TEMPO nanofibrillated cellulose as template for controlled release of antimicrobial copper from PVA films

Changle ***Jiang***[a], *Gloria* ***OPORTO***[a*], *Tuhua* ***ZHONG***[a], *and Jacek* ***Jaczynski***[b]

[a] Division of Forestry and Natural Resources, West Virginia University

[b] Division of Animal and Nutritional Sciences, West Virginia University

ABSTRACT

TEMPO nanofibrillated cellulose (TNFC) was used in different concentrations (0 wt. %, 30 wt. %, 50 wt. % and 70 wt. %) as template to synthesize copper nanoparticles (CuNPs) from copper sulfate and the resulting hybrid material was mixed with polyvinyl alcohol to prepare films. The final composite films were evaluated effectively in terms of their antimicrobial properties against *Escherichia coli* DH5α. More importantly, copper release, using deionized water as receptor media, was evaluated by ICP-OES. The results indicate that increasing the cellulosic material concentration will facilitate the control of copper release from the films. The copper release rate data were modeled by the empirical models but there was an alternation as TNFC concentration increased. The result shows that the release of copper obeys the Power law when TNFC is at a low concentration (<30%). However, as the TNFC concentration increased to 70%, the copper release rate obeys exponential mode with a high coefficient value (R^2) of 0.9951.

SYNTHESIS

CuNPs were synthesized on TNFC using a chemical reduction method. PVA composite films were prepared by incorporating this TNFC-CuNPs hybrid material into the PVA matrices using a solvent casting process.

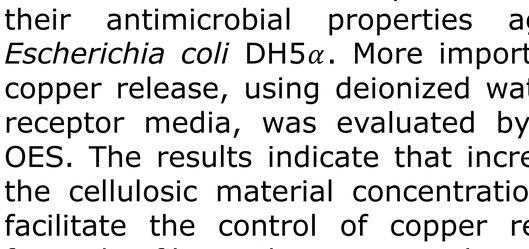

Figure 1. Preparation of TNFC-CuNPs hybrid material and PVA/TNFC-CuNPs film

CHARACTERIZATION

- Transmission electron microscopy (TEM) for morphology and Energy-dispersive X-Ray spectroscopy (EDS) analysis of TNFC-Cu
- Antimicrobial test against *E.coli* DH 5α
- Inductively coupled plasma optical omission spectroscopy (ICP-OES) for copper release
- Determination of copper release rate

To measure the concentration of released copper (μ_1), the films were cut into 1cm×1cm pieces and immersed in 10ml deionized water. To measure the concentration of copper still in film (μ_2), the immersed film pieces were solved using 1 ml nitric acid and subject to a digestion process then followed with a dilution process. The copper release rate (φ) was measured from 2 to 14 days with an interval of 2 days. The formula used for calculating is:

$$\varphi = \mu_1/(\mu_1+\mu_2)$$

Where:
φ: copper release rate
μ_1: mass of copper released to media
μ_2: mass of copper still in film

RESULTS AND DISCUSSION

➢ Morphology and elemental analysis

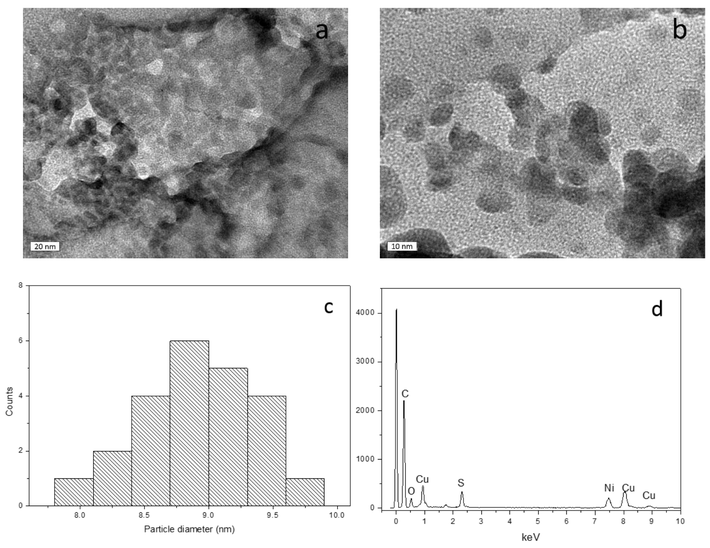

Figure 2. (a) TEM image of TNFC-CuNPs under scale of 20 nm; (b) TEM image of TNFC-CuNPs under scale of 10 nm; (c) Particle size distribution of Cu nanoparticles; (d) Energy-dispersive X-ray spectroscopy (EDS) of TNFC-CuNPs.

