



Nanoporous carbon from waste egg shells modified with copper-nanoparticles – An Efficient material for removal of microbial contaminants from polluted water

Thompson Izuagie¹, Saifya A. Muazu¹ and Halilu A. Anka²

¹Department of Chemistry, Sokoto State University, Nigeria

²Department of Chemistry, Zamfara State College of Education, Maru, Nigeria

Corresponding email: tomvi2012@yahoo.com

Received on: October, 2022

Revised and Accepted on: November, 2022

Published on: December, 2022

ABSTRACT

The paper examines the efficiency of nanoporous carbon modified with copper nanoparticles (nC@CuNPs) for the removal of microbial contaminants from polluted waters. The modified material was prepared by wet impregnation of the unmodified carbon material in a solution of as-prepared Cu-nanoparticles. The materials were characterized by UV-Visible Spectroscopy, Fourier Transform-Infrared (FTIR) Spectroscopy, and Thermogravimetric Analysis. The materials were then investigated for their ability to remove copper and lead using Atomic Absorption Spectroscopy (AAS), methylene blue using Ultraviolet-Visible (UV-Vis) Spectroscopy and microbial contaminants from simulated polluted water. The results showed that in addition to retaining its heavy metals (Cu and Pb), and methylene blue removal capacity, the modified material, nC@CuNPs was efficient in removing microbial contaminants (*E. coli* and *Salmonella*) from the polluted water. The study provides an avenue for the provision of easy access to a range of such water purification materials to the increasing world population and contributes towards meeting the United Nations Sustainable Development Goals (UN SDGs).

Keywords: nanoporous carbon, copper nanoparticles, polluted water, microbial contaminants, egg shells

1.0 INTRODUCTION

Water treatment and purification remains a fundamental research area in sustainable chemistry. This is primarily because it aims to provide easy access to clean water to the increasing world populace, which is one of the United Nations Sustainable Development Goals (SDGs). Several materials have been studied and applied in the treatment and purification of waste or polluted water. These materials include adsorbents such as zeolites, chitosan, clay minerals and activated carbons (Yua & Han, 2015; Kozera-Sucharda et al., 2021).

The preparation of activated or nanoporous carbon from a wide range of sources and its utilization is several applications especially water treatment is well-known as it is considered one of the earliest and widely utilized water-purification adsorbents (Tadda et al, 2016; Li et al, 2020). Due to its high porosity and large surface area, it is widely applied for the removal of heavy metals and organics in waste water with great efficiency (Thomas & George, 2015; Mestre et al., 2019). Despite the wide use of activated carbon in for removing heavy meals

and organics, not much have been reported in terms of its application in treating microbial contaminants, which are also major contaminants in waste water.

Recently, it was reported that the immobilisation of antimicrobial polyoxometalate ionic liquid (POM-IL) on nanoporous carbon from coconut shell support improved its capacity for the removal of microbial contaminants from polluted water (Izuagie et al., 2022a). This inspired the idea whether modifying nanoporous carbon with other antimicrobial agents such as copper nanoparticles could improve its activity against microbes in polluted water. Nanoparticles have been reported for the treatment of polluted waters (Nassar et. al, 2014). Copper and copper oxide nanoparticles for instance are reported to have antimicrobial properties (Ekthammathat, 2013; Betancourt-Galindo et al., 2014 Verman & Bharadvaja, 2022). They have also been applied in controlling hematophagous parasites including larvae of *Anopheles subpictus Grassi*, *filariasis vector*, *Culex quinquefasciatus*, Say (*Diptera: Culicidae*), and the larvae of cattle tick

Rhipicephalus (Boophilus) microplus, (Ramyadevi et al, 2011).

Also, there are several reports on depositing Cu nanoparticles on carbon support for applications in catalytic reactions (Sharghi et al., 2009; Alonso et al., 2010; Alonso et al., 2011; Sharghi et. al, 2011; Alonso et. al, 2012; Alonso et al., 2013; Gawande et al., 2016). Hence, the current paper aims to examine the efficiency of nanoporous carbon modified with copper nanoparticles for removal of microbial contaminants in polluted water.

2.0 EXPERIMENTAL

2.1 General Procedures, Solvents, Reagents and Instrumentation

All reagents and solvents used in this study were procured from VWR, Fischer or Sigma Aldrich and were used without further purification. Double distilled water was used throughout the study. Fourier Transform Infrared (FTIR) spectra were recorded on a Bruker Alpha spectrometer fitted with a Platinum ATR module (4000 – 400 cm^{-1}). Spectra were recorded for solid samples after drying for at least 1 h. Ultraviolet-Visible (UV-Vis) analyses were done on a UV-1800 Shimadzu UV spectrophotometer using 1-cm quartz cells with a resolution of 1 nm between 200 and 800 nm. Thermogravimetric analysis (TGA) of nC@CuNPs (sample weight 11.957 g) was conducted using a NETZSCH TG 209F1 Libra instrument in pinholed aluminium crucibles at a heating rate of 10.0 $^{\circ}\text{C}/\text{min}$ between 25 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$ under N_2 purging (10 ml/min). Simulated polluted and filtered waters were analysed directly for heavy metals (Cu and Pb) using Atomic Absorption Spectroscopy (AAS) and for methylblue using UV-Vis.

