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GREEN SYNTHESIS OF ZERO VALENT IRON NANOPARTICLES USING THE LEAVES EXTRACT OF *MORINGA OLEIFERA*

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KeyWords
Fourier transform infrared spectroscopy (FTIR), Iron, Moringa Oleifera, Nanoparticles, Synthesis, Zero-Valent.

ABSTRACT

The Importance of synthesizing nanoparticles using plant extracts is being emphasized globally, as an alternative to traditional methods because they are cost-effective, nontoxic, biocompatible and eco-friendly. In this study, green synthesis and characterization of zero-valent iron nanoparticles (ZVIN) using the leaves extract of *Moringa oleifera*, zero-valent iron nanoparticles were synthesized by mixing 6ml of *Moringa oleifera* leaves extract with 4ml of Fe_2SO_4. The synthesized zero-valent iron nanoparticles (ZVIN) were characterized by the use of Fourier transform infrared spectroscopy (FTIR). Fourier transform infrared spectroscopy (FTIR) reveals that the polyphenols present in the *Moringa oleifera* leaves extract are responsible for the reduction and stabilization of the zero valent iron nanoparticles (ZVIN). FT-IR spectra of the extracts and nanosuspensions were similar, with peaks observed at around 3300–3400 cm 1, 1600 cm 1, 1050–1150 cm 1 and 500 cm 1, corresponding to O–H, C=O, C–O and C–H stretching, indicating the participation of biomolecules in the zero-valent iron nanoparticles (ZVIN) synthesis process. TheFT-IR spectra reveals that the polyphenols present in the *Moringa oleifera* leaves extract are responsible for the reduction and stabilization of the zero valent iron nanoparticles (ZVIN). The results obtained in this study confirmed that *Moringa oleifera* leaves extract can play an important role in the bioreduction of Fe ions to zero- valent iron nanoparticles (ZVIN).

1. Introduction

Nanoparticles are gaining importance in different fields which include engineering, chemical science, physical science, biomedical science, food and feed cosmetics, space technology, environmental, drug and gene delivary. Nanoparticles, which are the basic building blocks of nanotechnology, are particles ranging from 1 to 100nm in size. Nanoparticles can be synthesized by two general approaches which are top-down and bottom-up. The top-down approach deals with synthesis of nanoparticles through physical methods such as milling, etching and machining of large size materials, while the bottom-up approach deals with synthesis of nanoparticles through chemical and biological methods such as precipitation, positional assembling and self-assembling [4].

The three main methods of synthesizing nanoparticles are the physical, chemical and biological methods [9]. Despite the fact that chemical and physical methods may successfully produce fine nanoparticles, they require a huge amount of energy and are very expensive and dangerous due to the involvement of expensive, flammable and toxic and reducing agents.Biological method which involves the use of plants is utalized as an alternative method for synthesizing nanoparticle, which is economical and eco-friendly in comparison to physical and chemical methods [3, 8]. Green synthesis of nanoparticles is gaining importance due to its eco-friendliness

and simplicity. Plant mediated synthesis can be carried out in any wet laboratory with few chemicals and instruments which is why it is emerging as an area of research for large-scale green synthesis of nanoparticles.

Zero-valent iron nanoparticles (ZVIN) have gained huge interest for the amending of both inorganic and organic pollutants from soil and water due to their large suface area, small size, and high reactivity [1,14]. The major physical methods through which zero valent iron nanoparticles (ZVIN) have been synthesized are grinding and ball milling. Chemically, zero valent iron nanoparticles (ZVIN) can be synthesized by using strong reducing agents such as hydrazine, sodium borohydride ($NaBH_4$) [15] and dimethylformamide [10] which are highly corrosive and toxic. Plant-mediated synthesis of zero valent iron nanoparticles (ZVIN) is a method which not only synthesizes but also stabilizes the nanoparticles against aggregation because plant metabolites may act as reducing as well as capping agent for the synthesis of zero valent iron nanoparticles (ZVIN) [2,3,12]. Plant extracts contain terpenoids, phenols, flavonoids, tannins, proteolyticenzymes,etc.,which act as reducing and capping agents in the production of zero valent iron nanoparticles (ZVIN). Based on the idea of green chemistry, previously zero valent iron nanoparticles (ZVIN) are synthesized from extracts like eucalyptus leaves [18], tea leaves [7], vine leaves [5], Rosadama scene, Thymus vulgaris, and Urticadioica[6]. But the recent observations showed that the sorption and dispersion capacity of ZVIN increased by the support of porous materials like carbon materials, clays and resins [13,16].

