SYNTHESIS AND CHARACTERIZATION OF ZINC SULPHIDE NANOPARTICLES FROM GARLIC AND ONION EXTRACT USING THE BIOSYNTHESIS METHOD

BY

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DECLARATION

I, Musene Benjamen, declare that this research has been done by myself. I confirm that this work is my own and it has not been submitted for any degree or examination at any institution.

..................Benje..

Musene Benjamen   Date: ....17th Nov 2023..............................

This research project report has been submitted to the Department of chemistry with the approval as supervisor:

....Pmusagala.....

Mr. Musagala Peter   Date: ....17/11/2023...................

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ABBREVIATIONS

ZnS: Zinc sulpide

NPs: Nanoparticles

FTIR: Furrier- transform infrared

XRD X-ray diffraction

ABSTRACT

ZnS nanoparticles were synthesized using garlic and onion extract. The green synthesis method was used since it was ecofriendly in that toxic gases and high temperatures are not involved. Additionally this method is also cheap. Garlic and onion gloves were obtained from nagongera town council, dried and 10g of each sample was measured and dissolved in 200mls of distilled water. 0.04 moles of zinc nitrate solution was made by dissolving 12g of zinc nitrate in 50mls of water. A solution of sodium sulphide was also made by dissolving 5.2g of sodium sulphide in 50mls of water. The two solutions are then mixed together followed by addition of the extract solution with constant stirring for 60minutes. During nanoparticle formation, there was color change from white to pale yellow for garlic extract and brown to green for onion extract. After the synthesized nanoparticles where dried, that from garlic extract gave 4g while that from onion extract gave 2g. The FTIR machine was used to characterize the nanoparticles and different spectrums where obtained as shown in the report. However the spectrums showed some peaks above 3000cm^{-1}. This would have come as a result of other phenolic compounds found in garlic.

CHAPTER 1 : INTRODUCTION

1.1 Background

Nanoparticles are tiny particles with dimensions ranging from 1 to 100 nanometers. They can be composed of various materials including metals, metal oxides, polymers and carbon based materials. Due to their small size, nanoparticles have exhibits unique physical, chemical and biological properties that makes them differ from their bulk counterparts(Ealia & Saravanakumar, 2017).Zinc sulphide nanoparticles (ZnS NPs) have gained significant attention in various fields, including optoelectronics, photo catalysis, and biomedical applications. The use of biosynthesis methods for nanoparticle synthesis offers several advantages, such as eco-friendliness, cost-effectiveness, and the potential to utilize renewable resources. In this research, garlic and onions (Allium sativum) are employed as a bio-reducing and capping agent to synthesize ZnS NPs. Zinc sulphide nanoparticles exhibit unique optical, electrical, and catalytic properties due to their size-dependent quantum confinement effects. Traditional synthesis methods for ZnS NPs involve chemical routes that often require toxic chemicals and generate hazardous byproducts. The biosynthesis method utilizing plant extracts has emerged as a sustainable alternative, offering green and facile nanoparticle synthesis. Garlic, a widely available plant with numerous bioactive compounds, has shown potential as a reducing and stabilizing agent for nanoparticle synthesis (Ahmad & et al, 2019).The synthesis of ZnS NPs using garlic involves the extraction of bioactive compounds from garlic bulbs, followed by their reduction and stabilization during nanoparticle formation. The bioactive compounds, such as flavonoids and sulfur-containing compounds, act as reducing agents and capping ligands, facilitating the formation and stabilization of ZnS NPs. The reaction parameters, such as temperature, pH, and reaction time, are optimized to control the size and morphology of the synthesized nanoparticles (Sharma.S & et.al, 2018; Yadav & et. al, 2019).A few portrayal methods are utilized to guarantee the fruitful combination of ZnS NPs. These techniques include transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and UV-Vis spectroscopy. TEM provides information on nanoparticle size, shape, and distribution, while XRD determines their crystalline structure. FTIR and UV-visible spectroscopy offer insights into the functional groups and optical properties of the synthesized ZnS NPs, respectively (Ahmad & et al, 2019; Yadav & et. al, 2019).