2.2 Preparation of Nanoporous Carbon (nC) from Eggshells

Egg shells were collected from a local food seller in Sokoto, Nigeria. The shells were washed thoroughly with distilled water to remove dirt and oven-dried at 60 $^{\circ}\text{C}$ for 24 h. The dried eggshells were then crushed and sieved through a 150-micron mesh to obtain a fine powder of the sample which was stored in an air-tight container for further studies. Nanoporous carbon was prepared and characterized from the powdered egg shell sample as described previously in Izuagie et al. (2022b). Briefly, 33 vol % H_3PO_4 was mixed with the fine powder in the ratio of 30% (30 egg

shell per 100 mL solution) and the mixture stirred for 1 h and allowed to stand for 24 h for activation. The sample was then filtered from the excess acid and oven dried for 3 h before carbonation. Carbonation was done using a tube furnace in an atmosphere of N_2 . The furnace was heated to 500 $^{\circ}\text{C}$ at a rate 10 $^{\circ}\text{C}/\text{min}$ and the temperature was maintained at 500 $^{\circ}\text{C}$ for 3 h. After cooling to room temperature, the carbonized material was washed thoroughly with distilled water until the pH was about 7 and dried at 110 $^{\circ}\text{C}$ for 1 h before further studies.

2.3 Preparation of copper-nanoparticles (CuNPs)

The method of Khan (2016) was adapted in the preparation of Cu nanoparticles via reduction of copper (II) sulphate pentahydrate as precursor and using starch as capping agent. In the preparation, starch solution (1.2%, 120 mL) was transferred into a round bottom flask. 0.1 M copper (II) sulphate pentahydrate solution (19 mL) was added into the solution with vigorous stirring for 30 min. 50 mL of 0.2 M ascorbic acid solution was then added to solution under continuous rapid stirring. Subsequently, 30 mL of 1 M sodium hydroxide solution was slowly added to the prepared solution with constant stirring and heating at 80 $^{\circ}\text{C}$ for 2 h. The colour of the solution turned yellow to ochre. The ochre solution was analysed using UV-Visible spectroscopy for formation of Cu-nanoparticles and was used in the preparation of the modified nanoporous carbon material in 2.4.

2.4 Preparation of Nanoporous Carbon Modified with Copper Nanoparticles (nC@CuNPs)

The prepared nanoporous carbon in 2.2 was modified adapting the methods of Alonso et al. (2012) by impregnation with the ochre solution. The nanoporous carbon from egg shells, nC (3 g) was added in the ochre solution and allowed to stir vigorously for 24 h. The solution was allowed to settle overnight and the supernatant solution was then discarded cautiously. The material was isolated from the solution by filtration and washed three times with double distilled water and ethanol to remove any excessive starch bound with the nanoparticles. The dark brown solid with a loading of 4% was dried at room temperature and stored in a glass vial for further studies.

2.5 Water Filtration Experiment

The modified nanoporous carbon material (Nc@CuNPs) was tested for its efficiency to remove heavy metals (Cu and Pb) and methylene blue from polluted water. The water filtration experiment was as described elsewhere (Izuagie et al, 2022a). Briefly, the adsorbent phase was made using a Pasteur pipette, glass wool and the prepared adsorbent materials (nC and nC@CuNPs respectively). Small quantity of the wool was used to plug the pipette and the adsorbent material (0.6 g) was filled on top of the wool and tapped gently to optimize the packing of the adsorbent. Batches of simulated aqueous solution (10 mL) containing Pb (2.2 mM) or Cu (1.4 M), which is 45, 000 times the WHO permissible limit of the respective metals (Pb = 0.01 mg/L or 0.048 μ M and Cu = 2 mg/L or 32 μ M)²² or methylene blue (32 mM) were passed over separate adsorbent phases of NC and POM-IL@NC at a flow rate of ca. 4 mL min⁻¹.¹⁷ Adsorption of the respective pollutant was determined by measuring the concentration of the pollutant remaining in the filtered solution using AAS for Cu and Pb and UV-Visible spectroscopy for methylene blue.