In this study, green synthesis method was used to synthesize zero valent iron (ZVIN) using the leaves extract of *Moringa oleifera*. In addition, the synthesized zero valent iron nananoparticles (ZVIN) were characterized by the use of FTIR spectroscopy.

2. Materials and Methods

2.1 Sample Collection

Fresh leaves of *Moringa oleifera* was obtained from Road 6922 Abuja Model City, Gwarimpa Estate, FCT Abuja Nigeria. The sample was transferred to the laboratory where it was washed with distilled water and dried at room temperature. The dried leaves were grounded into powder form by the use of mortar and pestle.

2.2 Sample Preparation

80g of the powdered leaves were extracted using a Soxhlet apparatus consisting of a chamber, a Soxhlet extractor and an extraction flask. 70% ethanol was used as the solvent for the extraction. The resulting solution was evaporated to dryness in a fume cupboard to obtain semi-solid extract. Partitioning was done on the crude ethanol extract with solvents of different polarity such as methanol (polarsolvent), n-hexane (non-polar), chloroform and ethylacetate (mediumpolar) using a separating funnel. Then the hexane fraction was carefully separated. Subsequently, the crude ethanol fraction thereof was partitioned with chloroform followed by ethylacetate and then finally the aqueous methanol fraction left behind the crude ethanol (residual aqueous fraction). The portions were subsequently referred to as n-hexane fraction, chloroform fraction, ethylacetate fraction, aqueous methanol fraction and residual aqueous fraction respectively.

2.3 Green Synthesis of Zero Valent Iron Nanoparticles

The zero valent iron nanoparticles were synthesized by adding 6ml of *Moringa oleifera* leaves extract to 4ml of 1M $FeSO_4$ for the reduction of Fe^{2+} ions. The synthesis of zero valent iron nanoparticles was carried out at room temperature. The colour of the solution changed immediately from green to black which indicates the formation of zero valent iron nanoparticles.

2.4 Characterization of Zero Valent Iron Nanoparticles

FTIR measurements were carried out to identify the possible biomolecules responsible for capping and efficient stabilization of the zero valent iron nanoparticles (ZVIN) synthesized using Moringa oleifera leaves extract.

Fourier Transform Infrared Spectroscopy (FTIR) analysis of FeNPs (Iron nanoparticles), and *Moringa oleifera* extracts was done over the range of 4000-600cm^{-1}. The measurements were carried out on a Cary 600 Series FTIR spectrometer.