There are numerous potential applications for the ZnS NPs mediated by garlic. They can be used as solar cells, photo detectors, and light-emitting diodes because of their distinctive optical properties. The photo catalytic movement of ZnS NPs empowers their application in water filtration and poison debasement. Besides, their biocompatibility makes them appropriate for biomedical applications, like medication conveyance and bio imaging (Suresh. S & et .al, 2020).

1.2 Statement of the problem

Zinc sulphide (ZnS) nanoparticles are described as semiconductor material with applications in optoelectronics, solar cells, sensors, photo catalysis, and biomedical applications(Xiao et al., 2017). However, the conventional methods of synthesizing ZnS nanoparticles often involve high temperatures, toxic chemicals, production of non-biodegradable byproducts, increased greenhouse gas emissions, and carbon footprint, which are dangerous to the environment, Eco toxicity of aquatic organisms, soil ecosystems, and overall ecosystem health (Karthik, Rajalakshmi, & Prakash, 2019; Zhang, Chen, Westerhoff, Crittenden, & Capco, 2019). Therefore, there is a need for developing a green and simple method of producing ZnS nanoparticles with desired properties.

Biosynthesis is a promising approach that uses biological agents such as plants, bacteria, fungi, or enzymes to synthesize nanoparticles in an eco-friendly and cost-effective way. Among various biological sources, garlic (Allium sativum) has been reported to have strong reducing and stabilizing abilities for metal ions due to its rich content of phytochemicals such as allicin, flavonoids, and polysaccharides(Pinto, Högger, & Bohm, 2019; Sharifi-Rad et al., 2020). However, there is limited research on the synthesis and characterization of ZnS nanoparticles from garlic using the biosynthesis method (Ahmad & et al, 2019; Karthik et al., 2019; Zhang et al., 2019). Therefore, this research aims at the alternative way of synthesizing ZnS nanoparticles from garlic extract using the biosynthesis method and to investigate their optical, structural, and morphological properties.

1.3 Objectives of the study

1.3.1 General objective

To synthesize zinc sulphide nanoparticles from garlic extract using the biosynthesis method.

1.3.2 Specific objectives

(i). to find the efficiency of onions and garlic in synthesis of ZnS nanoparticles

(II). to characterize ZnS nanoparticles synthesized from garlic and onion extracts

(III). to compare the functional groups of the zinc sulphide nanoparticles from onions and that from garlic.

1.4 Justification

The biosynthesis method is a green method for the synthesis of nanoparticles because it does not use hazardous chemicals. This makes it a more environmentally friendly option than traditional methods, such as chemical synthesis. Additionally, the use of garlic extract is a novel approach to the synthesis of ZnS nanoparticles because it has the potential to produce ZnS nanoparticles with unique properties and garlic can be easily obtained at a low cost making it an available material for nanoparticle synthesis.

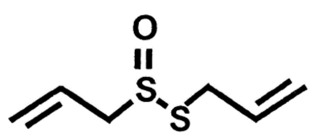
1.5 Literature review

Nanoparticles have attracted much attention due to their unique properties and potential applications in various fields. Green synthetic methods using natural resources have emerged as an environmentally friendly and sustainable approach to nanoparticle synthesis. Garlic (Allium sativum), a commonly available plant, has emerged as a promising bio-source for the synthesis of zinc sulfide (ZnS) nanoparticles.

Garlic and onions contains bioactive compounds such as allicin, diallyl sulfide (DAS), and S-allyl cysteine (SAC), which possess reducing and stabilizing properties that can promote the biosynthesis of ZnS nanoparticles (Gopinath, Kumaraguru, Bhakyaraj, & Nehru, 2012). Various studies have reported the successful biosynthesis of these ZnS nanoparticles using garlic extract as a reducing and capping agent (Xiao.Y., Qian, Zhang, Zhang, & Luo, 2017). The presence of sulfur-containing compounds in garlic extracts plays an important role in the formation of these ZnS nanoparticles by the reduction of zinc ions and subsequent nucleation and growth (Gopinath et al., 2012)