2.6 Antibacterial Analysis

The antimicrobial activity of the samples (nC and nC@CuNPs) were determined against *Escherichia coli* and *Salmonella* (both Enteric bacteria) by measuring turbidity (absorbance) using UV-Visible Spectrophotometer as described in Akinduti (2019). The isolates of *E. coli* and *Salmonella* were obtained from the

Department of Microbiology, Faculty of Science, Sokoto State University, Sokoto. Their purities were confirmed using standard methods and the colonies from the subculture plates were suspended in 10 mL of Luria Bertani (LB) broth (Tryptone 10.0 g, Yeast extract 5.0 g, NaCl 10.0 g in 1000 mL distilled water) and incubated at 37 °C for 18–24 h in an orbital shaker at 150 rpm to attain logarithmic phase culture. Sterile Muller-Hinton Broth (MHB (g/L) (Beef infusion: 300; Casein hydrolysate 17.5; Starch: 1.5; pH 7.2±0.2) was prepared. The media was sterilized at 121 °C at 15 lbs for 15 min. For each bacteria species (*Escherichia coli* and *Salmonella*), 4 mL of prepared Mueller Hinton Broth (MHB) was dispensed into four sterilized test tubes. The standardized test materials (nC and nC@CuNPs) were added into two of the test tubes, Gentamycin was added to one as a positive control whereas the fourth contained only the broth. A loop full of the diluted bacteria cultures adjusted to a 0.5 McFarland turbidity (1×10⁸ CFU mL⁻¹) was then inoculated into all the test tubes. After a period of pre-incubation (15 min), the absorbance of each of the test tubes (samples, positive control and broth) were measured at zero hour (T₀) using a Lasany Advanced Microprocessor UV-Vis Spectrophotometer at 600 nm. The test tubes (samples, positive control and broth) were then incubated at 37°C for 24 h and the absorbance of the test tubes were again measured at 600 nm (T₂₄). The absorbance of each test tube which is proportional to the turbidity of the bacteria growth was noted while the rate of inhibition (%) was calculated using the formula:

$$\text{Inhibition rate (\%)} = 1 - \frac{T_{24_{\text{test}}} - T_{0_{\text{test}}}}{T_{24_{\text{broth}}} - T_{0_{\text{broth}}}} \times 100$$

Where:

T_{24_{test}} = Absorbance of test samples (mixture of MHB + sample + bacteria cells) at 24 hours

T_{0_{test}} = Absorbance of test samples (mixture of MHB + sample + bacteria cells) at 0 hour

T_{24_{broth}} = Absorbance of broth culture (mixture of MHB + bacteria cells) at 24 hours

T_{0_{broth}} = Absorbance of broth culture (mixture of MHB + bacteria cells) at 0 hours

For the positive control:

T_{24_{test}} = Absorbance of Gentamycin (mixture of MHB + gentamycin + bacteria cells) at 24 hours

T_{0_{test}} = Absorbance of gentamycin samples (mixture of MHB + gentamycin + bacteria cells) at 0 hour

2.7 Statistical Analysis

Analyses were performed in triplicates and results were expressed as mean ± SD. SPSS 19 was used to determine statistical significant difference (P>0.05) in parameters among groups using one-way ANOVA.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Cu-nanoparticles via UV-Visible Spectroscopy

The change in colour to ocher during the preparation of Cu-nanoparticles indicate the reduction of Cu²⁺ to zero-valent copper. The

formation of Cu-nanoparticles was confirmed by subjecting the ocher solution to UV-Visible analysis. The spectrum obtained is shown in Figure 1. The spectrum shows a peak around 570 nm which is attributed to the surface plasmon

band of nanoparticles. This is within the range 570 to 580 nm stated in Pan et al. (2020) and lies between 566 nm reported by Sierra-Ávila (2015) and 575 nm reported by Ramyadevi (2011) for Cu-nanoparticles.

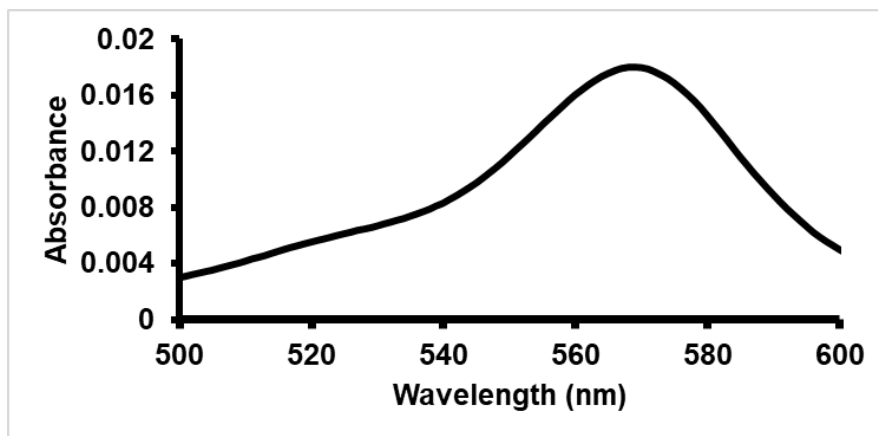


Figure 1: UV-Visible spectrum of Ocher solution of synthesized cu-nanoparticles.

