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Fabrication of Copper Nano-Filter Membrane and its use in the Purification of Contaminated Water

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ABSTRACT

Copper nanoparticles were synthesised by the green method using African spinach and peppermint leaves extract as both reducing and capping agents. The synthesized nanoparticles were then characterized by Energy Dispersive Spectroscopy, (EDS), Scanning Electron Microscopy (SEM) and Fourier Transform Infra-Red Spectroscopy (FTIR). EDS confirmed the formation of copper nanoparticles and SEM images showed spherical nanoparticles with an average size of 3.44 µm. FTIR showed that the functional groups on the leaves' extracts were capped on the surface of the nanoparticles. The nanoparticles were then casted into a nano-filter membrane using cellulose actetate and used to filter contaminated water gotten from a canal at the University of Lagos. The filtration efficiency of this nano-filter was compared with the ordinary cellulose acetate membrane and the result showed that the copper nano-filter membrane gave an odourless, cleaner water than that of ordinary cellulose acetate membrane. The microbial analysis also revealed that about 96.5 % of the bacteria was removed using the copper nano-filter membrane.

Keywords: Green synthesis, Copper nanoparticles, Waste water purification, Nano-filter membrane, Antimicrobial

1.0. Introduction

Globally, there is a general problem of water pollution. Most of our water bodies are polluted and are not fit for usage. As a result, a lot of water treatment methods have been developed. However, most of these methods are very expensive, not easily available and some of them are not as efficient. Therefore, there is need to provide easy, cost friendly and environmental benign method of treating our water. This can be achieved with the use of copper nanoparticles.

Copper nano particles possess unique characteristics which include catalytic (Judai *et al*., 2011), high electrical conductivity (Din and Rehan 2017), magnetic (Ghasemi *et al*., 2011) optical (Wu *et al*., 2010) and antibacterial/antifungal activities (Ramyadevi *et al*., 2012, Zain *et al*., 2014). The antimicrobial activity has led to numerous applications such as in cosmetics, food processing (Pal, 2017) drug delivery (Varshney *et al*., 2012, Kailasa *et al*., 2018) sensors (Ghotto *et al*., 2019) and in water treatment (Chen *et al*., 2014). In comparison with precious metals, such as gold, silver, or platinum, copper has the advantage of being in high abundance and it is cheap. The property of copper nanoparticles mainly depends on the synthesis route and their reaction parameters. Various synthetic routes have been employed for the synthesis of copper nanoparticles including chemical reduction (Dong *et al*., 2018, Gajera, 2014), electrochemical (Fernandez *et al*., 2017), hydrothermal (Seku *et al*., 2018), microwave assisted techniques (Galletti *et al*., 2013) and biological synthesis (Kulkarni and Kulkarni, 2013).

These days, the emphasis has been shifted towards the green synthesis of Cu-NPs by using plant extracts as stabilizers and reducing agents (Subbaiya and Selvam, 2015). This will eliminate the use of toxic chemicals and so promote environmental friendliness. In this research, copper nanoparticles were prepared using the green synthesis method. The copper nanoparticles were synthesized from copper sulphate solution with African spinach and peppermint leaves extract as capping/reducing agents under nitrogen to prevent oxidation of the copper nanoparticles. The synthesized nanoparticles were then characterized by Energy Dispersive Spectroscopy (EDS), Scanning Electron Microscopy (SEM) and Fourier Transform Infra-Red Spectroscopy (FTIR). The synthesized copper nanoparticles were made into a nano-filter membrane filter using cellulose acetate as support. The nano copper filter membrane was then tested by using it to filter water collected from a canal in the University of Lagos. The efficiency of this nano-filter membrane was compared with the ordinary cellulose acetate membrane by studying the extent to which they can successfully treat colour, odour and micro - organisms.

2.0. Methodology

2.1. Preparation of spinach and peppermint leaves extract

Fresh African Spinach and peppermint leaves were bought from a local market in Lagos. The leaves were washed several times with distilled water and were air dried for a few days. Then the leaves were ground to a fine powder and kept separately in different air-tight containers. 5 g of spinach or peppermint powder was weighed and transferred to a beaker. 50 ml of distilled water was measured and transferred to the beaker. It was placed on a hot plate and allowed to boil for 15 minutes. After boiling, it was allowed to cool and filtered using a filter paper. The filtrate was kept in a bottle and kept refrigerated until needed (Abdulwahab *et al*., 2019).