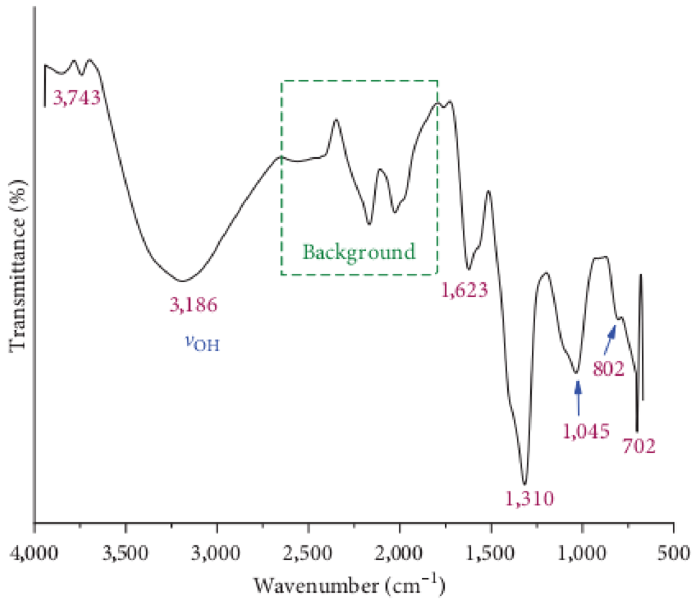
Characterization of ZnS nanoparticles is important for understanding their physicochemical properties and potential applications. Transmission electron microscopy (TEM) is commonly used to measure the size, shape, and morphology of nanoparticles. TEM analysis confirms the formation of spherical ZnS nanoparticles with an average size of 5–10 nm using garlic extract as a reducing agent. X-ray diffraction analysis (XRD) is used to characterize the crystalline nature and crystal structure of the synthesized nanoparticles. Fourier transform infrared spectroscopy (FTIR) provides information on the functional groups present on the nanoparticle surface and indicates the presence of bioactive compounds derived from garlic (Xiao.Y. et al., 2017). UV-visible spectroscopy is used to study optical properties such as absorption and bandgap energy of ZnS nanoparticles (Gopinath et al., 2012)

ZnS nanoparticles derived from garlic and onions biosynthesis show promising properties for various applications. Their unique size-dependent optical properties make them suitable for optoelectronic devices such as solar cells and light-emitting diodes (Xiao.Y. et al., 2017). ZnS nanoparticles have also shown potential for catalytic applications due to their large surface area and tunable reactivity Furthermore, the antimicrobial properties of garlic-derived nanoparticles make them attractive for biomedical applications such as drug delivery and antimicrobial coatings (Gopinath et al., 2012). Allicin is a sulfur containing compound found in garlic and onions that is responsible for its characteristic odor and taste. It is formed when the enzyme alliinase acts on the precursor molecule alliin which is found in garlic and onion cloves. Allicin contains two allyl groups as carbon chain, two sulfur atoms forming disulfide bonds including a thiol group. One of the sulfur atoms is a lone pair donor to an oxygen atom which therefore has a formal negative charge (Cavallito, Buck, & Suter, 1944). The structure of allicin is shown below which is a reducing and capping agent.



Allicin

In this research, garlic has been used and its nanoparticles formed have been characterized. The FTIR machine has been used to determine the functional groups present in the zinc sulphide nanoparticle obtained from garlic as shown below.