3. Result and Discussion

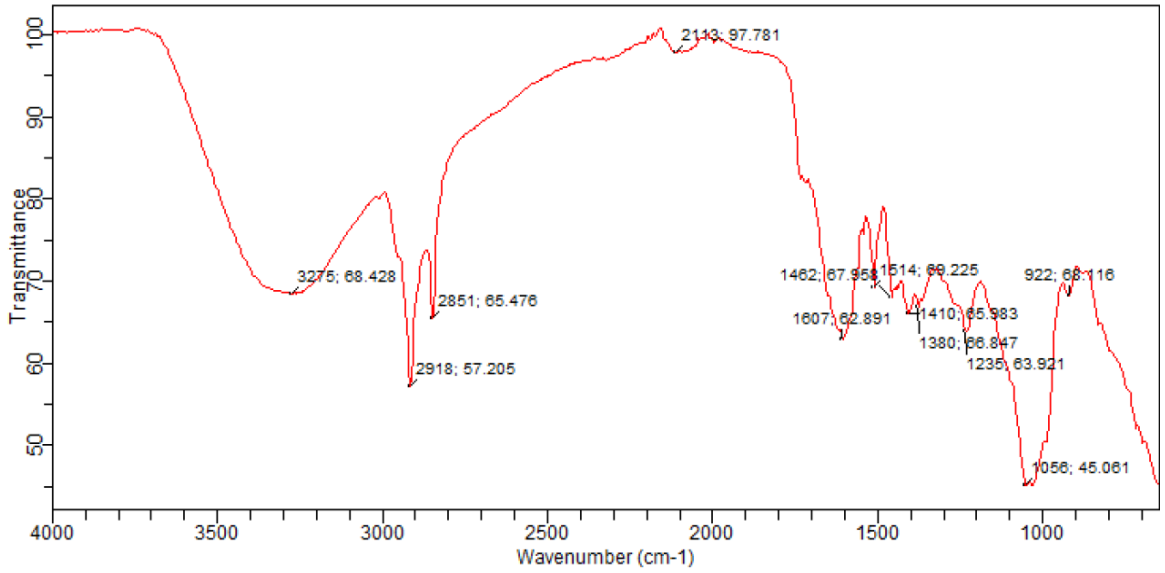

Figure1. FTIR spectrum of Crude extract of powdered dry leaves of Moringa oleifera

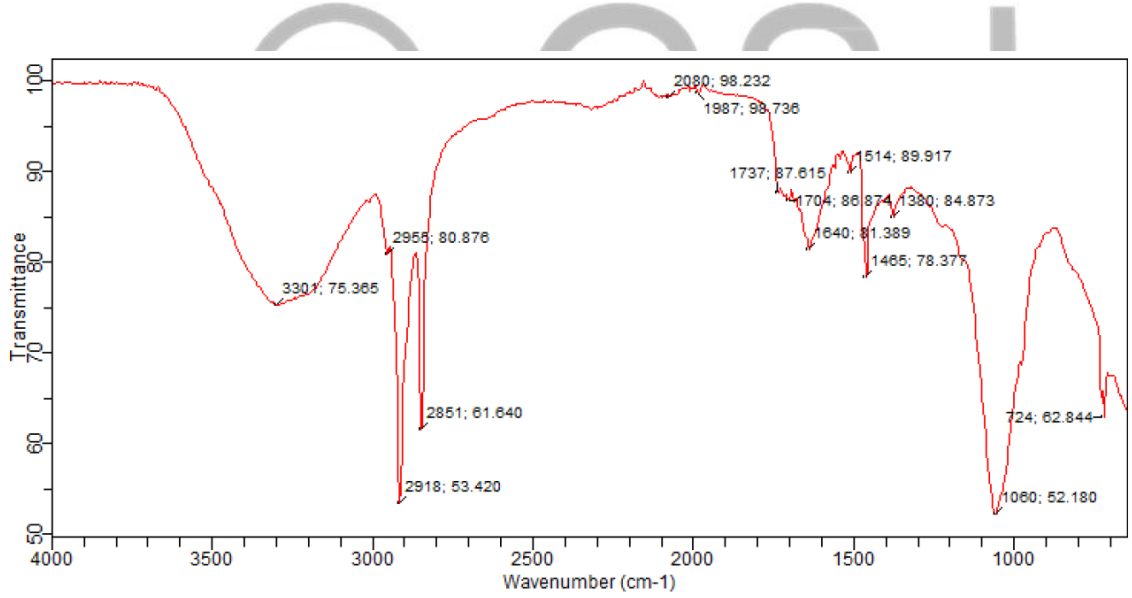

Figure 2. *FTIR spectrum of Chloroform fraction of powdered dry leaves of Moringa oleifera.*

