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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 minutes 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).

Keywords

drinking water treatment; copper nanoparticles; point-of-use water treatment; sustainable nanotechnology

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

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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*, *E. 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 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/m², respectively. Copper sulfate (CuSO₄), ascorbic acid (C₆H₈O₆), 30% hydrogen peroxide (H₂O₂), concentrated sulfuric acid (H₂SO₄), dipotassium phosphate (K₂HPO₄), monopotassium phosphate (KH₂PO₄), 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 hour to 2 days. Alkaline copper hydroxide solution was prepared by adding 1 M NaOH to 0.32 M CuSO₄ 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 minutes. 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 al, 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 grams 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 *Escherichia 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 K₂HPO₄ and 0.212 g/L of KH₂PO₄) with either 5x10⁴ or 4x10⁹ 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 24h 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.

3. Results and Discussion

3.1 Paper characterization

In order to sorb copper ions on the surface of cellulose paper fibers, we evaluated a range of dissolved copper compounds to determine which conditions showed the greatest copper absorption. We found that a high pH of the dissolved copper solution was a pertinent factor for copper sorption, as observed previously (Davidson and Spedding, 1958). Optimal copper absorption into the cellulose fibers occurred from concentrated sodium hydroxide with dissolved cupric hydroxide (cuprate), and took several hours for papers to become saturated with copper ions (abbreviated to alkali-cellulose II(Cu)). Following copper uptake from these cuprate solutions, the copper nanoparticles were readily formed on the cellulosic blotter papers via a reduction with ascorbic acid dissolved in a hot aqueous bath (85°C). (Figure 1).

The x-ray diffraction patterns confirm the formation of copper particles from the ascorbic acid reduction method. (Figure 2). The largest peaks were observed from copper powder formed from ascorbic acid reduction of cuprate in suspension and corresponded to the fcc copper phase ($2\theta = 43.3^\circ, 50.4^\circ, 74.1^\circ$, JCPDS 85 – 1326). Lower peak intensities were observed in the ground CuNP paper samples and most peaks were in the same locations with the additional peak at 2θ at 36.4° , which corresponds to Cu_2O (111) (JCPDS 77 – 0199). This indicates some minor oxide formation on the copper surface in the air, which is not unexpected, as other researchers have also observed the presence of copper oxides along with CuNPs following CuNP formation on fiber surfaces (Cady et al, 2011; Vainio et al, 2007). No peaks were observed for the untreated paper.

Following the reduction of copper with ascorbic acid on the paper, the surface of the paper fibers was covered with large nanoparticles, as shown in the SEM images (Figure 3 a,b). The size of the copper nanoparticles varied from less than 100 nm to over 600 nm in diameter, with an average diameter of 274.2 nm (Figure 3c). The larger particles appear to be aggregated smaller particles, and particle size appears to be consistently within this range for all CuNP paper samples. The particle aggregation is likely due to the lack of any stabilizing polymers or ligands in this system. A high intensity EDS peak for copper at 0.93

keV confirmed the formation of copper nanoparticles in the papers, which is consistent with the results obtained from XRD data (Figure 3d).

Copper uptake from cuprate solutions is time dependent. The sodium hydroxide swelling of cellulose fibers occurs within a few minutes and paper shrinkage is nearly immediately apparent. However, to achieve high levels of copper uptake, the fibers required many hours of soaking in cuprate solutions. In alkaline solutions, copper ions penetrate slowly the cellulose fiber, and have been suggested to alter the crystalline structure of cellulose (Ogawa et al, 2013). These cellulose copper complexes are stable in basic solutions, but in acidic solutions of ascorbate, copper leaches out of the fibers and is reduced to nanoparticles on the surface of the fibers.

Following nanoparticle synthesis, we performed acid digestions of the CuNP papers to determine the copper content, which ranged from ~10 mg Cu per g paper to 65 mg Cu per g paper for 1 to 48 hours of soak time. (Figure 4). Empirical research has shown copper uptake into cellulosic materials from cuprate solutions to be as high as 225 mg Cu per g of cotton cellulose, which corresponds to 0.57 atoms of Cu per glucose unit and led to the hypothesis that bound copper forms cross-linkages between adjacent cellulose chain molecules (Davidson and Spedding, 1958). From the dark field microscopy imaging, the CuNP papers showed an incomplete coverage of the paper fibers at our highest copper content, the 65 mg Cu per g paper sample (Figure 5). The paper's outer most fibers have a high degree of copper on the surface, whereas the inner fibers appear white and do not seem to have any copper bound to them. This suggests the copper uptake occurs completely at the outer most surfaces and a thinner paper would allow for a more uniform distribution of CuNPs within the paper.

