ECO-FRIENDLY PREPARATION AND CHARACTERIZATION OF Cu NANOPARTICLES USING *Citrus limon* FRUITS EXTRACTS FOR POTENTIAL WATER AND WASTEWATER REMEDIATION.

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ABSTRACT

In light of the sustainable benefits of green synthesis, the synthesis and stabilization of Cu nanoparticles [Cu NPs] using extracts from *Citrus limon* fruits were reported in this research work. The prepared nanoparticles were characterized using Transmission Electron Microscopy [TEM], Scanning Electron Microscopy/Electron Dispersive X-ray [SEM/EDX] analysis, X-Ray Diffraction analysis [XRD], Bruanner-Emmett-Teller [BET], and Fourier-Transform Infrared Spectroscopy [FTIR] analysis. The TEM together with SEM micrograph shows the spherical shapes of the nanoparticles with the average size of ~11.30 nm. The SEM micrograph illustrates rough surface and presence of heterogeneous cavities that can enhance adsorption. The XRD results reveals Face-Centered Cubic [FCC] crystal structure of the nanoparticles and the peak positions matches the JCPDS [Joint Committee on Powder Diffraction Standards] card No. 04-0836. BET reported specific surface area of 47.3382 m^2/g, pore size of 3.174nm, and pore volume of 0.0215 cm^3/g. The FTIR reveals Cu-O stretch, suggesting the formation of the Cu NPs. The presence of the hydroxyl [OH] groups was evident in the FTIR spectrum of the nanoparticles, which is good for surface functionality. The obtained results shows the green synthesis is an efficient method for preparation of Cu NPs for potential water and wastewater remediation.

INTRODUCTION

As civilization advances, there is rapid expansion of urbanization and industrialization, which significantly contributes to pollution intensity due to higher emissions, increased waste production, and environmental degradation. Industrial effluent and urban run-off consistently contaminate the water bodies leading to a significant global threat due to the direct impact of access to sufficient clean water on human well-being and quality of life [7, 8, 12, 17, 19]. Industrial wastewaters in the developing countries, such as Nigeria, receive inadequate or in some cases, no treatment before discharge into waterways. This is partly due to the lack of stringent law as regards the discharge of such wastewater into the environment [3]. To mitigate

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the effects of water pollution, it is necessary to prioritize clean water, adopt sustainable practices, invest in remediation techniques, and promote environmental stewardship. There is need for accessible, inexpensive, and eco-friendly wastewater remediation methods that could be easily practiced by industries in developing countries [12, 17]. Water remediation is cogent to the Sustainable Development Goal 6 [SDG 6] and the Target 10 of Objective 7 of the Millennium Development Goals [MDGs] due to its effect on the availability of sufficient water supply and preventing environmental degradation, subsequently improving public health and the ecosystem [18].

Nanotechnology is an inexpensive and feasible method of harnessing the unique properties of nanoparticles for efficient environmental remediation of the water bodies [12, 24]. Nanoparticles are synthesized by both physical and chemical means, which leads to subsequent environmental degradation. Thus, the development of biological or green approach of synthesizing nanoparticles was researched into to avoid the environmental problems further caused by the physical and chemical approaches. This green approach involves the use of biological agents or agricultural materials such as plants, yeast, enzymes, bacteria, and fungi, and the process is observed to be economical, eco-friendly, and with minimal or no toxicity [2, 12]. In recent researches, plants are greatly utilized for production of phytochemicals necessary in nanotechnology for the maintenance of the water cycle, balancing the ecosystem, and especially synthesis of nanoparticles used for water remediation [2].