The FTIR machine used was limited to the range of 650 to 4000 cm^{-1} .in this range, indicated peaks where Identified. In this range, indicative peaks of the NPs, as well as the traced organics involved in the NPs production, can be identified. The broad band centered at about 3,186 cm−1 is characteristic of different hydroxyls (–OH, such as alcohols, phenols, and carboxylic acids) and amines (–NHn) functional groups. Peaks on the wavenumber (e.g., above 3,500 cm^{-1}) are commonly of nonhydrogen bonded OH, while broadness indicates contribution from carboxylic acids [24]. Peaks observed in the range of 1,800–2,600 cm−1 are instrument-based backgrounds. The absorption peak at 1,623 cm−1 can be attributed to C=C stretching bands associated with alkene and aromatic functional groups. The absorption band at 1,310 cm−1 coincides to C–C bond. Peak observed at 1,045 cm−1 may indicate vinyl of allicin (the principle component in garlic extract) and C–O bond. Bonds at 802 and 702 cm−1 could be assigned to C–O asymmetric stretching and ZnS bending bonds, respectively. As a result of the complex structure of capping agents sourced from the target plant, the peaks tend to broaden and combine with shoulders for different functional groups.

Onions and garlic which also belong to the Allium genus can however be used in the synthesis of zinc sulphide nanoparticles. In this research therefore, onions and garlic was used. The nanoparticles have been synthesized but they are not characterized so this research will aim at characterizing the ZnS nanoparticles obtained from onions and then comparing them to that formed from garlic. During nanoparticle formation, the color will change from white to brown due to nanoparticle formation.

CHAPTER TWO

EXPERIMENTAL

2.1 Materials

Deionized Water, Conical flask, centrifuging machine (model: OMEGA 6, power: 220V 50 Hz) Magnetic stirrer (DWB; MS7-H550-S), test tubes was all got from the university laboratory (Busitema university Nagongera campus laboratory).

Zinc precursor was obtained from zinc nitrate hex hydrate; Sulphur was obtained from source sodium sulphide**;** Characterization was done by use of the FTIR machine which was got from main campus of Busitema University. Fresh onions and garlic bulbs was obtained from Nagongera town council daily market in Torero and all measurements of was of analytical grade.

1.2 METHOD

2.2.1 Preparation of Onions and Garlic Extract.

Fresh onions and garlic cloves were collected from the Nagongera town council daily market, peeled and washed with water to ensure that they are clean and crushed well using a mortar and pestle. The sample was left to dry under direct sunshine and sieved to obtain a fine powder. 10g of onion was dissolved in 200 ml of deionized water differently and mixed with constant stirring for 60 minutes at 25^0C. The aqueous solution was then filtered and the filtrate was onion extract.

Likewise for garlic extract, fresh garlic gloves was collected from Nagongera town council daily market. The cloves was washed with water, peeled and crushed using mortar and pestle, dried in the oven for 24hours at 40^0C. The dried garlic was then sieved to obtain fine powder. 10g of the garlic powder was weighed, placed in the conical flask and 200ml of distilled water was added. The mixture was stirred constantly for 60 minutes at 25ºC. The mixture was then filtered and the filtrate obtain was garlic extract.

2.2.2 Synthesis of ZnS Nanoparticles

The stoichiometric (0.04 mole) solutions of zinc nitrate (12 g in 50 mL) and sodium sulphide (5.2g in 50 mL) will be prepared separately by dissolving the corresponding salt in the specified volume of deionized water with magnetic stirring for 30min. The two solutions will be mixed together and 60 mL of the freshly prepared onions extract will be added and then stirred at 25°C for 60 min. The obtained precipitate will be centrifuge at 4000 rpm for 10 minutes using a centrifuging machine , washed with deionized water, and dried at 25°C for 48 hr. The obtained powder will further be annealed at 100°C for 60 min. The resulting powder will be then collected carefully for characterization appropriately.

Zinc nitrate and sodium sulphide dissolve in water to form their respective ions

$$Zn(NO_3)_2 \longrightarrow Zn^{2+} + 2\,NO_3^-$$

$$Na_2S \longrightarrow 2\,Na^+ + S^{2-}$$

$$Zn^{2+} + S^{2-} \longrightarrow ZnS$$

The ZnS complex formed can then be stabilized by adding the garlic and onion extracts differently which contains substances like allicin which acts as stabilizing agent during nanoparticle formation and prevents agglomeration of the nanoparticles by providing the protective coating on the surface. Onion and garlic extract can act as a reducing agent facilitating the reduction of metal ion (Zn^{2+}) to their elemental form (Zn) (Alnehia, Al-Odayni, Al-Hammadi, Almaradhan, & Sharaf, 2023). During the formation of ZnS nanoparticles, the color changed from white to pale yellow for garlic and color change from brown to green for onion extract. This color changes showed that the nanoparticles have been formed.