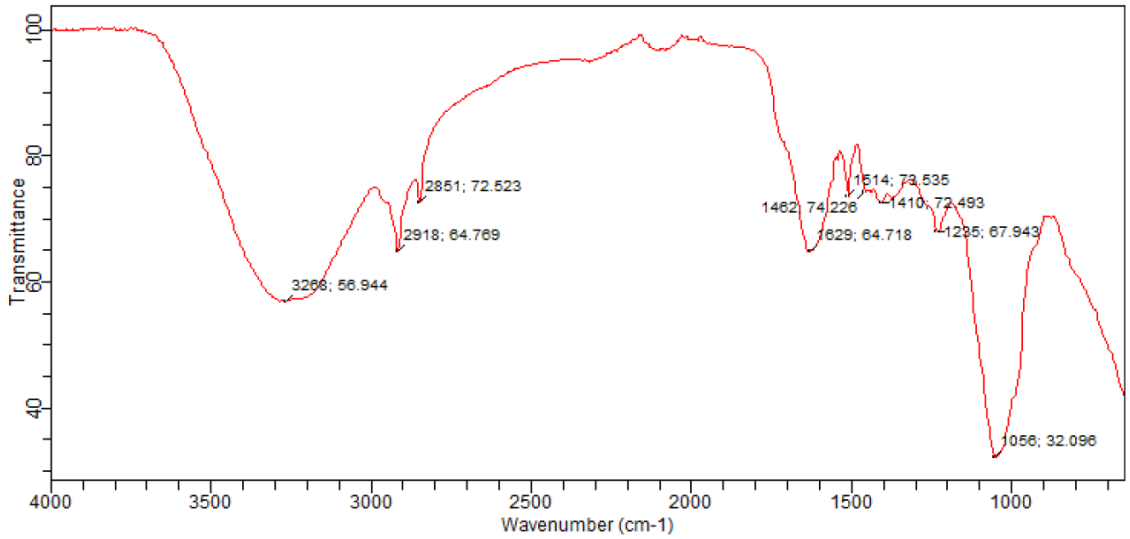

Figure 3. *FTIR spectrum of Ethylacetate fraction of powdered dry leaves of Moringa oleifera.*

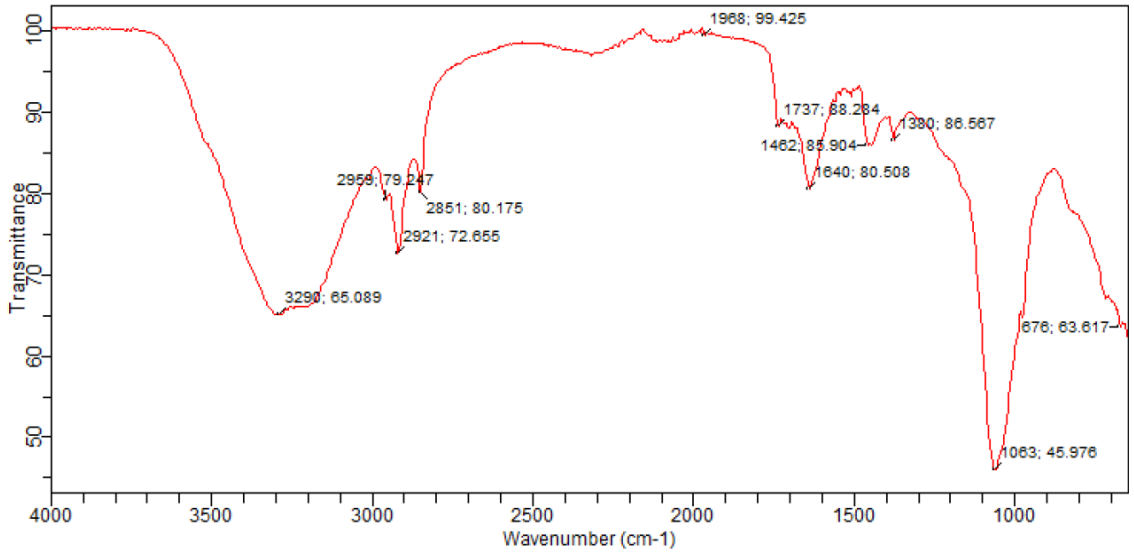

Figure 4. *FTIR spectrum of n-hexane fraction of powdered dry leaves of Moringa oleifera.*