The copper nanoparticles [Cu NPs] have garnered substantial research interest owing to its unique properties such as the catalytic, mechanical, electrical, optical, and antibacterial properties [5, 21, 24]. In addition, Cu NPs are gaining attention because it is inexpensive, widely available, and possess extensive application range such as adsorption, photocatalytic degradation, and antimicrobial activity against various bacterial and fungal strain [5]. It has high surface area and large number of active sites that allows it to be used alone as photocatalysts without doping with any semiconducting metal oxide [21, 23]. Cu NPs were conventionally synthesized by methods like exploding wire method, metal vapours synthesis, vacuum vapour deposition, and microemulsion, which are difficult due to their low redox potential, prone to oxidation when exposed to air, high cost, pressure, radiation and toxic chemicals usage [24]. Recently, green synthesis method has become a viable approach which is simple to utilize, cost effective, eco-friendly, and with reduced raw materials and energy wastage [23, 24]. The synthesis method, good conditions, and physical properties of nanoparticles all influence the nanoparticle's photocatalytic ability. The copper nanoparticles size also differs due to the synthesis method, the influence of pH, reaction

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time, and concentration of the capping or reducing agent [21].

Citrus limon [lemon] fruit is an agricultural material that has been harnessed by several researcher for synthesis of nanoparticles such as Ag NPs [4], TiO_2 NPs [20], and Cu NPs [5]. In this study, Cu NPs were synthesized using *Citrus limon* juice extract and it was characterized by standard techniques.

MATERIALS AND METHODS

Preparation of Citrus limon fruit extract

The *Citrus limon* [lemon] fruits was bought from Sabo market, Ile-Ife, Osun State, Nigeria. The fruits were duly washed, diced, and heated in distilled water at 80 ºC for 10 min. The fruits were squeezed out of the mixture and the mixture was then filtered to obtain the aqueous extract, which was stored in a reagent bottle and kept in the refrigerator prior the experimental work [5].

Green synthesis of copper nanoparticles

On a magnetic stirrer, the prepared *Citrus limon* extract [200 mL] was added drop wisely to 400 mL of 0.01M copper sulfate pentahydrate [$CuSO_4 \cdot 5H_2O$] [2] at 50 ºC and it was stirred continuously for 4 hours. The successful fabrication of Cu NPs were signified by noticeable colour change from clear blue to cloudy green [Figure 1]. The obtained nanoparticles solution were centrifuged at 3000 rpm for 30 min. The prepared green synthesized Cu NPs was dried in an oven at 90ºC for 4 h following the modified methods of Amjad *et al*. [2] and Amer and Awwad [5].

Figure 1: pictorial illustration of the green synthesis of Cu NPs

Characterization methods

The TEM analysis was done by the Verios 460L of the JEM-ARM200F-G TEM. SEM-EDX imaging was done by Hitachi SU 3500 scanning microscope, Tokyo, Japan. The XRD analysiss was carried out by the Rigaku D/Max-lllC X-ray diffractometer, Tokyo, Japan. The FTIR

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identified the present functional group using a SHIMADZU Infrared spectrometer. The BET was done using a JWGB Surface Area Analyzer, model JW-DA:76502057en, Beijing, China.

RESULTS AND DISCUSSION

TEM Analysis of Cu NPs

The TEM micrograph of the Cu NPs is shown in Figure 2. TEM has higher resolution and better imaging of internal structures of nanoparticles compared to SEM analysis. Thus, the size and shape of the Cu NPs were more clearly analysed using the transmission electron microscopy technique. The Cu NPs was obsereved from the TEM analysis to be spherical in shape with average size of 11.30 nm similar to the white tea extract synthesized Cu NPs size of 10nm as reported by Huang *et al*., [14]. Similarly, related researches by Shende *et al*., [22] and Elisma *et al*. [11] also reported synthesis of small size Cu NPs using citron juice from Citrus medica Linn. and *Uncaria gambir* Roxb., respectively, as bio reducing agent and $CuSO_4$ as the precursor.

