Fabrication of polyaniline-coated Kapok (*Ceiba pentandra*) fibers embedded with copper-based particles

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**Abstract.** Polyaniline-coated kapok (*Ceiba pentandra*) fibers that were embedded with Cu-based particles were fabricated for antimicrobial application. Kapok fibers were coated with polyaniline molecules using oxidative polymerization. The coated fibers were embedded with copper-based particles using soaking method in prepared CuO suspension. X-ray diffraction (XRD) pattern shows presence of Cu and Cu\(_2\)O particles on the modified fibers. Scanning electron microscopy (SEM) supports the presence of embedded particles on the modified fibers. The samples showed antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*.

1. Introduction
Metal-based materials [1-5] such as Ag, Zn, and Cu have been studied for antimicrobial properties. Moreover, copper-based materials have shown potential as bactericidal agent at low cost and ease of synthesis. Copper-based materials in powder form or in film have various possible applications [5-7] such as paints, fabrics, and agriculture.

Kapok (*Ceiba pentandra*) fiber (KF) [9-10] is one of the less given attention agricultural products. The fiber exhibits large hollow lumen, which can be an excellent template for growing polymers. However, one of the drawbacks of the fiber is the hydrophobic character due to its waxy cutin. In such, embedding of particles using aqueous medium requires a hydrophilic substrate such as modified kapok fiber. Conversion of hydrophilic from hydrophobic kapok fibers can be achieved through polymerization of hydrophilic material on the fiber surface.

Polyaniline (PAni) [11-13] is an intrinsically conducting polymer that has been studied for its unique structure, ease of polymerization and applications. The high content of amine and imine groups of PAni makes it an excellent polymer for application of polar environment. Depending on the pH, PAni can exist in different form such as pernigraniline, emeraldine, leucoemeraldine. PAni has been applied as sorbent [14-15] for heavy metals such as chromium (VI) and copper. The sorbent property of PAni makes it efficient for embedding metal oxides.
In this study, copper-based particles will be embedded on PANi-coated kapok fiber and tested for its antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*.

2. Methodology

2.1 Materials
Kapok fibers were obtained from Nueva Ecija, Philippines and taken out from their pod. Aniline (99.5%, AR) (95%, AR) was purchased from Loba Cheme. Glacial acetic acid (99.7%, AR) was purchased from Macron Fine Chemical. Sodium Chlorite (80%, AR) and hydrazine monohydrate (98% AR) were from Sigma Aldrich. Ethanol (EtOH) (95%, AR) was from Ajaxfinechem. Hydrochloric acid (HCl, 37%, AR) was from RTC laboratory service and supply house. Ammonium persulfate (98%. AR) was from HIMEDIA. Copper oxide (99% AR) was from Nacalai Tesque. All reagents were used without further purification.

2.2 Pretreatment of Kapok fiber
The cutin of kapok fibers was removed to easily adhere the polyaniline molecules on the fiber. About 1.20 g of NaClO$_2$ was dissolved in 100 mL of distilled water in a three-neck flask and 1.90 mL of glacial acetic acid was also added. The mixture was added with 1.50 g of KF and stirred for 60 min at 700 rpm at 90ºC. The treated kapok fibers were washed with distilled water until filtrate reached pH 6-7. The fiber was oven dried at 60 ºC.

2.3 Coating of Polyaniline on kapok fibers
Coating of polyaniline on kapok fibers (PAni/KF) was prepared via oxidative polymerization by method of Zheng et al.(2012) [12]. Using 2.0 g of aniline dissolved in 66.0 mL of 1.0 M HCl. The mixture was cooled in an ice bath where 0.40 g of untreated KF was added and stirred for 30 minutes to disperse the fiber. In a separate beaker, 4.0 g of APS was dissolved in 16 mL 1.0 M HCl and cooled in an ice bath. APS mixture was added to the aniline and KF mixture dropwise and stirred for 1 hour. The resulting mixture was left for 16 hours at room temperature. The fibers were filtered then washed with distilled water until the supernatant became colorless. Further washing was done using ethanol. The product was air dried before drying in an oven at 60 ºC.

2.4 Embedding of Copper-based particles on Polyaniline/Kapok fiber
Copper-based particles were embedded by soaking PAni-coated kapok fiber in suspension containing CuO mixture. The mixture was prepared by method of Balela and Amores (2015)[16]. The CuO suspension was prepared by dissolving 4.87 g CuO powder in 42.0 mL deionized water by sonication. In a separate vessel, hydrazine solution was prepared using 3.06 g hydrazine in 42.0 mL deionized water. Around 18.0 g gelatin mixture (10%) was added to CuO and hydrazine mixtures. The pH of the mixtures were adjusted to pH 12 using aqueous NaOH. The mixture was purged with nitrogen for 30 The hydrazine solution was added to CuO mixture slowly while stirring at 500 rpm. The reaction was allowed for 2 hours at 353 K under nitrogen environment. The product was collected by centrifugation then washed with deionized water to remove excess hydrazine.