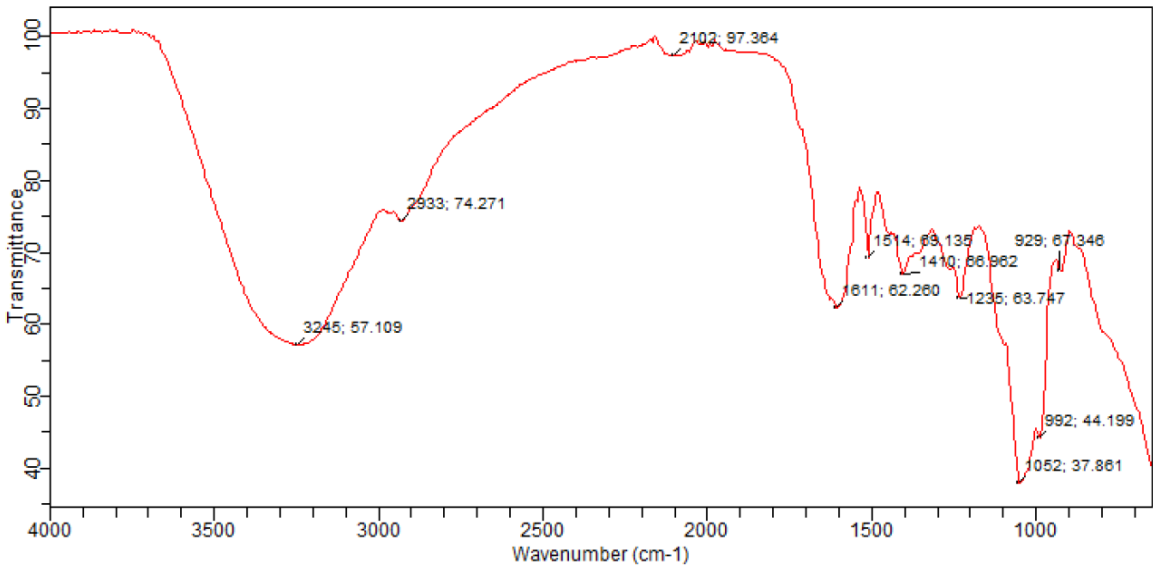

Figure 5. *FTIR spectrum of methanol fraction of powdered dry leaves of Moringa oleifera.*

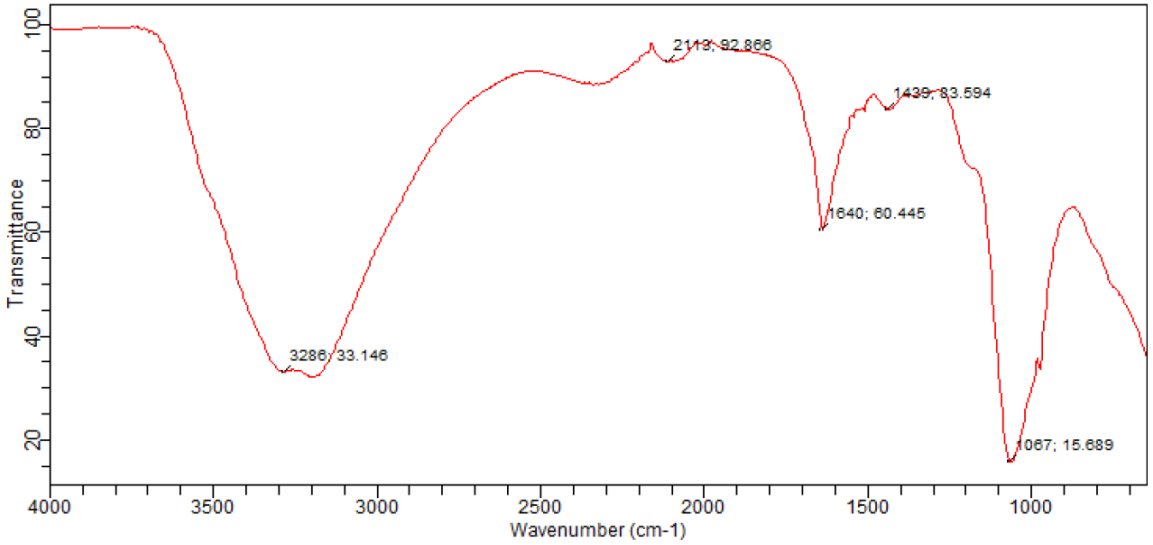

Figure 6. FTIR *spectrum of $FeSO_4$ / Crude extract of powdered dry leaves of Moringa oleifera.*

