were stirred over a magnetic stirrer for 2hours at 40°C and sonicated for 30 minutes at the temperature range from 30°C to 47°C. The obtained suspensions were then centrifuged. The brownish black nano-powder of MnO_2-NPs settled down and was washed with ethanol followed by distilled water several times. The washed powder was dried in oven at 90°C for 4 hours preserved in sealed plastic bottles for characterizations and antimicrobial activities.

Results and Discussion

Fourier transform infrared characterization was done in the wavelength range at 400-4000 cm^{-1} as shown in the figure 10 and 11. The spectrum obtained with boiled extract of AVLP is closer to earlier studies. MnO_2NPs use the extract of AV plant. The characteristic peaks are obtained at 3378 cm^{-1}, 1633 cm^{-1}, 1383 cm^{-1}, 1060 cm^{-1} and 545 $cm^{-1}$with peaks of O-H, C=O, C=C, C-C, C-Mn and Mn-O bonds respectively on the surface of MnO_2NPs[13].

The brown colour of the prepared nanocomposite was the result of the surface plasmon resonance (SPR) caused by the oscillation of electrons on the surface of the nanocomposite. The shade of the compound depends on two main factors, namely, the shape of the compound and the size of the NPs. The UV–Vis spectrum of the MnO NPs solution shows a peak in the visible region at 410 nm. Theoretically, MnO_2NPs possess an absorption peak in the range of 350–410 nm. As shown in figure 4A, the functional groups in green tea extract were identified and their role in MnO NP synthesis was analysed. The size distribution was around 18 nm[20].

The FTIR analysis results indicate the existence of bio-components on the NPs' surface such as alkaloids, tannins and glycosides. FTIR measurements were utilised to determine the interaction between manganese salts and protein molecules capable of reducing Mn ions and stabilising MnONPs. FTIR analysis revealed some remarkable bands of the vibrations of the hydroxyl group, C–O, MnO and others. This corresponds to the MnO NPs and bio-compounds on the surface[2,6]

Conclusion

The FTIR spectrum obtained by boiled AVLP extract is better method than un-boiled AVLP extract for the synthesis of MnO_2-NPs at 3350.49 cm^{-1}, 1621.85 cm^{-1}, 1455 cm^{-1}, 1396 cm^{-1}, 1076 cm^{-1} and 516 cm^{-1}, six peaks corresponding to O-H, C=O, C=C, C-C, C-Mn and Mn-O bonds respectively. This NM has antimicrobial activity and we can modify it for many other applications such as conductance, sensors etc. with innovative ideas.

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