

Potential of Silver Nanoparticle-Coated Polyurethane Foam As an Antibacterial Water Filter

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Abstract: Silver nanoparticles can be coated on common polyurethane (PU) foams by overnight exposure of the foams to nanoparticle solutions. Repeated washing and air-drying yields uniformly coated PU foam, which can be used as a drinking water filter where bacterial contamination of the surface water is a health risk. Nanoparticles are stable on the foam and are not washed away by water. Morphology of the foam was retained after coating. The nanoparticle binding is due to its interaction with the nitrogen atom of the PU. Online tests were conducted with a prototypical water filter. At a flow rate of 0.5 L/min, in which contact time was of the order of a second, the output count of *Escherichia coli* was nil when the input water had a bacterial load of 10^5 colony-forming units (CFU) per mL. Combined with the low cost and effectiveness in its applications, the technology may have large implications to developing countries. © 2005 Wiley Periodicals, Inc.

Keywords: silver nanoparticles; polyurethane; antibacterial

INTRODUCTION

Water is the common breeding ground for many pathogens. The presence of bacteria is the main indication of water contamination. In countries such as India, 80% of the diseases are due to bacterial contamination in drinking water. The World Health Organization (WHO, 1996) recommended that any water intended for drinking should contain fecal and total coliform counts of 0, in any 100-mL sample. When either of these groups of bacteria is encountered in a sample, immediate investigative action should be taken. The removal or inactivation of pathogenic microorganisms is the last step in the treatment of wastewater. To achieve this, chemical and physical agents, such as chlorine and its derivatives, AgNO₃, ultraviolet light and radiation, are commonly used (Droste, 1997). During the past few decades, several investigations have been carried out concerning the use of synthetic and natural zeolites, polymer films, and metal ions (Ag, Cu, Zn, Hg, Ti, Ni,

Co) as bactericides for water disinfection (Feng et al., 2000; Shearer et al., 2000; McLean et al., 1993; Chohan et al., 2004; Ulkuseven et al. 2002; Chen et al., 2003; Cik et al., 2001; Islam et al., 2003). The use of metal nanoparticles for water disinfection is relatively new (Stoimenov et al., 2002; Zhang et al., 2003). Because of their high reactivity due to the large surface to volume ratio (Ichinose, 1992), nanoparticles are expected to play a crucial role in water purification (Stoimenov et al., 2002; Zhang et al., 2003) when water becomes an important commodity (Barraque, 2003). Several investigations have been carried out on the bactericidal effect of nanoparticles and their applications in the plastics, health, textile, and paint industry (Zuhuang, 2003; Chen and Chen, 2002; Lee et al., 2003; Fechner and Zimmer, 2003; Reimer and Fleischer, 1999). Pesticide removal from drinking water with the help of nanoparticles was reported in our previous work (Nair and Pradeep, 2004). The aim of this study is to demonstrate the antibacterial properties of the polyurethane foam coated with silver nanoparticles. The mechanism of antibacterial effect of silver nanoparticles has been reported in the literature (Sondi and Salopek-Sondi, 2004), which suggests that the particles are bactericidal. Experiments showed that the treated *Escherichia coli* cells were damaged, showing formation of "pits" in the cell wall of the bacteria. This support was chosen because the -N(H)COO- (carbamate) group is expected to bind with the surface of the nanoparticles. It is also one of the most cost-effective, food-grade polymers available, and it has a considerable application possibility in rural communities. *E. coli* was chosen in this study as indicators of fecal contamination. Several investigations have been done on supports such as polypropylene and textile fabrics (Yeo et al., 2003) for exploring bactericidal effect.

EXPERIMENTAL

AgNO₃ and trisodium citrate were obtained from Qualigens Fine Chemicals, India, and used as received. Polyurethane

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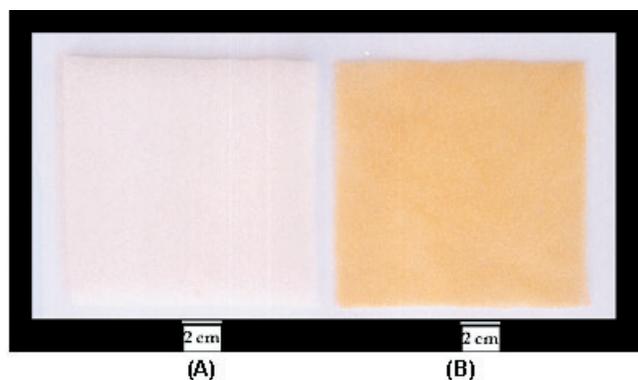