In Fig.3c, the average diameter of CuNPs obtained in this study is 8.9 nm with a standard deviation of ±0.4 nm.

➢ Antimicrobial Test against *E. coli*

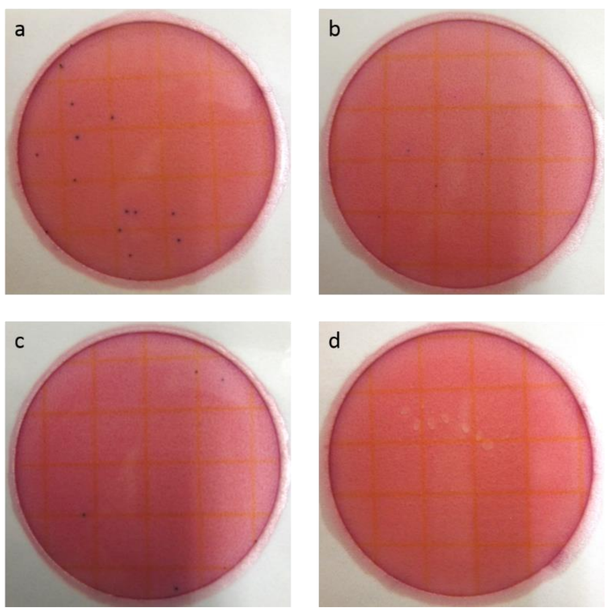

Figure 3. Antimicrobial test against *E. coli*: a) *deionized water*; b) PVA film; c) PVA/TNFC film; d) PVA/TNFC-CuNPs film

E. coli broth was exposed to those substance for 7 days. All population of *E. coli* were counted after 10^7 times dilution of exposed broth other than Fig. 3d which was 10^2 times. The reason is that *E. coli* colony has not been observed after 10^2 times dilution. The results show that original population of *E. Coli* broth before exposure are (a) 1.5×10^8 CFU/ml, (b) 5×10^7 CFU/ml, (c) 6×10^7 CFU/ml and (d) 1×10^2 CFU/ml.

➢ TNFC concentrations and copper release

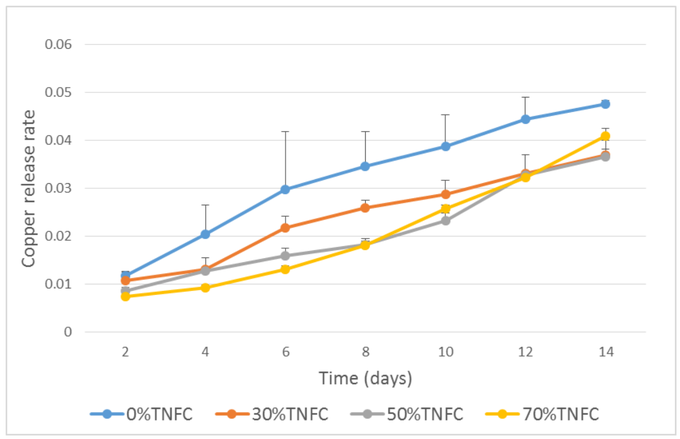

Figure 4. copper release rate over time

In Fig.4, the average copper release rates are 0.770 (0% TNFC), 0.768 (30%), 0.650 (50%) and 0.590 (70%) respectively.

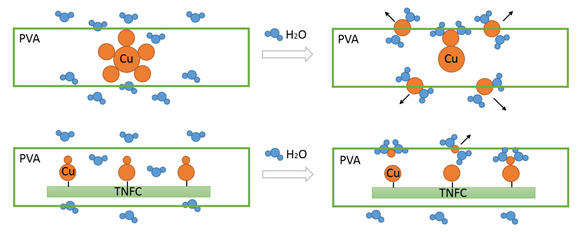

Figure 5. Scheme of release behavior of PVA/CuNPs film (top) and PVA/TNFC-CuNPs (bottom) films in deionized water.