3.2 Preparation of Cu-nanoparticles-modified nanoporous carbon (nC@CuNPs)

As described in Alonso et al. (2012), a preweighed amount of nanoporous carbon was modified by adding a given amount in the ocher solution and stirring it for 24 h to obtain a 4% loading dark brown solid, which was subjected to FT-IR and TGA analysis.

3.3 FT-IR Analysis of Materials

The prepared nanoporous carbon (nC) was stirred in the ocher solution of the Cu-nanoparticles to prepared the Cu-nanoparticles-modified nanoporous carbon (nC@CuNPs). After the

preparation, both nC and nC@CuNPs were subjected to FT-IR analysis in a bid to ascertain the groups present in the materials. The FT-IR spectra are shown in Figure 2. The spectrum for nC showed notable bands especially a broad peak around 1404 cm^{-1} associated to carbonate and Ca-O vibrations and peaks at 1074 , 924 and 874 cm^{-1} assigned to P-O group. The spectrum for the modified nanoporous carbon (nC@CuNPs) was similar to that of nC except for minor changes in the peaks position which was due to the presence of Cu-nanoparticles in the modified material. This is in line with the observation in Sierra-Ávila (2015).

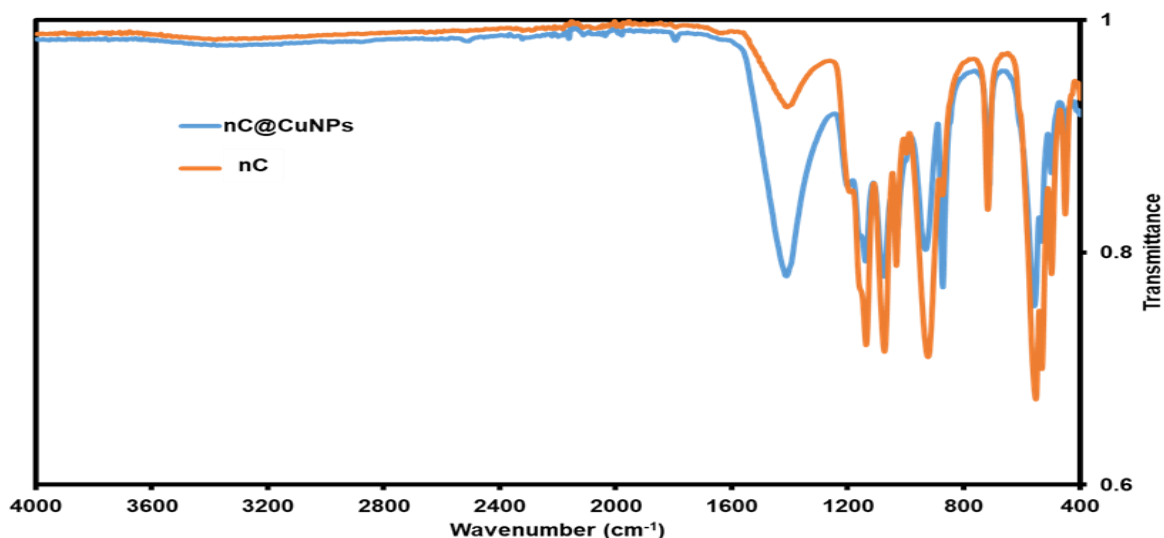


Figure 2: FT-IR spectra of nanoporous carbon and cu-nanoparticles modified nanoporous carbon.

3.3 Thermogravimetric Analysis of nC@CuNPs

The nC@CuNPs material was further subjected to TG analysis. The thermogram of nC@CuNPs shown in Figure 3 exhibits two major weight loss events: The first with an onset degradation temperature at about 300°C (about 24% loss) possibly due to devolatilization arising from degradation of some functional groups present and the second at around 780 to 800°C (about 7.79% loss). No weight loss was observed prior to these, indicating the anhydrous nature of the

material. Generally, a residual mass of 68.13% was obtained up to a temperature of 999.4°C indicating the material to be thermally stable. This is consistent with literature where fixed content of activated carbon of 67.60 to 75.61% and onset degradation temperature range of 225.45 to 295.99 °C were reported for different activated carbons from coconut shells (Sumaila et al., 2022).