Figure 1. Photographs of pure polyurethane (PU) (A) and PU coated with silver nanoparticles (B). Golden yellow color in B is due to the saturation coverage of silver nanoparticles.

foams were obtained from local sources and used after through washing with distilled water. Triple distilled water was used for all the synthesis and measurements. Standard cultures of the organisms were obtained from Microbiology Laboratory, Apollo Hospital, Chennai and Aquamall Water Research Lab, Eureka Forbes Ltd., Bangalore. Nutrient broth and Nutrient and m-Endo agars were obtained from HIMEDIA Chemicals, India, Pvt. Ltd. M-Endo agar is coliform specific and shows a metallic sheen for all the coliforms.

The synthesis of Ag@citrate was done according to the literature procedure (Kamat et al., 1998). Briefly, the synthesis involves the following materials and methods: 25 mL of 0.005 M stock solution of silver nitrate in water was diluted to 125 mL and heated until it begins to boil. Then 5 mL of 1% sodium citrate solution was added; heating continued until the color was pale yellow. The solution was cooled to room temperature. The synthesized nanoparticles were characterized by ultraviolet (UV)-visible spectroscopy, transmission electron microscopy (TEM), and infrared (IR) spectroscopy (FTIR). The UV-visible spectra were recorded

with a Perkin-Elmer Lambda 25 spectrometer. The TEM images were taken with a Philips CM12 microscope working at 120-kV acceleration.

Polyurethane (PU) foams were soaked in silver nanoparticle solution overnight. For the saturated coating of 20 cm × 25 cm foam of 8 mm thickness ~1.5 L of the nanoparticle solution was required. This leads to saturation coverage. Partial coverage can be achieved for shorter exposure times or reduced nanoparticle concentrations. The sheets were washed repeatedly with water to remove any adsorbed ions like citrate and were air-dried. The as coated PU foams were characterized by optical microscopy, electron microscopy, and diffused reflectance spectroscopy. Scanning electron micrographs (SEMs) were taken with a JEOL 30-kV machine. UV-Vis-NIR diffuse reflectance spectra were recorded with a Varian 5E spectrometer. Optical microscopic images were taken with a Leica DC 150 microscope. FTIR studies were conducted using a Perkin-Elmer Spectrum One spectrometer.

Microbiological Experimentation

E. coli ATCC 25922 and *E. coli* MTCC 1302 were selected as indicators of fecal contamination of water. Nutrient broth was used as the growing medium. Bacteria were grown aerobically in nutrient broth at 37°C for 12 h. The cultures were centrifuged and the cells were washed and suspended in distilled water, reaching a final concentration of 1×10^5 – 1×10^6 CFU/mL.

Test Tube Test

For the test tube test, 10 mL *E. coli* suspension in distilled water was taken in sterilized test tubes. 1 cm × 9 cm × 0.6 cm pieces of the foam were put into the test tubes (one piece in each test tube). After 5 min and 10 min, the foam samples were taken out from the test tubes and were put

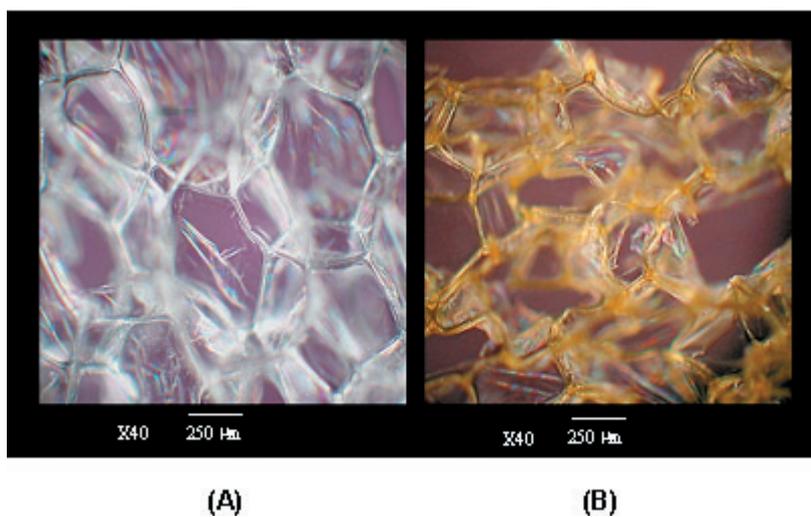


Figure 2. Optical microscopic image of pure polyurethane (PU) (A) and PU coated with silver nanoparticles (B).