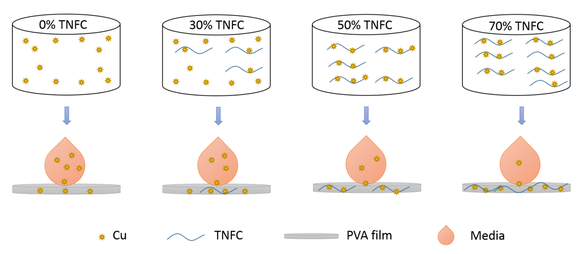

Figure 6. Scheme of copper release process subject to increasing TNFC concentration

➢ Kinetic study of copper release

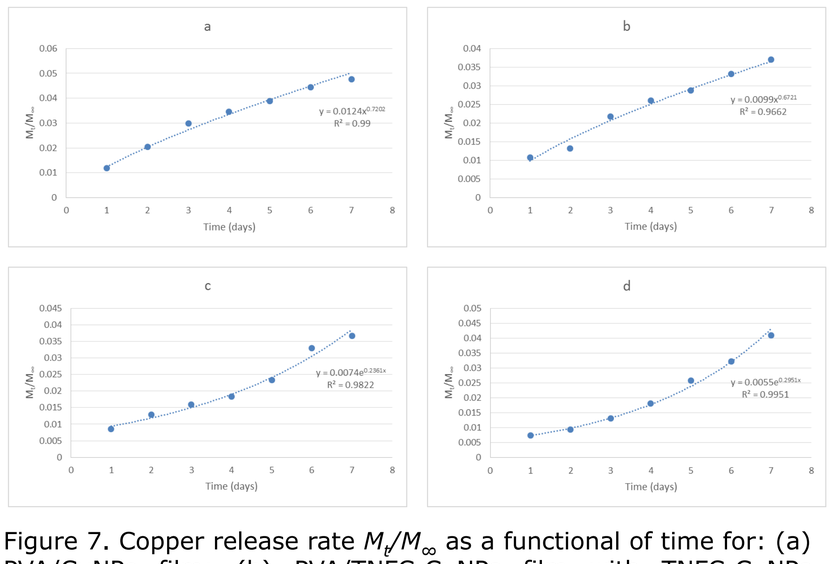

Figure 7. Copper release rate M_t/M_∞ as a functional of time for: (a) PVA/CuNPs film; (b) PVA/TNFC-CuNPs film with TNFC-CuNPs containing 30% TNFC; (c) PVA/TNFC-CuNPs film with TNFC-CuNPs containing 50% TNFC; (d) PVA/TNFC-CuNPs film with TNFC-CuNPs containing 70% TNFC

In Fig.7, M_t stands for the mass of copper released to the deionized water. M_∞ stands for the mass of copper which was still in the films after releasing.

CONCLUSIONS

TEMPO nanofibrillated cellulose was successfully used as bio-based template for synthesis of copper nanoparticles with resulting particle size around 9 nm. Comparing to directly embed CuNPs into PVA film, TNFC-CuNPs hybrid nanomaterial was demonstrated more effectively against *E. coli* growth, leading by 5 log reduction. TNFC can regulate the copper release rate and improve the long-term antimicrobial properties of the PVA films. It indicates that the average copper release rate decreases by 38% when the concentration of TNFC increases from 0 wt.% to 70 wt.%. The copper release rate of CuNPs obeys well to the Power law, while the one of TNFC-CuNPs obeys well to exponential model with a high coefficient of determination (R^2=0.9951) when TNFC increases to 70 wt.%. TNFC-CuNPs is a promising agent to achieve controlled delivery of copper for antimicrobial application.

ACKNOWLEDGMENTS

Funding for this work has been provided by the USDA NIFA Grant No. 2013-34638-21481 "Development of novel hybrid cellulose nanocomposite film with potent biocide properties utilizing low quality Appalachian hardwoods" and NIFA McStennis WVA00098 "Efficient utilization of biomass for biopolymers in central Appalachia".

CONTACT INFORMATION

* Corresponding author: Dr. Gloria S. Oporto

Assistant Professor, West Virginia University

E-mail: gloria.oporto@mail.wvu.edu