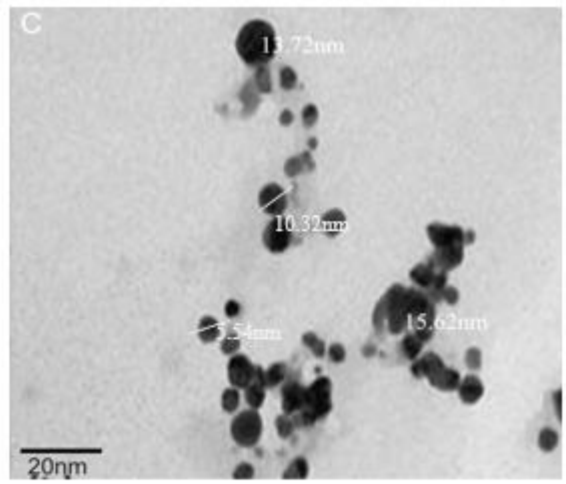

Figure 2: TEM Micrograph of Cu NPs

SEM/EDX Analysis of Cu NPs

The SEM micrograph of Cu NPs is presented in Figure 3b while the result of the EDX analysis is presented in Figure 3a. It was observed from the SEM analysis that the surface of the nanoparticles were filled with spherical shaped particles, with numerous pores and cavities, and some aggregated particles [2, 14]. The presence of multiple pores will enhance adsorption capabilities by facilitating the infiltration of adsorbate solution through the pores. The observed agglomeration of particles was owing to the exhibited polymeric nature of the nanoparticles [15]. The presence of the aggregated particles could also be due to the presence of water molecules in the reaction mixture of the synthesis process and the adsorbed active biomolecules from the lemon juice extract [9, 10, 13, 15].

The EDX analysis results [Figure 3a] illustrates high elemental Cu percentage which suggests successful production of the Cu NPs. The EDX spectrum also shows high percentage of elemental oxygen [24] that could originate from residual organic molecules from the *citrus limon,* ambient oxygen in the environment, and water adsorption leading to the presence of hydroxyl groups [-OH] on the nanoparticle surface that is revealed by the FTIR results [13]. The presence

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of minimal amount of other elements was also illustrated by the EDX spectrum owing to the presence of residual organic molecules from the precursor or from impurities during handling.

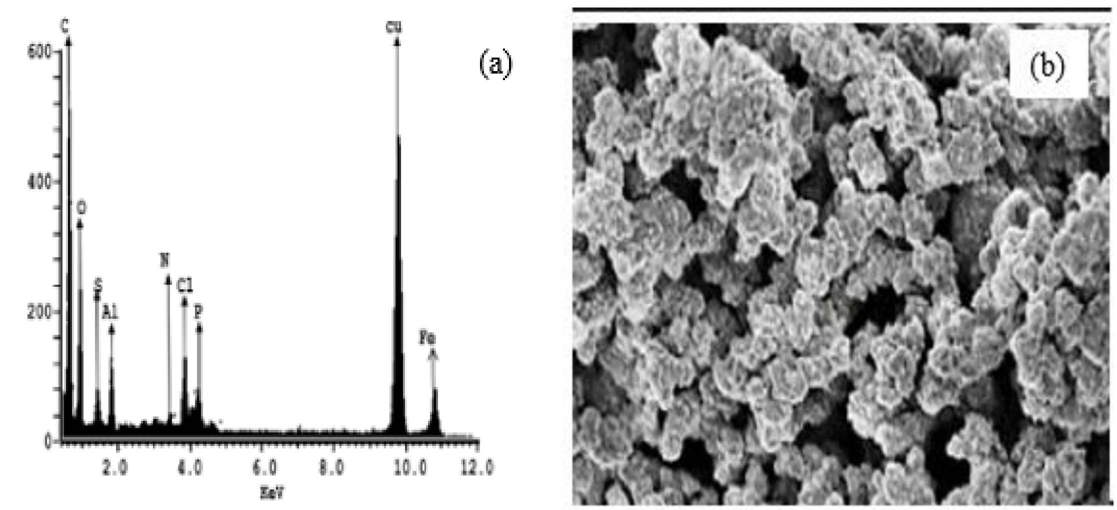

Figure 3: [a] SEM micrograph and [b] EDX spectrum of Cu NPs

XRD Analysis of Cu NPs

The results of the XRD analysis were presented in the XRD spectrum in Figure 4. The observed XRD diffraction peaks of synthesized Cu NPs at 2θ, are detected at 40.34°, 49.53°, 75.65°, and 92.54° corresponding to the plane of Miller indices [111], [200], [220], and [311], respectively.