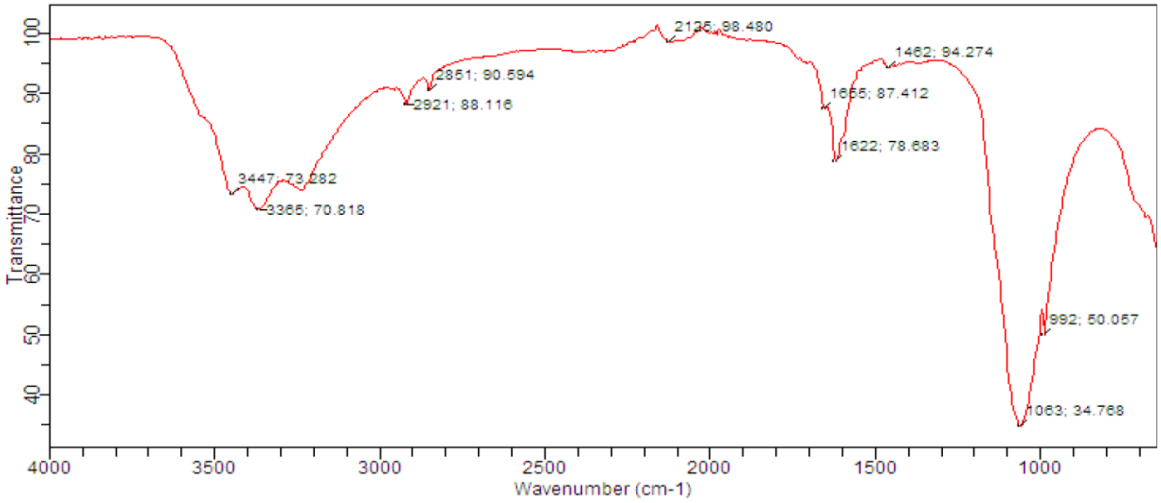

Figure 7. *FTIR spectrum of $FeSO_4$/ Chloroform fraction of powdered dry leaves of Moringa oleifera.*

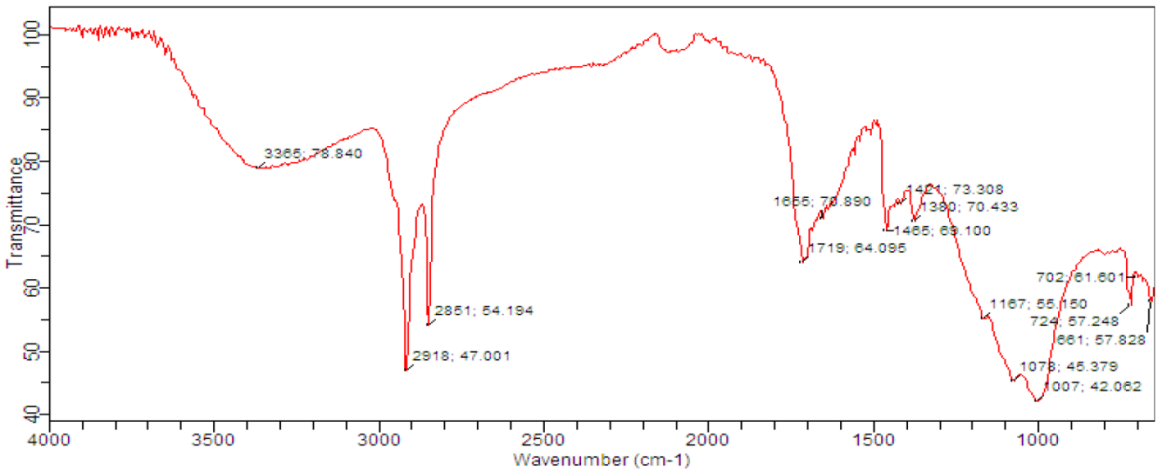

Figure 8. *FTIR spectrum of $FeSO_4$/ Ethyl acetate fraction of powdered dry leaves of Moringa oleifera.*