3.2 Antibacterial effectiveness

To assess the bactericidal effectiveness of CuNP papers, we re-grew the effluent bacteria, after passage through the paper. To verify that paper does not filter out bacteria, we also tested for the viable bacteria in the effluent water after filtering through untreated paper. For the 65 mg Cu per g paper CuNP paper, the log reduction value was log 8.8 and log 4.6 reductions of viable *E. coli* bacteria, in the effluent, as compared to the initial concentration of bacteria (4.4×10^9 CFU/mL and 5.2×10^4 CFU/mL) (Figure 6). The CuNP paper with lower copper content (10 mg Cu per g paper) showed a lesser degree of bacterial inactivation. The untreated paper showed a minor filtration effect with a log reduction of 0.5. These results are similar to our previous study of AgNP paper filtration of *E. coli* bacteria (Dankovich and Gray, 2011a). The average flow rate of bacterial suspensions through the CuNP was 1.81 liters per hour, which is three times as fast as flow through our previous AgNP papers (Dankovich and Gray, 2011a). In contrast, the flow rate of the untreated filter papers was much slower, only filtering at 0.3 liters per hour. Swelling from the NaOH soaking step causes the increase in paper thickness and air to be trapped in the swollen sheet, and as a result, a greater inter fiber pore space of the filter paper (Richter and Glidden, 1940).

Copper is an essential trace element for human health, but ingesting levels higher than 3 ppm in drinking water for two weeks can cause gastrointestinal irritation (Agency for Toxic Substances & Disease Registry, 2004). The average copper concentration in the filter

effluent was 206.9 ± 34.1 ppb (Figure 7) from filtering deionized water through the 65 mg Cu per g paper sample, which is well below the EPA secondary limit for copper in drinking water (1000 ppb) (US EPA, 2002). Because the antibacterial tests were conducted after filtering 100mL of bacterial suspensions, the expected copper concentration in the effluent during the bactericidal tests should be between 200 – 600 ppb. Because the graphite furnace atomic absorption spectrometer does not distinguish between the specific forms of the analyte, there is no information from this method on whether the copper released is in the nanoparticle or ionic form. Dissolved carbon dioxide and oxygen from the atmosphere are present in the deionized water, which causes surface corrosion of the copper nanoparticles, and as a result, the surface layer of the nanoparticles to be in the ionic form and this is supported by the copper oxide XRD peak (Figure 2). It has been observed in similar systems that the corroded copper readily releases dissolved copper ions (Dortwegt and Maughan, 2001), and as is likely in this case as well. The copper release from the CuNP paper was 0.14% of the initial copper content of the filter papers per liter of water filtered. The very low copper release per liter suggests the CuNP paper could be a long-lasting water purifier.

3.3 Discussion

Our hypothesis on the mechanism of this CuNP paper is that *E. coli* bacteria accumulate copper ions from direct contact with CuNPs in the paper, and over time become inactivated. Since the IDEXX method requires 24 hours to analyze for bacteria viability, it is not possible to know exactly how long copper takes to inactivate bacteria from our study. However, from other studies, it appears copper ions can rapidly inactivate bacteria from a few minutes (Esperito Santo et al, 2011; Molteni et al, 2010; Jia et al, 2012) to several hours (Varkey and Dlamini, 2012), depending upon the environmental conditions. In this particular study, we cannot conclude whether dissolved copper or copper absorbed by the bacterial cells contributes to bacterial inactivation, but in subsequent work, which is published elsewhere (Dankovich et al, 2014), we used another method to test for bacterial viability, i.e. membrane filtration, which separates the effluent water from the bacteria cells immediately following filtration through the CuNP paper. This work also showed strong antibacterial activity of the CuNP papers, which supports the idea that bacterial inactivation is due to the direct contact with CuNPs during filtration through the CuNP paper (Dankovich et al, 2014). Other researchers have examined the specific mechanism of copper inactivation of bacteria and suggest that the copper ions cause irreversible damage to bacterial membranes by increasing membrane permeability and destabilizing the cells (Esperito Santo et al, 2011).

This study is a proof-of-concept example of water purification using papers embedded with copper nanoparticles, and other variables not tested in this work also can affect the overall bactericidal performance of these filter papers. For example, the particle retention size of cellulosic filter papers can be altered in the paper making process to fit the particular filtration application. The fiber arrangement and density will dictate the overall flow rate through the paper sheet. Environmental variables, such as turbidity in water sources, will lead to determining an optimal filter paper. High turbidity leads to clogged filters, which could be avoided if the particle retention of the paper is large enough to allow adequate flow

through. Possibly, the final version may contain some mix of untreated paper (or other material) to remove turbidity and the CuNP paper to reduce bacteria count.