2.2 Preparation of precursor solutions

Copper sulphate pentahydrate salt was weighed (0.50 g, 0.04 M) and dissolved in 10 ml distilled water in a beaker. The resulting mixture was transferred into a 50 ml standard flask and distilled water was added up to the mark. 5 g of ascorbic acid was dissolved in 50 ml dissolved water. It was stirred until a clear solution was obtained.

2.3 Green synthesis of copper nanoparticles with peppermint and spinach extracts

50 ml of the copper sulphate pentahydrate solution was measured into a three-necked round bottom flask. Then 50 ml ascorbic acid was added to the copper sulphate solution followed by 25 ml of the extracts (peppermint and spinach). The resulting mixture was heated on a hot plate for 1 hour with rapid stirring at 80 °C using a magnetic stirrer under nitrogen atmosphere (Abdulwahab *et al*., 2019).

On the addition of ascorbic acid, the colour changes from blue to light green. The green solution now turned reddish brown after adding the extracts indicating the formation of copper nanoparticles. The brown solution was then centrifuged, washed with distilled water and left to dry completely.

2.4 Casting of cellulose acetate membrane

The casting of cellulose acetate membrane was carried out following procedure in literature but with modifications (Kaiser *et al*., 2017). 5 g of cellulose acetate was weighed into a conical flask and 75 ml of acetone was added and stirred using a magnetic stirrer for 1 hour. After 1 hour, 3 g (0.05 mole) of sodium chloride and 3 ml of glycerol were added to the mixture and was left to stir for 30 minutes. The resulting polymer was casted onto the glass plate and left to dry. The dried glass plate containing the membrane was put into a tray of distilled water for 10 minutes to etch out the sodium chloride so that pores can form on the membrane to enable filtering.

2.5 Casting of copper nano-filter membrane

0.1 g of copper nanoparticles was dissolved in 3 ml of dimethyl sulphoxide and then added to the already made polymer solution and was stirred for 30 minutes. The functionalized polymer mixture was the casted onto a glass plate and left to dry. The copper nano-filter membrane was then put in a tray of distilled water for 10 minutes to etch out the sodium chloride and create pores in the nano-filter cellulose acetate membrane to enable it filter.

The ordinary cellulose membrane and the copper nano-filter membrane were then used to filter contaminated water from a canal by passing a 100 ml of the water each through the ordinary membrane and the copper nano-filter membrane.

2.6 Microbiological analysis of water

The microbial activity was determined using the pouring plate counting method. The media used for the bacteriological analysis of water include plate count agar (PCA), nutrient agar (NA), potato dextrose agar (PDA) and eosin methylene blue agar (EMB). All the media used were weighed out and prepared according to the manufacture's specification, with respect to the given instructions and directions. The microbes present in the sample were determined by plating out 0.1ml of 10^{-1} dilution series of water sample on the nutrient agars. Duplicates were made and incubated aerobically at 37 ºC for 24 hours (nutrient agar plates) while the potato agar plates were incubated at room temperature for 3 – 5 days. The thermo-tolerant bacteria were incubated at 44 ºC (Bartram and Pedley 1996). The pure cultures of the isolates were subjected to various morphological and biochemical characterization tests to determine the identity of the isolates with reference to Bergey's Manual of Determinative Bacteriology (Buchanan and Gibbons, 1974).

3.0. Results and Discussion

3.1 Characterization of copper nanoparticles

After copper nanoparticles have been successfully synthesized from African spinach and peppermint leaf extracts, the brown coloured powder obtained was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The EDS and FTIR results are similar to what was obtained in an earlier study by the authors (Abdulwahab *et al*., 2019) on copper nanoparticles using the same procedure.

3.2 Fourier Transform Infrared Spectroscopy

The peak at 3321 cm^{-1} is attributed to OH stretching. This peak became broadened and there is a shift in the IR spectrum of nanoparticles capped with extract indicating that there is adsorption of OH bond on the surface of the nanoparticles (Figure 1). The C=O stretching peak (1637) found in the extract disappeared in the synthesized nanoparticles capped with extract suggesting that oxidation must have taken place, hence confirming the use of the extracts as reducing agent.