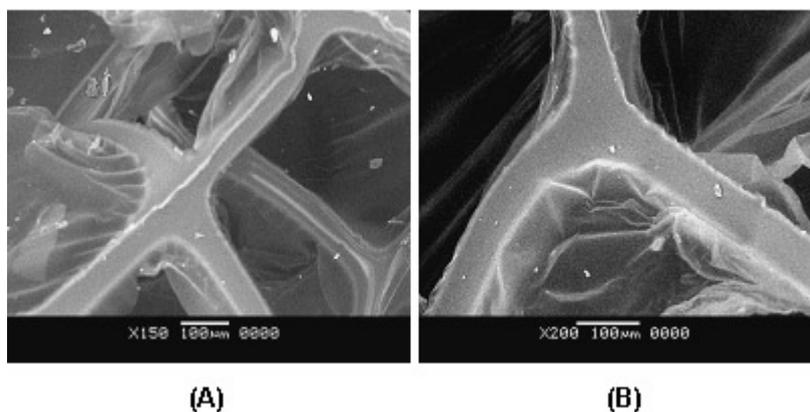


Figure 3. SEM of pure polyurethane (PU) (A) and PU coated with Ag nanoparticles (B).

into an empty test tube. They were squeezed to get the treated water. Plating was done with this treated water by series dilution method for 10^0 , 10^{-2} and 10^{-4} dilutions with nutrient agar and m-Endo agar. Plating was also done for the initial CFU count and with uncoated PU-treated solution. For every dilution, 10 μ L of the solution was plated. Plating was done by the pour plate method. Plates were incubated at 37°C for 24 h.

Flow Test

Antibacterial action was also checked at flow rates used in domestic water purifiers (0.5 L/min). Bulk solution (200 L) of *E. coli* MTCC 1302 of load 10^5 CFU/mL was prepared in tap water. This was passed through the material, which was wrapped around a ceramic water filter candle at a constant flow rate of 0.5 L/min. The foam was of 6-mm thickness and was wrapped twice on the candle of 157-mm diameter and 20-cm length, making the prototype. Output

water samples were taken at the regular intervals of 1 h for 4 h in sterilized conical flasks. Plating was done as above.

Zone of Inhibition

For the zone of inhibition test, nutrient agar was poured onto disposable sterilized Petri dishes and was allowed to solidify; 10 μ L of the bacterial water (10^5 CFU/mL) was streaked over the plate and was spread uniformly. Square pieces of both the coated and uncoated PU were gently placed over the solidified agar gel in different Petri dishes. This was done for both the bacterial strains. Plates were incubated at 37°C for 24 h. The above processes were repeated with m-Endo agar as the medium instead of nutrient agar.

RESULTS AND DISCUSSION

Morphology

Color of polyurethane foam changes from white to yellow when it is soaked in silver nanoparticle solution overnight.

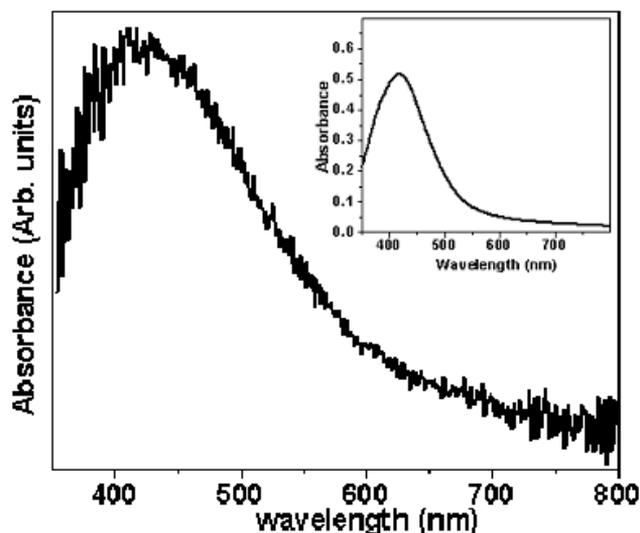


Figure 4. Diffused reflectance spectrum of polyurethane (PU)@Ag after baseline correction. UV-Vis spectrum of silver nanoparticles in solution is shown in the inset. PU@Ag shows a peak at 419 nm, which matches with UV-Vis peak of silver nanoparticles in solution.