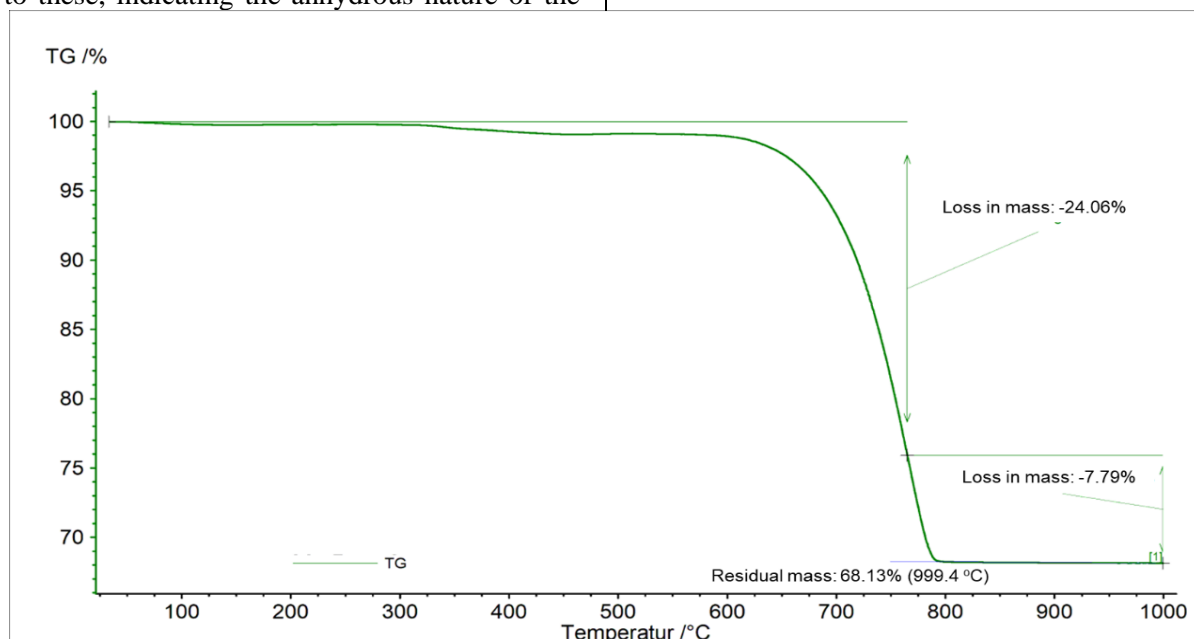


Figure 3: TGA thermogram of cu-nanoparticles modified nanoporous carbon.

3.4 Heavy Metals Removal Efficiency of Materials

The nanoporous carbon and modified materials were firstly tested for their ability to remove heavy metals (Cu and Pb) from polluted water and the results are shown in Figure 4. The results show that the modified material retained its

capacity for removal of heavy metal as over 99.9% of the heavy metals (Cu and Pb) were removed from the polluted water compared to the unmodified materials. The efficiency of activated carbon materials for heavy metals remediation is well-known (Gupta et al., 2015).

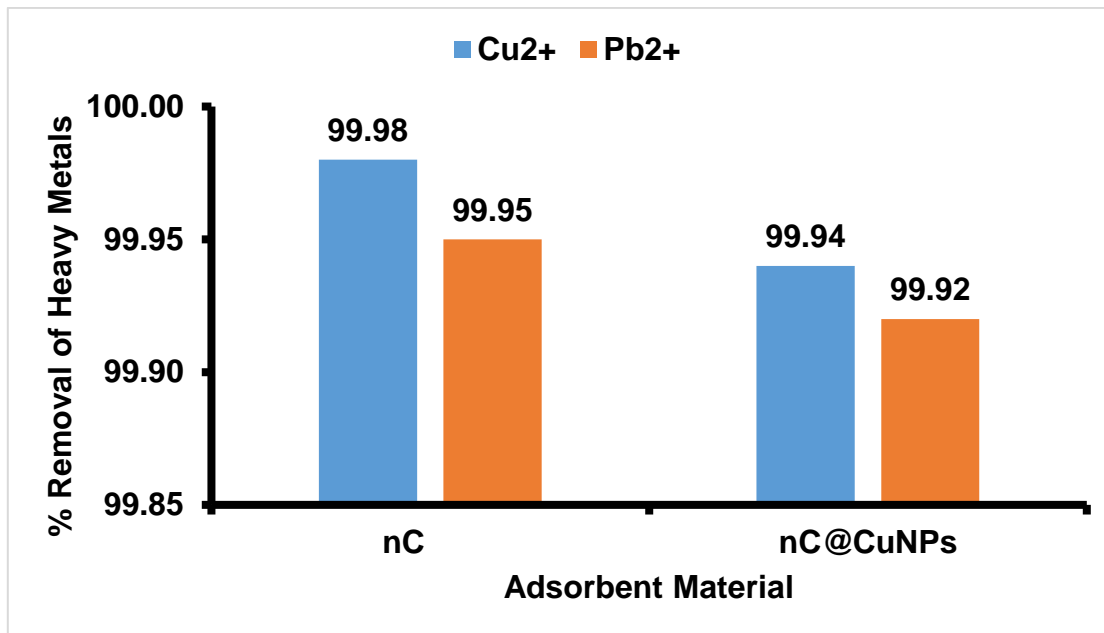


Figure 4: % Removal of Heavy metals by nC and nC@CuNPs.