2.2.3 Characterization of ZnS Nanoparticles using furrier transform infrared spectroscopy

Fourier Transform Infrared spectroscopy is a powerful machine for determining functional groups of compounds. To determine the functional groups, present in the zinc sulphide nanoparticles, the following shall be followed.

Sample preparation, ZnS nanoparticles will first be prepared in a suitable solvent such as chloroform. The sample will then be deposited onto an infrared-transparent substrate such as potassium bromide pellets. The FTIR machine is then set in the wave length of 650 to 4000 cm^{-1}. The instrument should be calibrated using a reference material to ensure accuracy. A background measure will be taken without a sample to account for any interference from the environment or substrate. ZnS nanoparticles sample will then be placed in the FTIR instrument and an infrared beam will be passed through it. The beam will interact with the sample and some of the infrared radiation will be absorbed by the functional groups present on the nanoparticle surface. The resulting absorption spectrum is obtained as a plot of absorbance (transmittance) against wave number or wave length. The results obtained was compared to the standard chart and then analyzed and discussed.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1. RESULTS

In this research, garlic and onions where employed in the synthesis of ZnS nanoparticles. 10g of garlic and onion powered was weighed independently. During nanoparticle formation, the color changed from white to pale yellow for garlic while that of from onions changed from brown to green. The synthesized nanoparticles where then kept under room temperature for 48hrs. After 48hrs of room temperature, they were heated at 100^0c for 60minutes. The solid obtained was then collected on the filter paper and then weighed. The mass of the nanoparticles from garlic was found to be 4g while that formed from onion was found to be 2g.

The FTIR machine was used to characterize the nanoparticles and the following results were obtained.