These CuNP paper filters fit into the greater picture of point-of-use water filtration on the very low cost end. The amount of copper in each paper amounts to less than a cent, and could be easily incorporated with other existing POU methods. Ongoing research is exploring various filter designs to add these antibacterial papers to. Potential uses include disaster relief and emergency response, backpacking filters, and rural household filters for developing countries. In our subsequent work, we have evaluated longer term use for this filter papers, which shows the potential for repeat usage with natural water sources (Dankovich et al, 2014). Future work will clarify the extent to how much water a single paper filter can purify. Performance limitations may be due to either the amount of CuNPs in the paper or the overall strength of the paper filter. In the current state, this proof of concept experiment of an antibacterial paper containing CuNPs shows the potential to be a very useful filter, but the filter design needs to be optimized prior to the evaluation of the relevant water purification metrics, such as antiviral, anti-protozoan, and long term antimicrobial performance.

With some of the papers containing high levels of copper nanoparticles, we observed slow wetting of the papers. Cellulosic materials and in particular blotting papers are hydrophilic materials and highly water absorbent (Dankovich and Gray, 2011b). We did not observe reduced hydrophilicity with the filters we tested in the study, which were all highly wettable and allowed water to flow through at rates even faster than the untreated papers. It is relevant to note that there is an upper limit to the amount of copper that can be added to this filter paper and other filtration materials. A hydrophobic water filter cannot filter water, and therefore for water filtration applications, it is not advisable to use copper levels higher than the 7% weight percent, which was our upper limit. Although, other potential uses of a hydrophobic copper nanoparticle embedded paper may not rely on wettability. For example, another application of nano-copper materials is to impart super-hydrophobic surfaces, such as with ceramic coatings (Reinosa et al, 2012).

4. Conclusion

Although many studies have shown the antimicrobial effects of copper surfaces in hospitals, the use of copper in drinking water treatment, has been limited to silver-copper ionization systems for the control of Legionnaire's disease (Stout and Yu, 2003) and copper pots in developing countries (Sudha, 2012). At the material cost of only a few cents per filter, one sheet of CuNP paper can be synthesized in the laboratory. This CuNP paper filter has the potential to become an extremely low-cost way to purify water. This is especially relevant for resource limited countries, and can be used in remote "off-the-grid" locations.

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Highlights

- Copper nanoparticles were readily formed by ascorbic acid on fiber surfaces.
- Paper sheets with Cu nanoparticles were characterized by XRD, SEM, EDS, and FAA.
- As a water filter, paper with Cu nanoparticles show superior antibacterial activity.
- We report a novel point-of-use paper filter for water treatment.

Figure 1. Blotter papers (a) untreated, (b) soaked in cuprate solution for 2 days (alkali-cellulose II(Cu)), and (c) alkali-cellulose II(Cu) heated in the 10% w/v ascorbic acid bath (85°C) for 10 minutes.

Figure 2.
XRD patterns of (a) copper powder produced through ascorbic acid reduction, (b) ground CuNP paper, and (c) ground untreated paper.

Figure 3. Characterization of copper nanoparticles embedded on paper fibers. Scanning electron microscope image of CuNP paper with 65 mg Cu/ g paper: (a) 1,200× and (b) 10,000× magnification. (c) Histogram of distribution of copper nanoparticle diameters, as measured from SEM images. (d) EDX spectra of CuNP papers. Samples were sputter coated with Au Pd.

Figure 4.
Copper content in paper filters, measured by flame atomic absorption spectrometry, with increasing paper soak time in cuprate solutions.

Figure 5. Dark field microscopy image of CuNP paper. CuNP coated fibers are more concentrated on the outer paper surface (maroon fibers) with uncoated fibers in the paper core (white fibers).

Figure 6.

Log reduction values of *E. coli* bacterial count after permeation through the CuNP paper with 65 mg Cu/g paper (black bars), CuNP paper with 10 mg Cu/g paper (gray bars), and untreated paper (white bars). Two different initial bacterial concentrations were evaluated, 4×10^9 CFU/mL (log 9.6) and, 5×10^4 CFU/mL (log 4.7). Standard error is reported.

Figure 7.

Copper concentration in effluent water with respect to volume of water filtered through the CuNP paper. The recommended Cu limit for drinking water is 1000 ppb.