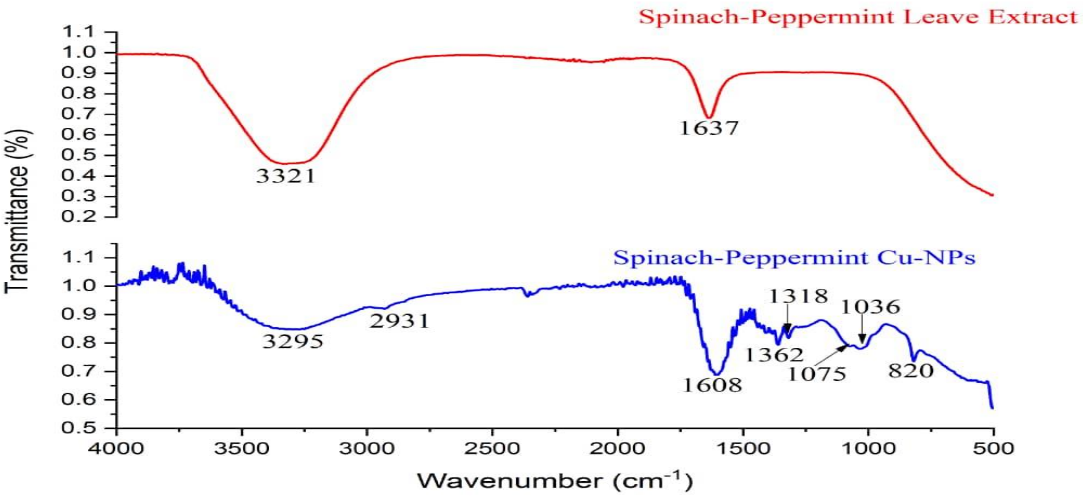

Figure 1: FTIR spectra of spinach-peppermint leave extracts (top) and spinach-peppermint capped Cu-NPs (bottom)

3.3 Energy dispersive spectroscopy (EDS)

The EDS result of the copper nanoparticles for the peppermint and spinach leaves was done. The result showed 55% of copper (Figure 2). The presence of oxygen showed it has undergone some form of oxidation. The carbon can be attributed to the organic compounds present in the peppermint and spinach leaf extracts which is confirmed by the FTIR result in Figure 1. In comparison with similar method reported earlier by Aher *et al.* (2019), they got 39.16 % of copper. This shows that the leaf extracts used in this study were better at reducing the copper ions and stabilizing them.

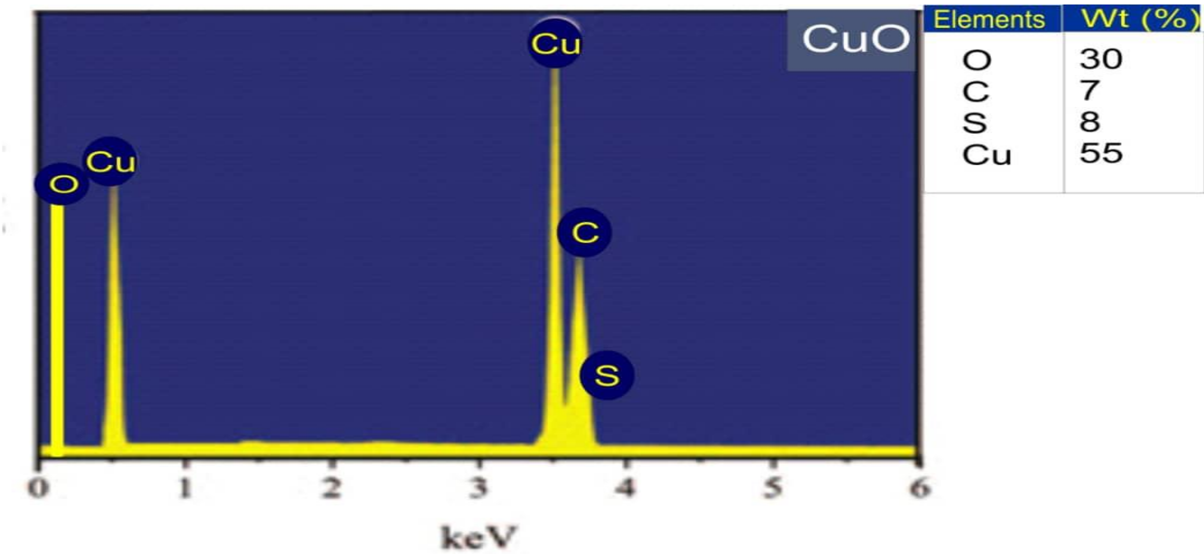

Figure 2: EDX spectrum of copper nanoparticles capped with spinach and peppermint leaves extracts

3.4 Scanning electron microscopy (SEM)

The SEM images are shown in Figure 3. The copper nanoparticles are spherical in shape and are evenly distributed with an average size of about 3.44 µm.