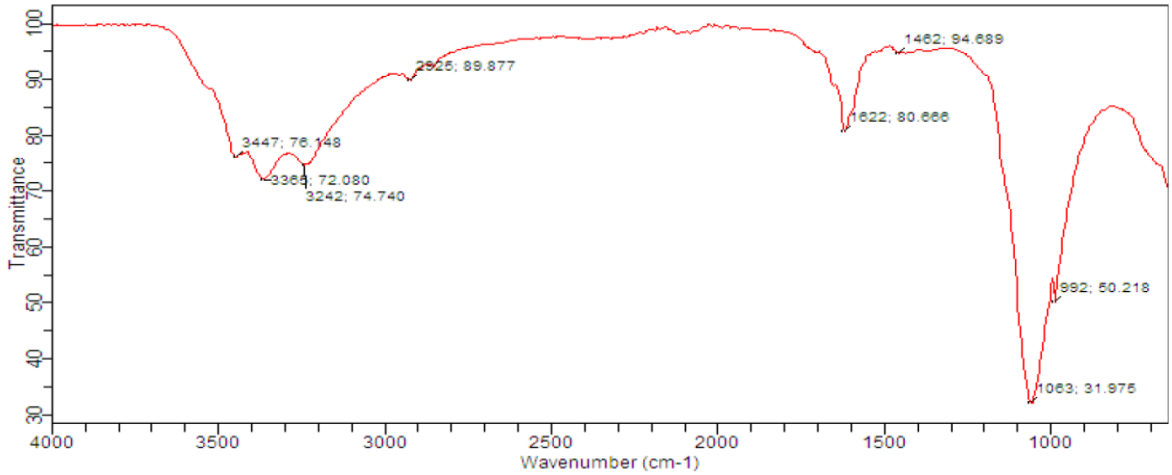

Figure 9. *FTIR spectrum of $FeSO_4$/ n-hexane fraction of powdered dry leaves of Moringa oleifera.*

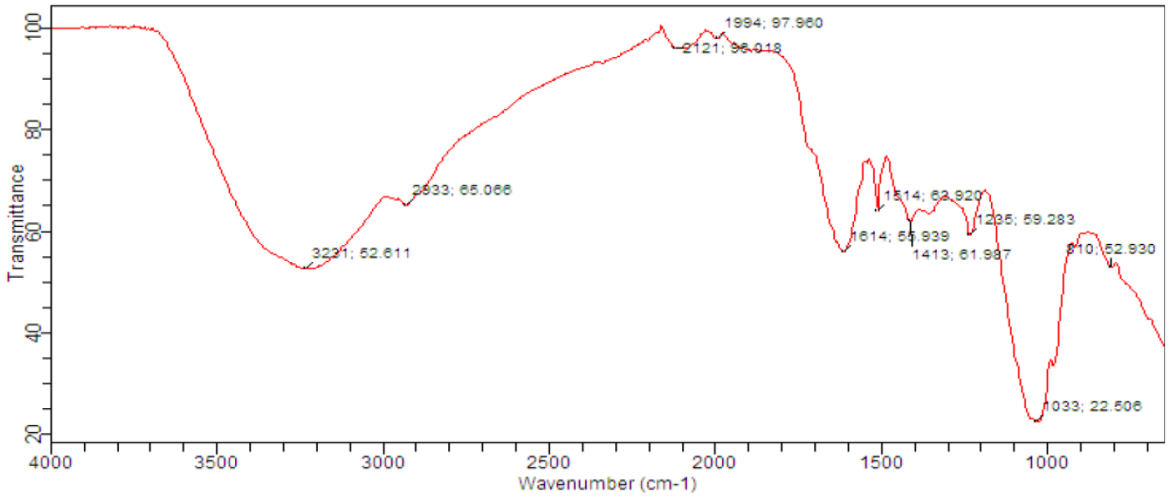

Figure 10. *FTIR spectrum of $FeSO_4$/ methanol fraction of powdered dry leaves of Moringa oleifera.*

3.1 FTIRSpectroscopy

Fourier transform infrared spectroscopy was performed to identify the presence of functional groups on the surface of the crude extract, chloroform fraction, ethylacetate fraction, n-hexane fraction, methanol fraction and also the ZVIN (Zero valent iron nanoparticles) synthesized from the crude extract. In Figure 1 which shows the FTIR spectrum of crude extract of powdered dry leaves of *Moringa oleifera*, the fundamental mode of vibration at 3275cm^{-1} is corresponding to the O-H stretching of hydroxyl compounds. The bands at 2918 and 2851 cm^{-1} could be due to alkane C–H stretch which is associated with lipid molecules in the leaf broth. The existence of carbonyl group (C=O) was indicated by the peak at 1607cm^{-1}. The peak shown at 1410cm^{-1} was assigned to the (C=C) stretching of aromatic ring. The peaks at 1235cm^{-1} and 1056cm^{-1} was assigned to C-O stretching of phenol group and primary alcohol respectively. The absorption peak at 922cm^{-1} was assigned to C-H out of plane bending.

In Figure 2 which shows the FTIR spectrum of chloroform fraction of powdered dry leaves of *Moringa oleifera*, The intense broadline at 3301cm^{-1} is characteristic of the hydroxyl functional group in alcohols and phenolic compounds. The band at 2918 and 2851cm^{-1} could be due to alkane C–H stretch which is associated with lipid molecules in the leaf broth. The peak at 1640cm^{-1} is due to amide II bond from proteins and at 1465cm^{-1} was assigned to the (C=C) stretching of aromatic ring.