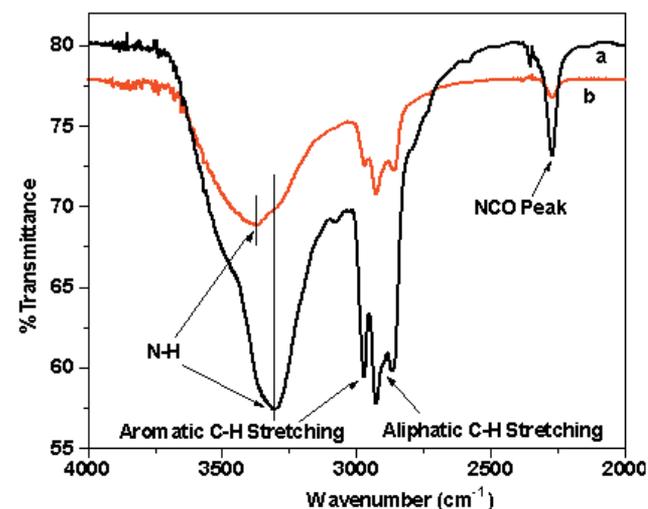


Figure 5. FTIR spectra of uncoated (a) and coated (b) polyurethane (PU).

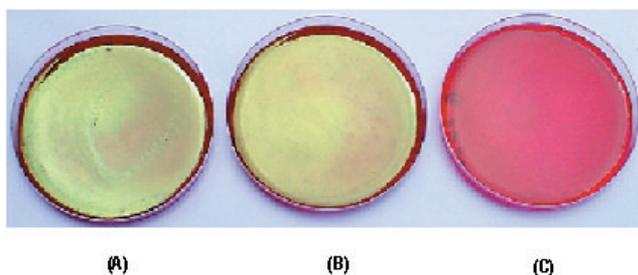


Figure 6. Test tube result for *Escherichia coli* MTCC 1302 for 10^{-2} dilution for 5-min exposure. **A:** Initial count. **B:** After exposure to pure polyurethane (PU). **C:** After exposure to nanoparticle-coated PU. Characteristic metallic sheen shown by *E. coli* is clearly visible in A,B, while the bacterium count was zero in C.

The saturated binding of nanoparticles on polyurethane gives a golden yellow color to it as is shown in Figure 1. There was no loss of nanoparticles after several (4–7 times) washing and drying operations and after keeping it for several months in a closed environment. Washing was done with distilled water and each time foam was kept in the water for ~20 min after which it was air dried.

Optical images of PU and PU coated with silver nanoparticles show incorporation of silver nanoparticles as yellow contours in the film as shown in Figure 2. The morphology of the film did not manifest any change as a result of nanoparticle incorporation.

SEM images of coated and uncoated PU are shown in Figure 3. The PU maintained its morphology upon coating with silver nanoparticles. It appears that the nanoparticle binding is on the surface. We have shown below that binding is due to interaction between nitrogen of the $-N(H-)$ of polyurethane and silver nanoparticles. We could not observe silver nanoparticles on the surface, probably due to specific surface characteristics of the foam. The surface of the foam is known to be highly porous which results in a large surface area. It is likely that the surface roughness of the foam is comparable to the dimensions of the nanoparticles and topography of the surface may not

reflect the presence of nanoparticles. At much larger magnifications, one could have observed the particles, but the insulating character of the film and the fact that its surface characteristics changed when the foam was gold coated to avoid charging, prevented us from observing the nanoparticles. However, EDAX analysis confirmed its presence.

Spectroscopy

Diffused reflectance spectrum of polyurethane coated with silver nanoparticles shows a peak at 419 nm, which clearly indicates the presence of silver nanoparticles (Fig. 4). The UV-Vis spectrum of the parent nanoparticle solution shows a peak around 420 nm (inset in Fig. 4). The data show that silver nanoparticles are not undergoing any change after coating onto the polyurethane surface.