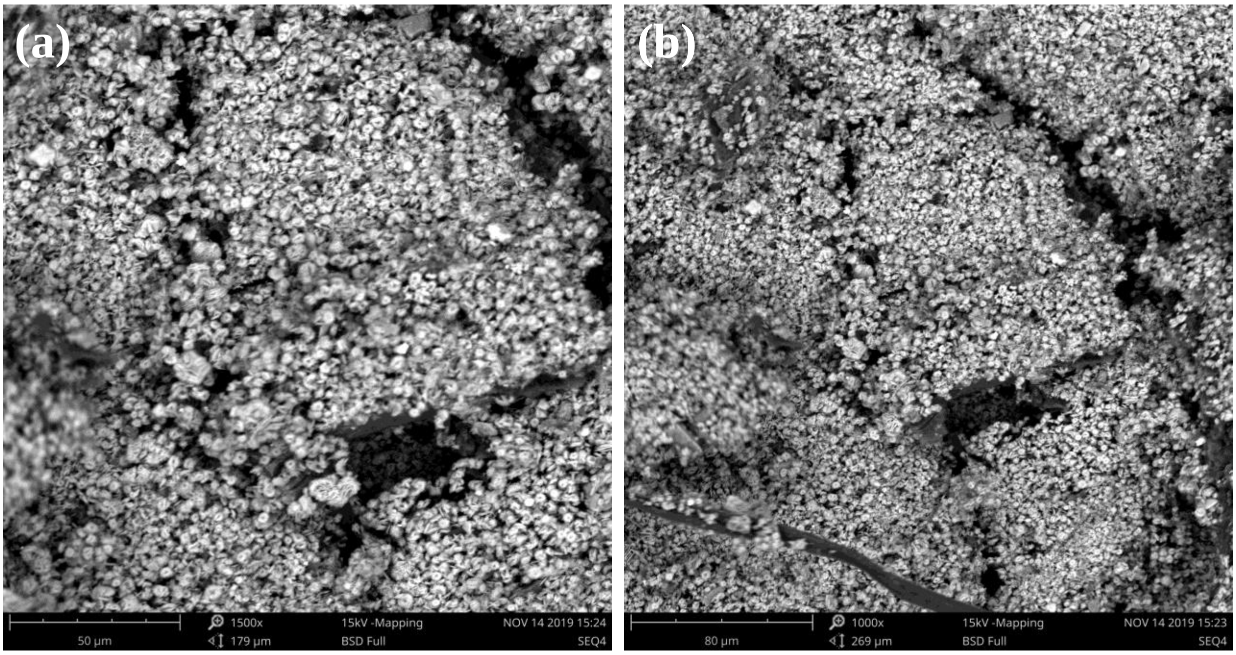

Figure 3: SEM images of copper nanoparticles at different magnifications (a) at 50 µm and (b) 80 µm

3.5 Comparison of the efficiency of ordinary cellulose acetate membrane with nano-filter membrane in the treatment of dirty canal water

Contaminated water was collected from a canal on campus and purified to study the efficiency of nano-filter membrane in the removal of colour, odour and micro-organisms. The filtrate collected using copper nano-filter membrane was clean, odourless and colourless while the filtrate collected using ordinary cellulose acetate membrane still had odour and was not as clean as that obtained from the nano -filter (Figure 4).