In a conical tube, 10 mg of PAni/KF was mixed with 10 mL of copper oxide suspension and PAni/KF was thoroughly dispersed. The mixture was stand for 3 hours. The fibers were recovered via filtration and dried. After drying, sonication of the product was done for 10 minutes to remove loosely attached copper oxide. The product was obtained using filtration. Drying was done at room temperature.
2.5 Characterizations
Morphological characterization of kapok and modified kapok fibers was done using Scanning electron microscope JEOL JSM 5310. X-ray diffraction analysis was done using SHIMADZU MAXima XRD-7000.

2.6 Antimicrobial activity of copper-based particles-polyaniline/kapok fiber
The test organisms used were Escherichia coli (UPCC 1195) and Staphylococcus aureus (UPCC 1143). The 24-hr old cultures were prepared as microbial suspensions in 0.1% peptone water. Inoculation was done using swabbing of applicator stick on a pre-poured nutrient agar about 3 mm thick. Even distribution of inoculum was ensured by rotating the plate 60° as the procedure was repeated twice. Samples were applied at three points on the plate. Incubation of NA plates was done at 35°C. Clearing zones were observed after 24 hours.

3. Results and Discussion
PAni-coated kapok fibers embedded with copper-based particles was fabricated. The XRD patterns of the sample are shown in Figure 1. The peaks at diffraction angles (2θ) 36.44°, 61.28 correspond to (111) and (220) of Cu2O. Peaks at 43.66°, 50.90° and 74.46° correspond to (111), (200) and (220) of Cu. The peak at 22.3° shows typical cellulose (200) plane from the kapok fiber. The XRD profile of the product shows the embedding of Cu and Cu2O particles on the modified fiber.

SEM images shows the coating PAni and embedding of copper-based particles on KF. Figure 2a-b shows SEM micrographs of kapok fiber while the coated kapok fiber can be seen on Figure 2c-d. The polyaniline coating on kapok fiber is not uniform. Some coating aggregated in some sites of the fiber. The rougher surface as compared to the raw KF image indicates PAni coating of KF. Meanwhile, the copper-based particles can be seen on Figure 2 d-e with some agglomeration of the particles. The aggregated materials are suspected to be Cu and Cu2O. The soaking method employed may have led to agglomeration of the nanoparticle on the surface of modified kapok fiber.

Figure 1. XRD pattern of copper-based particles embedded on modified kapok fiber.
The copper-based particles/PAni/KF showed antimicrobial activity against *E. coli* and *S. aureus*. Clearing zones were observed around the two samples and one sample with no clearing zone for *E. coli*. The exact antimicrobial of copper particles has not yet been studied. Various mechanism proposed includes disruption enzymatic activity due to release of Reactive Oxygen Species (ROS). The release of ROS leads to production of different radicals which disrupt the cell activity leading to cell death[4] thus, formation of clearing zones. While the zone for *S. aureus* shows the reduced growth instead of clearing zone for the three samples tested as summarized in Table 1. The existence of clearing zone beneath the sample while only having reduced growth of *S. aureus* around the sample suggest that the copper-based particle on modified KF has more effect in contact inhibition where there is an intimate contact of bacteria to sample.

### Table 1. Antimicrobial activity of Copper-based particles/PAni/KF on *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive).

| Test organism                  | Clearing zone present (+) or absent (-) | Growth beneath the sample | Antimicrobial activity |
|-------------------------------|----------------------------------------|---------------------------|------------------------|
|                               | 1       | 2   | 3     |                         |                        |
| *Escherichia coli* (Gram-negative) | +      | +   | -     | none                   | Present                |
| *Staphylococcus aureus* (Gram-positive) | reduced | reduced | reduced | none                   | Present                |

4. **Summary and conclusion**

In this study, copper-based particles were embedded on polyaniline-coated kapok fibers. The fibers were coated with polyaniline using oxidative polymerization. Embedding of copper-based particles was done using soaking method in a prepared copper oxide suspension. Embedding of Cu and Cu$_2$O particles were shown by XRD profile and SEM images. The product was subjected to agar disc
diffusion test. Clearing zones were observed against *E. coli* while reduced growths were observed against *S. aureus*. Results showed the potential of copper-based embedded PANi-coated KF as an antimicrobial material.

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