Figure 1: shows the spectrum of ZnS nanoparticles formed from garlic

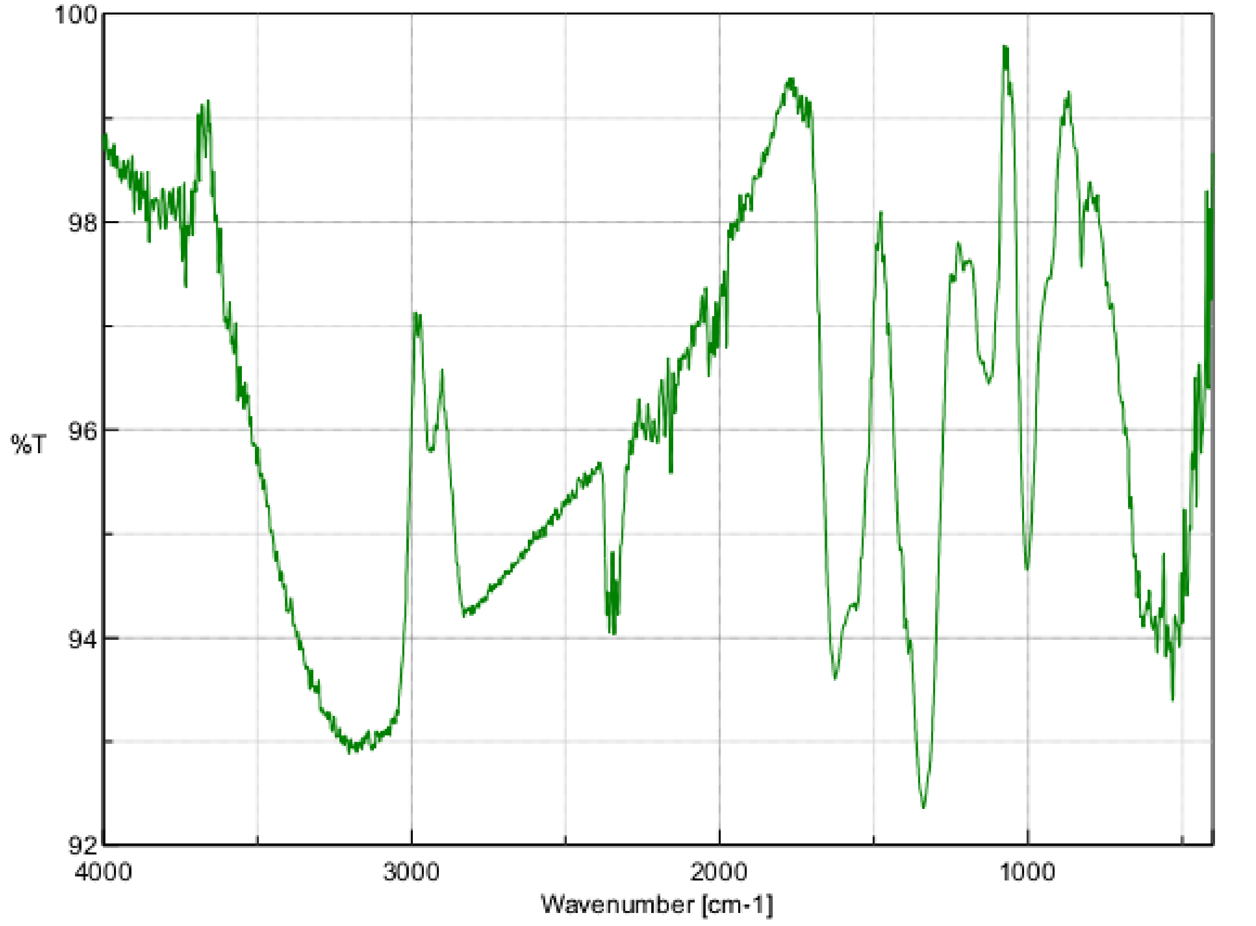
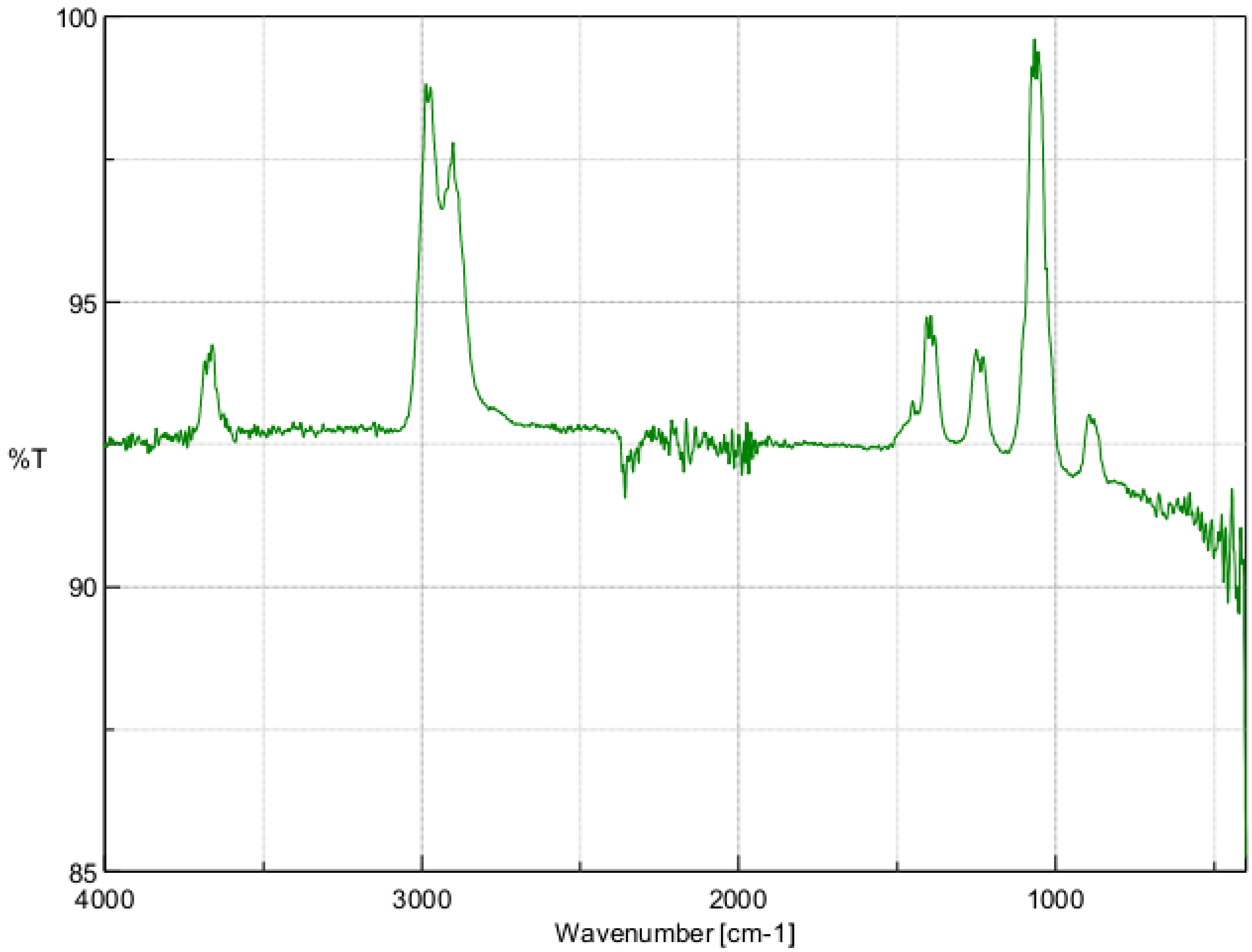


