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Incorporation of copper nanoparticles into paper for point-of-use water purification

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ABSTRACT

As a cost-effective alternative to silver nanoparticles, we have investigated the use of copper nanoparticles in paper filters for point-of-use water purification. This work reports an environmentally benign method for the direct *in situ* preparation of copper nanoparticles (CuNPs) in paper by reducing sorbed copper ions with ascorbic acid. Copper nanoparticles were quickly formed in less than 10 min and were well distributed on the paper fiber surfaces. Paper sheets were characterized by x-ray diffraction, scanning electron microscopy, energy dispersive x-ray spectroscopy, and atomic absorption spectroscopy. Antibacterial activity of the CuNP sheets was assessed for by passing *Escherichia coli* bacteria suspensions through the papers. The effluent was analyzed for viable bacteria and copper release. The CuNP papers with higher copper content showed a high bacteria reduction of log 8.8 for *E. coli*. The paper sheets containing copper nanoparticles were effective in inactivating the test bacteria as they passed through the paper. The copper levels released in the effluent water were below the recommended limit for copper in drinking water (1 ppm).

1. Introduction

The lack of clean drinking water in many rural communities throughout the world is a significant human-health concern. Point-of-use (POU) water purification offers an affordable and convenient way to reduce exposure to pathogenic microorganisms (Clasen, 2010). Paper-based filters coated with biocidal agents are easy to produce and distribute to remote locations. Filters containing nanoparticles do not require energy inputs for water purification. Paper and cotton fabrics are very abundant and regularly used in water filtration. Recently, for POU applications, we have designed a paper sheet embedded with silver nanoparticles to purify drinking water contaminated with bacteria (Dankovich and Gray, 2011a; Dankovich, 2014). As a more affordable alternative to silver, researchers have turned to using copper to purify drinking water (Sudha et al., 2012; Stout and Yu, 2003; Varkey and Dlamini, 2012).

Copper and copper compounds have been demonstrated to eliminate a wide variety of microorganisms, including *Vibrio cholerae, Shigella, Escherichia coli, Salmonella,* fungi, viruses, and other types (Sudha et al., 2012; Esperito Santo et al., 2011; Molteni et al., 2010). Metallic copper surfaces have been used to prevent bacterial growth in hospitals (Esperito Santo et al., 2011; Molteni et al., 2010). Copper nanoparticles can be incorporated into fibrous materials to act as a long-lasting reservoir of copper ions for enhancing antimicrobial and catalytic activity (Vainio et al., 2007; Bendi and Imae, 2013; Ben-Sasson et al., 2013). Recently, researchers have

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demonstrated the application of copper nanoparticles to cellulosic materials (Vainio et al., 2007; Bendi and Imae, 2013; Jia et al., 2012; Cady et al., 2011). However, none of these researchers have evaluated these copper nanoparticle membranes as antibacterial drinking water purifiers. A similar membrane technology is a membrane containing copper oxide particles for virus removal from breast milk (Borkow et al., 2007). Recently, a related application using a porous ceramic substrate doped with copper nanoparticles as a filter material showed strong bactericidal activity (Klein et al., 2013).

A novel and facile method for embedding copper nanoparticles in cellulosic papers is described. This involves the preparation of copper nanoparticles *in situ* on the fiber surfaces with a mild reducing agent, ascorbic acid, and a heat source. To test for the bactericidal effectiveness of the CuNP papers, we passed *E. coli* bacterial suspensions through a CuNP paper sheet, and analyzed the effluent water for viable bacteria. This paper was selected due to the fact that the particle retention size is greater than the size of bacteria, which allows for exposure to copper nanoparticles, not removal due to filtration removal (Dankovich and Gray, 2011a).

2. Materials and methods

2.1. Materials

We used absorbent blotting papers made from bleached softwood kraft pulp (made by Domtar Inc. and supplied by FP Innovations, Pointe-Claire, QC). The sheet thickness and grammage are 0.5 mm and 250 g/m^2, respectively. Copper sulfate ($CuSO_4$), ascorbic acid ($C_6H_8O_6$), 30% hydrogen peroxide (H_2O_2), concentrated sulfuric acid (H_2SO_4), dipotassium phosphate (K_2HPO_4), monopotassium phosphate (KH_2PO_4), tryptone, yeast extract, and sodium chloride were purchased from Fisher Scientific and used as received. Colilert® Quanti-Trays 2000 were purchased from IDEXX Laboratories, Westbrook, Maine. Water treated with a Barnstead Nanopure system was used throughout.