3.5 Methylene Blue Removal Efficiency of Materials

The nanoporous carbon and modified materials were further analysed for their methylene blue removal ability and the results are shown in Figure 5. It can be observed that the contaminated solutions that passed through both nC and

nC@CuNPs materials show no UV-Visible absorption for methylene blue indicating that virtually all the contaminants had been removed by the adsorbents. Thus the results equally show that the modified again retained its capacity to remove methylene blue from polluted solution. This agrees with previous report (Izuagie et al, 2022a).

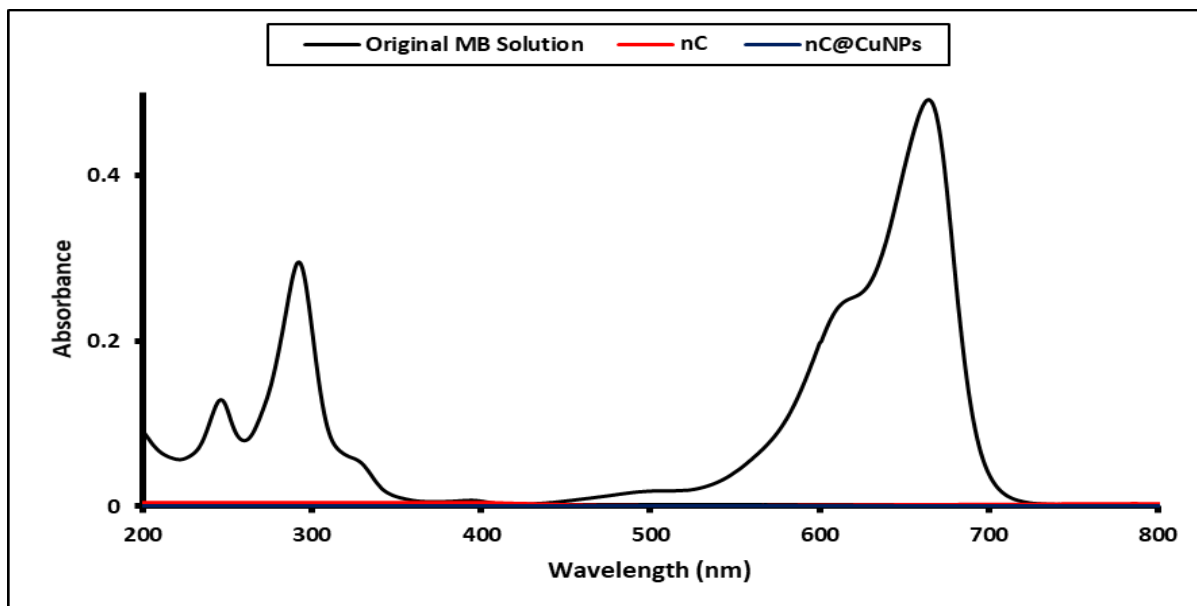


Figure 5: % Removal of methylene blue by nC and nC@CuNPs.

3.6 Antimicrobial Studies

In a bid to determine their ability for removal of microbial contaminants from waste water, the materials (nC and nC@CuNPs) were equally

subjected to antimicrobial studies against *E. coli* and *Salmonella*, which are both Enteric bacteria and are common in polluted water especially in developing countries. The results (see Table 1)

indicate that the modified material, nC@CuNPs exhibited significantly higher inhabitation rate on both organisms (*E. coli* and *Salmonella*) than the unmodified nanoporous carbon. This is attributed to the presence of the Cu-nanoparticles on the modified carbon materials. Copper nanoparticles

have been reported to show antimicrobial properties (Ekthammathat, 2013; Betancourt-Galindo et al., 2014 Verman & Bharadvaja, 2022). The activity of nC@CuNPs was however less than the control (Gentamycin).

Table 1: Antimicrobial Activity of nC and nC@CuNPs materials

	Inhibition Rate (%)	
	<i>E. coli</i>	<i>Salmonella</i>
Nc	2.10	1.75
nC@CuNPs	86.34	73.49
Gentamycin (Positive control)	91.20	89.45

4.0 CONCLUSION

This study has successfully prepared a copper nanoparticles-modified nanoporous carbon material (nC@CuNPs), which showed an improved ability as compared to the unmodified carbon material (nC), to remove microbial contaminants from waste water in addition to removing both heavy metals and organic dyes such as methylene blue. This improved ability of nC@CuNPs has been attributed to the presence of Cu-nanoparticles in the material. This result has great implication for the provision of clean water to the ever-increasing world population and contributes towards meeting the UN SDGs.