In Figure 3 which shows the FTIR spectrum of ethyl acetate fraction of powdered dry leaves of *Moringa oleifera.* The fundamental mode of vibration at 3301cm^{-1} is corresponding to the O-H stretching of hydroxyl compounds. The bands at 2918 and 2851cm^{-1} could be due to C–H stretching of alkanes. The peak at 1629cm^{-1} was assigned to the amide (C=O) functional group, while the peak shown at 1410cm^{-1} was assigned to the (C=C) stretching of aromatic ring.

In Figure 4 which shows the FTIR spectrum of n-hexane fraction of powdered dry leaves of *Moringa oleifera.* The intense broadline at 3290cm^{-1} is characteristic of the hydroxyl functional group in alcohols and phenolic compounds. The bands at 2931 and 2851cm^{-1} could be due to C–H stretching of alkanes. The peak at 1640cm^{-1} is due to amide II bond from proteins and at 1462cm^{-1} was assigned to the (C=C) stretching of aromaticring. The peak at 1056cm^{-1} represents C-OH stretching vibrations.

In Figure 5 which shows the FTIR spectrum of methanol fraction of powdered dry leaves of *Moringa oleifera.* The fundamental mode of vibration at 3245cm^{-1} is corresponding to the O-H stretching of hydroxyl compounds. The band at 2933cm^{-1} could be due to C–H stretching of alkanes. The peak at 1611cm^{-1} was assigned to the amide (C=O) functional group, while the peak shown at 1410cm^{-1} was assigned to the (C=C) stretching of aromatic ring. The peaks at 1235cm^{-1} and 1052cm^{-1} was assigned to C-O stretching of phenol group and primary alcohol respectively.

The FTIR spectra of ZVIN (zero valent iron nanoparticles) synthesized from the crude extract and its fractions in aqueous methanol, chloroform, ethylacetate and n-hexane are shown in Figure 6-10. The spectrum exposed some peaks ranging from 3301 to 3345cm^{-1} which was attributed to the free OH molecule, other peaks that can be seen at 2918 to 2851cm^{-1} were due to the asymmetric and symmetric aliphatic C-H stretching vibrations, the existence of carbonyl group (C=O) was indicated by the peaks at 1704 to 1607cm^{-1}. Lastly, peaks shown at 1465 to 1410cm^{-1} and 1060 to 1052cm^{-1} were assigned to the (C=C) stretching of aromatic ring and C-OH respectively. All the sepeaks indicated the presence of the phenolic structures with in the crude extract and its different fractions. Our findings showed great similarity with what was obtained by [17].

According to one study, FTIR spectra for FeNPs synthesized by leaf extract of *Platanus orientalis* were obtained by scanning the FeNP sample between the range of 400–4500cm^{-1}. Its spectrum displays stretching of the C–H group at 2096 cm-1 and bending of H–C–H at 1315 and 1410cm^{-1}. C–O and C–C stretching was observed at a range of about 1000–1450 (cm−1).Another example includes FTIR analysis of FeNPs synthesized by flower extract of *Musa ornata.* FTIR analysis was performed between the range of 400–4000cm^{-1}. Three sharp peaks at 480.69, 3383.42, and 1634.15cm-1 were displayed on FTIR spectra of previously mentioned example [11] these studies supported our results and revealed that the presence of O–H and C=O bonds due to phenol/alcohol and Alkene functional groups are involved in the synthesis and stability of FeNPs from *Moringa oleifera*.

Conclusion

Green synthesis of ZVIN (zero valent iron nanoparticles) using plant extracts is a good alternative to chemical synthesis. The results obtained in this study confirmed that *Moringa oleifera* leaves extract can play an important role in the bio reduction of Fe ions to zero-valent iron nanoparticles (ZVIN). The formation of zero-valent iron nanoparticles (ZVIN) was confirmed by FTIR spectroscopy. FTIR results confirm the presence of functional groups such as hydroxyl, alkanes, carboxyl group in the extract and the synthesized nanoparticles. FTIR spectral data confirm that the polyphenols present in the *Moringa oleifera* leaves extract are responsible for the formation of ZVIN.

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