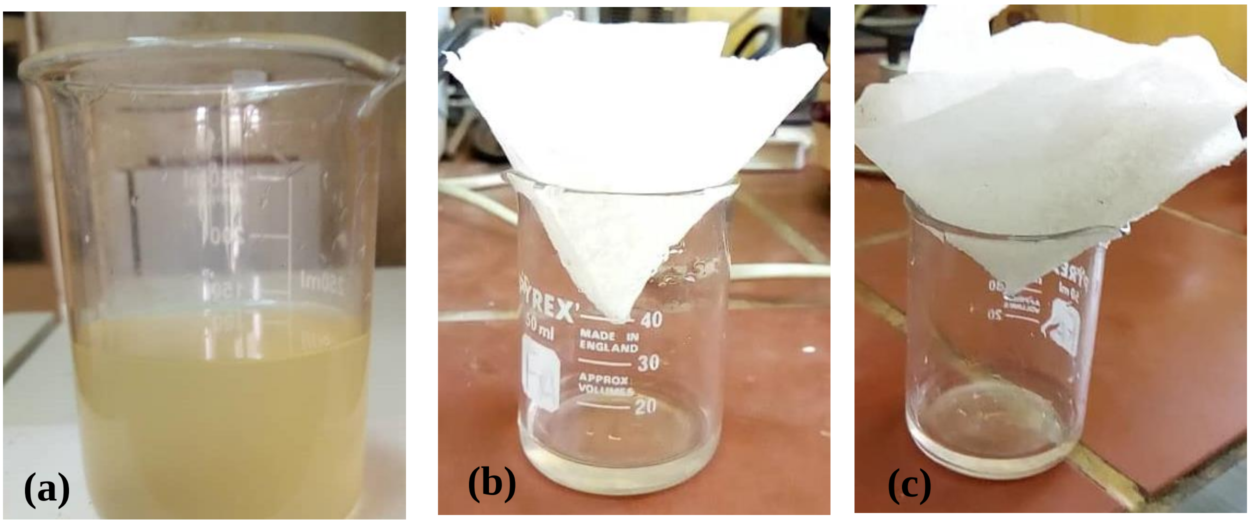

Figure 4: (a) water sample before purification (b) filtrate obtained using ordinary cellulose membrane (c) filtrate obtained using nano-copper filter membrane

Table 1: Microbial analysis obtained for the water before and after treatment

Sample	Total Heterotrophic Bacteria (cfu/ml)	Total Heterotrophic Fungi (cfu/ml)	Total Faecal Coliforms (cfu/ml)	Predominant Species
Canal water (before filtration)	2.30×10^5	3.0×10^4	1.10×10^3	*Aspergillus niger* *Fusarium spp* *Pseudomonas aerugious,* *Staphylococcus aureus* *Escherichia coli* *Bacillus sps*
Water filtered through ordinary membrane	1.10×10^4	0.00	0.00	*Bacillus spp*
Water filtered through copper nano-membrane	8.0×10^3	0.00	0.00	*Bacillus spp*

The microbial analysis done on the water before and after treatment revealed that the contaminated water was heavily contaminated with lots of disease-causing bacteria such as *Escherichia coli* (an indicating organism) that shows the water sample is heavenly polluted with faecal contaminants. Also isolated in the contaminated water are *Pseudomonas aerugious*, *Staphylococcus aureus* and *Aspergillus niger* (*Fungus*) which secretes Alflotoxin that affects the nerves of humans. In the treated water only *Bacillus* sps was isolated. All the fungi and faecal contaminants have been removed in the process of treatment.

The contaminated water was found to have a total count of 230,000 cfu/ml for heterotrophic bacteria; while in the treated water a total count of 8000 cfu/ml was obtained from water treated with copper nano-filter membrane and 11,000 cfu/ml was obtained from water treated with ordinary cellulose membrane. These results show that the nano-filter membrane not only succeeded in removing poisonous bacteria but also has removed 96.5 % of the heterotrophic bacteria found. The killing of 96.5 % microbes within a short contact time (less than 10 minutes) shows that the nanofilter membrane is very efficient as compared to method reported in literature that requires a longer contact time for this to be achievable (Jia *et al.*, 2012). This indeed revealed the potency of copper nanoparticles as anti-microbial and antifungal substance as sighted in literatures (Yoon *et al.*, 2007, Camacho-Flores *et al.*, 2015). Research has shown that one of the mechanisms by which copper carries out its antimicrobial property involves the release of copper ions into the water resulting in rapid membrane damage and DNA degradation of the microbes when they come in contact with the copper surface (Ren *et al*., 2009, Santo *et al*., 2012, Zain *et al*., 2014).

4.0. Conclusions

Copper nanoparticles were successfully synthesized from copper sulphate salt by the green method using peppermint and African spinach leaves extracts as natural reducing and capping agents. The copper nanoparticles were characterized using SEM, FTIR and EDS.

The synthesized copper nanoparticles were casted into a nano-membrane and then tested as filter for waste water. Its efficiency was tested for waste water filtration by comparing with ordinary cellulose acetate membrane and was found to give cleaner and odourless water than that obtained from ordinary cellulose acetate membrane. The microbial analysis also revealed that the poisonous micro-organisms were removed during filtration showing the anti-microbial potency of copper nanoparticles. This nano-filter is very efficient in removing about 96.5 % of the microbes.

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