ACKNOWLEDGEMENTS

The authors are thankful to Mal. Muhammad Bello of Microbiology Laboratory, Sokoto State University, Sokoto for assisting with the antimicrobial studies.

REFERENCES

Akinduti, P. A., Motayo, B., Idowu, O. M., Isibor, P. O., Olasehinde, G. I., Obafemi, Y. D., Ugboko, H. U., Oyewale, J. O., Oluwadun, A. & Adeyemi, G. A. (2019). Suitability of spectrophotometric assay for determination of honey microbial inhibition, IOP Conference Series: Journal of Physics, 1299, 012131. doi:10.1088/1742-6596/1299/1/012131

Alonso, F., Moglie, Y., Radivoy, G. & Yus, M. (2011). Multicomponent click synthesis of 1,2,3-triazoles from epoxides in water catalyzed by copper nanoparticles on activated carbons. The Journal of Organic Chemistry, 76, 8394–8405. <https://doi.org/10.1021/jo2016339>.

Alonso, F., Moglie, Y., Radivoy, G. & Yus, M. (2010). Multicomponent synthesis of 1,2,3-triazoles in water catalyzed by copper

nanoparticles on activated carbon. Advanced Synthesis & Catalysis, 352, 3208–3214. <https://doi.org/10.1002/adsc.201000637>

Alonso, F., Moglie, Y., Radivoy, G. & Yus, M. (2012). Multicomponent click synthesis of potentially biologically active triazoles catalyzed by copper nanoparticles on activated carbon in water. Heterocycles, 84, 1033–1044. DOI: 10.3987/COM-11-S(P)81.

Alonso, F., Moglie, Y., Radivoy, G. & Yus, M. (2013). Alkenes as azido precursors for the one-pot synthesis of 1,2,3-triazoles catalyzed by copper nanoparticles on activated carbon. The Journal of Organic Chemistry, 78, 5031–5037. <https://doi.org/10.1021/jo400110m>.

Betancourt-Galindo, R., Reyes-Rodriguez, P. Y., PuenteUrbina, B. A., Avila-Orta, C. A., Rodríguez-Fernández, O. S., Cadenas-Pliego, G., Lira-Saldivar, R. H. & García-Cerda, L. A. (2014). Synthesis of copper nanoparticles by thermal decomposition and their antimicrobial properties. Journal of Nanomaterials, 2014, 1–5. <https://doi.org/10.1155/2014/980545>.

Ekthammathat, N., Thongtem, T. & Thongtem, S. (2013). Antimicrobial activities of CuO films deposited on Cu foils by solution chemistry. Applied Surface Science, 277, 211–217. <https://doi.org/10.1016/j.apsusc.2013.04.027>.

Gawande, M. B., Goswami, A., Felpin, F. X., Asefa, T., Huang, X., Silva, R., Zou, X., Zboril, R., & Varma, R. S. (2016). Cu and Cu-based nanoparticles: synthesis and applications in catalysis. Chemical Reviews, 116, 3722–3811. DOI: 10.1021/acs.chemrev.5b00482.

Gupta, V. K., Nayak, A., Bhushan, B. & Agarwal, S. (2015). A critical analysis on the efficiency of activated carbons from low-cost precursors for heavy metals remediation. Critical Reviews in Environmental Science and Technology,