Figure 2: shows the FTIR spectrum of ZnS nanoparticles formed from onions



3.2. DISCUSSION OF RESULTS

From figure one

Has several peaks including a peak at approximately 3180cm^{-1} which signifies OH, a peak at approximately 3000cm^{-1} is as a result of sp3 C-H, a peak at approximately 1630 cm^{-1} is as a result of C=C double bond, a peak at approximately 1300cm^{-1} is a result of C-C, A peak at approximately 1000cm^{-1} is as a result of S=O bond and lastly a peak at 700cm^{-1} is as a result of zinc sulphide bending bond.

From figure two

Has several peaks including a peak just below 3000cm $^{-1}$ which is for sp3 C-H bond, a peak at approximately 1300cm-1 is for C-C , a peak at approximately 1050cm^{-1} is as result S=O and lastly a peak at approximately 812cm^{-1} indicates the ZnS bending bond.

However the following comparisons were made

- In both spectrums, there C-C bond at approximately 1300cm$^{-1.}$
- In both spectrum, there was a peak for s=o at approximately 1000cm-1 for garlic and at approximately 1050cm^{-1}
- There is a peak at approximately 3180cm^{-1} for garlic which signifies OH and for onions there was no OH.
- In both spectrums there is a peak which signifies the ZnS nanoparticle due to the bending bond. At approximately 700cm^{-1} for garlic and 812cm^{-1} for onions.
- In the spectrum of the nanoparticles formed from garlic there was C=C bond while that from onions didn't have the C=C bond
- In both spectrums there is a peak for sp3 C-H bond which is just below 3000cm^{-1}.

CHAPTER FOUR

CONCLUSION AND RECOMMENDATION

4.1 Conclusion

From the results obtained, it can be concluded that garlic has a high potential in ZnS nanoparticle synthesis compared to onions. This is because the mass after drying was found to be 2g more than that obtained from onions. Garlic also gave a high yield because it has a high levels of allicin which is used as a stabilizing agent compared to onion with low levels.

4.2 Recommendation

My first specific object was to find the efficiency of garlic and onions in the synthesis of ZnS nanoparticles. I therefore recommend garlic for the synthesis of ZnS nanoparticles.

I would also recommend other researchers to researchers to use other machines like scanning electron microscope for morphology and XRD for determining the crystalline nature of the nanoparticle.

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