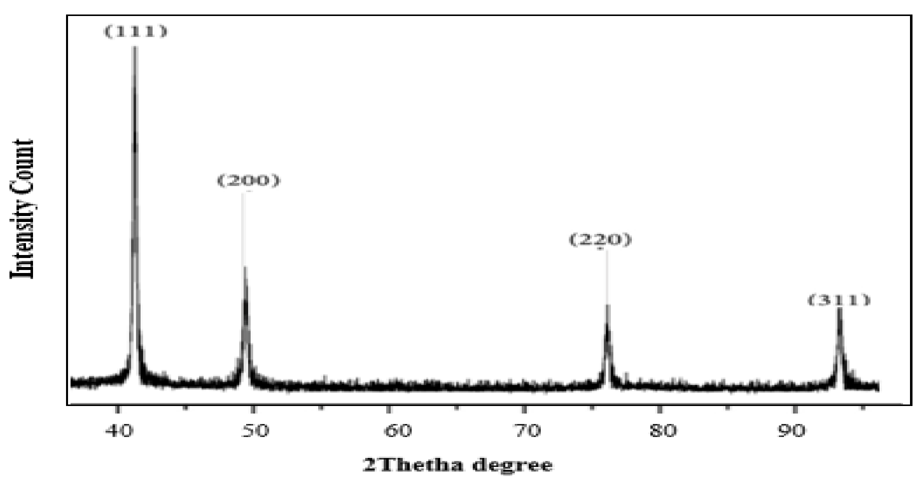

Figure 4: XRD spectrum of the Cu NP

The average crystallite size was noticed as 16.81 nm when subjected to the Debye Scherrer's equation. The observed XRD peaks in this study are consistent with existing literature

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on green synthesized Cu NPs and this is owing to the interaction between the plant extracts and Cu NPs [12, 14, 16, 22]. The presence of high intensity peaks in the planes of [111] and [200] suggests a Face-Centered Cubic [FCC] crystal structure and the peak positions matches the Joint Committee on Powder Diffraction Standards [JCPDS] card No. 04-0836 [9, 22].

FTIR Analysis of Cu NPs

The FTIR spectrum of the Cu NPs is shown in Figure 5 and it indicates broad peaks around 3375 cm^{-1} and 1427 cm^{-1}, which are attributed to the O-H stretching vibrations of the hydroxyl group and the C-H bending vibrations of the methyl group or the C-O stretch of the carboxylate ions, respectively. The presence of the hydroxyl group suggests surface functionality that could be due to adsorbed water molecules present on the surface of the nanoparticles and from the organic compounds in the *Citrus limon* extracts.