- 45:613–668. DOI: 10.1080/10643389.2013.876526.
- Izuagie, T., Mira, A. & Streb, C. (2022b, November, 10-11). Nanoporous carbon from waste sources as support for polyoxometalates-ionic liquid hybrid materials for waste water treatment [Poster presentation]. Chemical Science Symposium 2022, London, United Kingdom.
- Izuagie, T., Sirajo, M. & Abubakar, M. G. (2022a). Immobilization of polyoxometalates-ionic liquid on coconut shell nanoporous carbon support: an improved material for water purification. *Caliphate Journal of Science and Technology*, 2, 213-220. <https://dx.doi.org/10.4314/cajost.v4i2.11>.
- Khan, A., Rashid, A., Younas, R. & Chong, R. (2016). A chemical reduction approach to the synthesis of copper nanoparticles. *International Nano Letters*, 6, 21–26. <https://doi.org/10.1007/s40089-015-0163-6>.
- Kozera-Sucharda, B., Gworek, B., Kondzielski, I. & Chojnicki, J. (2021). The comparison of the efficacy of natural and synthetic aluminosilicates, including zeolites, in concurrent elimination of lead and copper from multi-component aqueous solutions. *Processes*, 9(5), 812. <https://doi.org/10.3390/pr9050812>.
- Li, B., Xiong, H. & Xiao, Y. (2020). Progress on synthesis and applications of porous carbon materials. *International Journal of Electrochemical Science*, 15, 1363 – 1377. doi: 10.20964/2020.02.04
- Mestre, A. S. & Carvalho, A. P. (2017). Nanoporous carbon synthesis: an old story with exciting new chapters. In T. H. Ghrib (Ed.), *Porosity - Process, Technologies and Applications*. IntechOpen: London. <http://dx.doi.org/10.5772/intechopen.72476>.
- Nassar, N. N., Arar, L. A., Marei, N. N., Ghanin, M. M. A., Dwekat, M. S. & Sawalha, S. H. (2014). Treatment of olive mill based wastewater by means of magnetic nanoparticles: Decolourization, dephenolization and COD removal. *Environmental Nanotechnology, Monitoring & Management* 1, 14-23. <https://doi.org/10.1016/j.enmm.2014.09.001>.
- Pan, Y., Chu, L., Liu, J., Lv, B., Belfiore, L. A. & Tang, J. (2020). Precise control of copper-localized surface plasmon resonance in the near infrared region for enhancement of up-conversion luminescence. *Metals*, 10(5), 628; <https://doi.org/10.3390/met10050628>.
- Ramyadevi, J., Jeyasubramanian, K., Marikani, A., Rajakumar, G., Abdul Rahuman, A., Santhoshkumar, T., Kirthi, A. V., Jayaseelan, C. & Marimuth, S. (2011). Copper nanoparticles synthesized by polyol process used to control hematophagous parasites. *Parasitology Research*, 109:1403–1415. DOI 10.1007/s00436-011-2387-3.
- Saleem, J., Shahid, U. B., Hijab, M., Mackey, H. & McKay, G. (2019). Production and applications of activated carbons as adsorbents from olive stones. *Biomass Conversion and Biorefinery*, 9, 775–802. <https://doi.org/10.1007/s13399-019-00473-7>.
- Sharghi, H., Khalifeh, R. & Doroodmand, M. M. (2009). Copper nanoparticles on charcoal for multicomponent catalytic synthesis of 1,2,3-triazole derivatives from benzyl halides or alkyl halides, terminal alkynes and sodium azide in water as a "green" solvent. *Advanced Synthesis & Catalysis*, 351, 207–218. <https://doi.org/10.1002/adsc.200800612>.
- Sharghi, H., Khalifeh, R., Mansouri, S. G., Aberi, M. & Eskandari, M. M. (2011). Simple, efficient, and applicable route for synthesis of 2-aryl(heteroaryl)-benzimidazoles at room temperature using copper nanoparticles on activated carbon as a reusable heterogeneous catalyst. *Catalysis Letters*, 141, 1845–1850. <https://doi.org/10.1007/s10562-011-0671-6>.
- Sierra-Ávila, R., Pérez-Alvarez, M., Cadenas-Pliego, G., Padilla, V. C., Ávila-Orta, C., Camacho, O. P., Jiménez-Regalado, E., Hernández-Hernández, E. & Jiménez-Barrera, R. M. (2015). Synthesis of copper nanoparticles using mixture of allylamine and polyallylamine. *Journal of Nanomaterials*, 2015, 1-9. <http://dx.doi.org/10.1155/2015/367341>.
- Sumaila, A., Sumaila, A. O., Usman, A. O., Abdullahi, A. S. & Abdullahi, Z. (2022). Thermal degradation and particle size distribution studies of activated carbon obtained from coconut shells. *Journal of Materials and Environmental Science*, 12(07), 739-746. <http://www.jmaterenvironsci.com/>
- Tadda, M. A., Ahsan, A., Shitu, A., ElSergany, M., Arunkumar, T., Jose, B., Abdur Razzaque, M. & Nik Daud, N.N. (2016). A review on activated carbon: process, application and prospects. *Journal of Advanced Civil Engineering Practice and Research*, 2(1):7-13. www.ababilpub.com/jacepr.

- Thomas, B. N. & George, S. C. (2015). Production of activated carbon from natural sources. *Trends in Green Chemistry*, 1, 1-5. [10.21767/2471-9889.100007](https://doi.org/10.21767/2471-9889.100007).
- Verma, A., & Bharadvaja, N. (2022). Plant-mediated synthesis and characterization of silver and copper oxide nanoparticles: antibacterial and heavy metal removal activity. *Journal of Cluster Science*, 33:1697–1712 <https://doi.org/10.1007/s10876-021-02091-8>.
- Yua, C & Han, X. (2015). Adsorbent material used in water treatment - a review. In M. Yao & H. Liang (Eds.), *Advances in computer science research - Proceedings of the 2015 2nd International Workshop on Materials Engineering and Computer Sciences (IWMECS 2015)* (pp. 286-289). Atlantis Press, <https://doi.org/10.2991/iwmecs-15.2015.55>.