2.2. Preparation of copper nanoparticle paper

We immersed sheets of blotting paper (10 cm by 10 cm) in freshly prepared alkaline solutions of copper hydroxide (0.8%) for 1 h to 2 days. Alkaline copper hydroxide solution was prepared by adding 1 M NaOH to 0.32 M $CuSO_4$ solution to form gelatinous copper hydroxide ($Cu(OH)_2$), and subsequently, $Cu(OH)_2$ was dissolved in 500 mL of 10 M NaOH to form $[Cu(OH)_4]^{2-}$, which typically was 30 mM $[Cu(OH)_4]^{2-}$. Following copper absorption by the blotting papers, they were soaked in deionized water to remove excess base. To reduce the copper ions embedded in the paper fibers, the blotting papers were placed in a 10% ascorbic acid aqueous bath at 85 °C for 10–30 min. Following reduction, the papers were soaked overnight in deionized water.

2.3. Characterization

Paper samples were imaged through standard photography and dark field microscopy (Hirox KH 7700). Qualitatively, color changes from white to red and/or maroon indicate the presence of copper nanoparticles (Jia et at., 2012). Additionally, the presence of CuNPs in the blotting paper was confirmed by x-ray diffraction (XRD) using PANalytical X'Pert Pro Multi Purpose Diffractometer (PANalytical B.V., The Netherlands). Paper samples were finely ground to a powder with a coffee grinder prior to XRD analysis.

The shape and size distribution of the copper nanoparticles in the sheet were examined by electron microscopy. Imaging and analysis of the CuNP paper was performed with a field emission scanning electron microscopy (Hitachi S-4700 FE- SEM) attached to an energy-dispersive X-ray spectroscopy detector (EDX). For SEM, samples were sputter coated with a thin, 12 nm, layer of AuPd prior to imaging. Nanoparticle diameters were measured for greater than 150 particles.

To quantify the amount of copper in the CuNP papers, we performed an acid digestion of the paper and analyzed the amount of dissolved copper with a flame atomic absorption (FAA) spectrometer (Perkin Elmer AAnalyst 200). To dissolve the copper and to degrade the cellulose fibers, ~0.05 g of CuNP paper was added to 2 mL concentrated sulfuric acid heated in a sand bath to between 50 °C and 60 °C and was followed by the addition of 2 mL 30% hydrogen peroxide. The copper content is reported for four replicates per sample concentration with standard error reported.

2.4. Bactericidal testing

The bactericidal activity of the CuNP paper was tested against a nonpathogenic wild strain of *E. coli*, a model organism for contaminated water, which was obtained from IDEXX (IDEXX Laboratories, Inc, Maine). The influent consisted of a 100 mL bacteria suspension in a 10 mM random motility buffer solution (0.4949 g/L of K_2HPO_4 and 0.212 g/L of KH_2PO_4) with either 5×10^4 or 4×10^9 colony-forming units (CFU)/mL of *E. coli*. This bacterial suspension was passed through a 6.5 cm by 6.5 cm sheet of CuNP paper, as described previously (Dankovich and Gray, 2011a). As a control paper, we also filtered *E. coli* through an untreated paper sheet. Prior to pouring the bacterial suspension through the paper filters, the filters were rinsed with 20–50 mLs of deionized water to check for a water tight seal in the filter holder. The effluent water was tested for live bacteria by shaking 100 mL of effluent water with an IDEXX Colilert® pack and subsequent sealing in IDEXX Quanti-Tray 2000. The Quanti-trays were incubated overnight at 37 °C for 24 h and the positive wells were counted (Edberg et al., 1990). Seven samples tested were evaluated at each influent bacteria concentration with standard error reported.

2.5. Copper release and retention

The effluent was analyzed for copper by graphite furnace atomic absorption spectrometry (GF-AA, Perkin Elmer AAnalyst 200 with HGA 900). The copper release was evaluated from 0.1 to 2 L of deionized water for six samples with standard error reported. The percent copper retention was determined from the copper release subtracted from the overall copper content of the paper.