FTIR studies show that binding is due to the interaction between the nitrogen of the $-N(H-)$ bond of polyurethane and silver nanoparticles. Spectra of the coated and uncoated samples in the region of relevance are shown in Figure 5. There is a significant shift in the $-N-$ peak upon nanoparticle coating, while all the other peaks remain unchanged. The shift observed for this peak is 63 cm^{-1} . It appears that not all the PU is involved in bonding as part of the $-NH$ stretch is unaffected, as expected.

Microbiological Results

After a contact time of 5 and 10 min with the PU coated with silver nanoparticles, there was no bacterium detected in the treated water (Fig. 6). For both *E. coli* strains, the output count was zero for all the dilutions. Control (pure PU) treated water showed substantial growth on nutrient as well as m-Endo agar. Initial water sample (input) showed overgrowth in almost all the cases.

There was no bacterium in the output water after passing through the coated foam for *E. coli* MTCC 1302 for a continuous and constant flow rate of 0.5 L/min. This was checked for input loads of 1×10^3 and 1×10^5 CFU/mL.

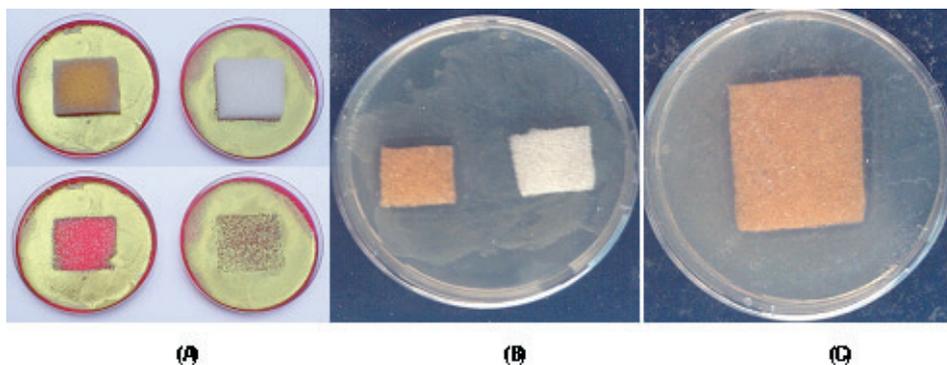


Figure 7. Zone of inhibition test results. **A:** Comparison of coated (yellow in color) and uncoated (white) for *Escherichia coli* ATCC 25922 with m-Endo agar plating. The pictures at the bottom were taken after lifting the polyurethane (PU) materials showing no growth below coated PU and growth below uncoated PU. Similar results were obtained for *E. coli* MTCC 1302. **B,C:** Comparison of the coated and uncoated PU for *E. coli*. ATCC 25922 with nutrient agar plating. Zone of inhibition is visible in B,C around coated PU.

There was no growth below the PU coated with nanoparticles while growth was seen in case of pure PU, which again confirms the antibacterial property of PU coated with silver nanoparticles (Fig. 7).

Using citrate-stabilized nanoparticles, the PU foams were also coated with Au. Color of the PU foams changed to purple after soaking it with gold nanoparticle solution. Antibacterial properties of this material were not evaluated. Similar experiments may be done with copper nanoparticles as well.

CONCLUSION

Silver nanoparticles can be coated onto polyurethane (PU) foams in diverse forms. This material can be washed, dried, and stored for extended periods without the loss of nanoparticles. The performance of the material as an antibacterial water filter was checked and no bacterium was detected in the output water when the input water had a bacterial load of 1×10^5 – 1×10^6 CFU/mL. The antibacterial action was also checked online for a flow rate of 0.5 L/min and no bacterium detected, which suggests that domestic use of this technology is possible. Other standard tests, such as the “zone of inhibition” and “test tube” tests, were also done to confirm the antibacterial properties of the material. The results are in line with the WHO requirements for drinking water. The experiments suggest the possibility of the use of this material in drinking water purification, air filtration, domestic and industrial air quality management, antibacterial packaging, etc. The chemicals involved in the synthesis of nanoparticles are commonly available, cheap, and non-toxic. The chemistry involved in the preparation of nanoparticle-coated foams is simple. These qualities make this technology adaptable to underdeveloped nations where bacterial contamination is the principal issue in drinking water. The technology can be implemented with minimum infrastructure and therefore offers a solution to the affected people without intermediaries. Along with other nanoparticles, the technology can offer complete anti-microbial solutions for rural communities.

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