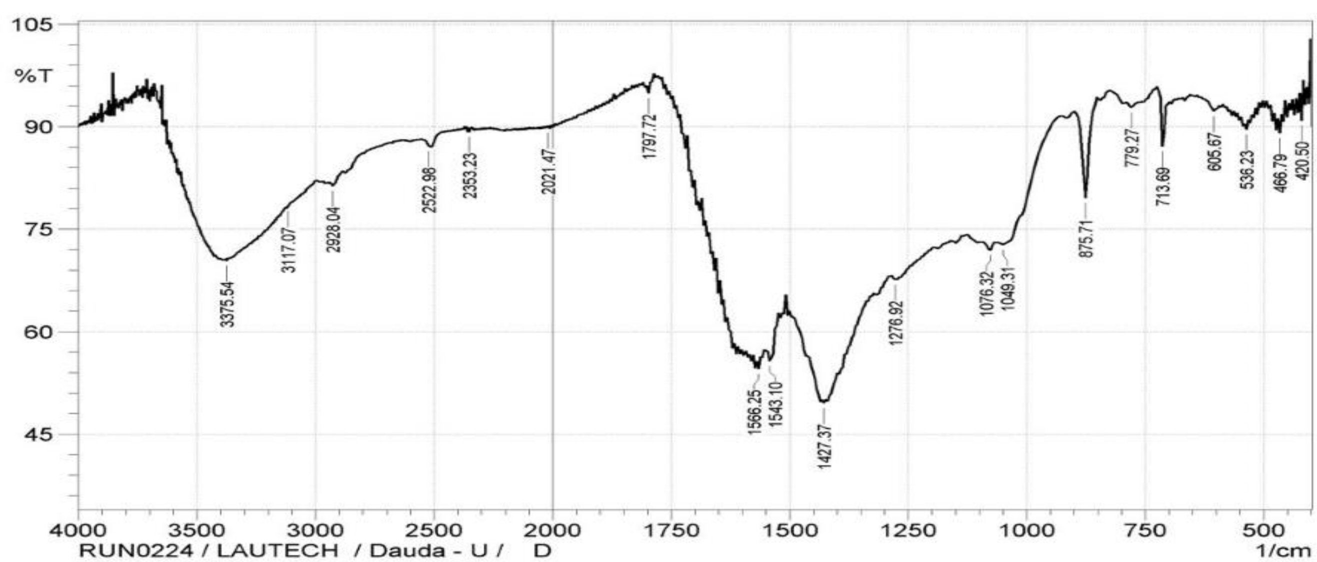

Figure 5: FTIR spectrum of Cu NPs

Peaks around 2928 cm^{-1} and 2853 cm^{-1} that are attributed to the C-H stretching vibrations from aliphatic groups were also identified. Presence of the aliphatic groups can originate from the alkaloids or other biomolecules in the lemon extracts used for the synthesis of the nanoparticles [1, 5]. The presence of the metal-oxygen peak [Cu-O] was also reported at 420.5 cm^{-1} confirming the formation of the Cu nanoparticles. Other peaks around 1797 cm^{-1}, 1630 – 1550 cm^{-1}, and peaks below 1500 cm^{-1} which corresponds to the C=O stretching vibration [carbonyl group], C=C stretching vibrations [aromatic rings or carboxylate ions], and peaks corresponding to C-O stretching vibrations [alcohols], respectively, were also revealed in the FTIR spectrum. All the observed

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peaks are linked to the organic content of the *Citrus limon* extracts used as the precursor in this study, confirming the ability of the extract to act as the capping and stabilizing agents of the Cu NPs. This is consistent with the research works by Akpanudo and Olabemiwo [1], Amer and Awwad *et al*., [5], and Neethu [6], Elisma *et al*., [11], Kumar *et al*., [16], and Wu *et al*., [24].

BET Analysis of Cu NPs

The BET analysis of the Cu NPs showed specific surface area of 47.3382 m^2/g, pore size of 3.174 nm, and pore volume of 0.0215 cm^3/g. The observed surface area of 47.3382 m^2/g suggests increased sorption capacity, high reactivity, and thus, enhanced catalytic performance of the Cu NPs. Its pore size is a mesoporous structure suitable for small to medium sized molecules. The small pore volume can be linked to small particle size identified by the TEM [5 – 15 nm] and the aggregated particles shown in the SEM micrograph. This observation could be attributed to the adsorbed active organic molecules present in the lemon extract [13, 14].

CONCLUSION

This study successfully synthesized Cu NPs from *Citrus limon* extracts and characterized the nanoparticle to ensure its credibility. The TEM analysis identified spherical shape which is consistent with the shape of Cu NPs in previous studies. The SEM analysis result revealed a rough surface with pores and cavities necessary for infiltration of adsorbate solution during adsorption. The EDX revealed presence of elemental Cu, confirming the formation of the nanoparticles and oxygen, necessary for surface functionalization. The XRD result also confirms the formation and crystalline structure of the nanoparticles. The FTIR spectrum presented functional groups that confirms the effectiveness of the *Citrus limon* extracts as a capping agents and also confirms the formation of the nanoparticles. The characterization results projects that the synthesized nanoparticles is a credible potential catalyst or adsorbent for water and wastewater remediation.

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