**Fabrication of antibacterial water filter by coating silver nanoparticles on flexible polyurethane foams**

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**Abstract:** In this paper, we fabricated silver-coated polyurethane foams and used it as a bacterial filter for contaminated drinking water. Flexible PU foams were soaked in silver colloidal solutions for 10 h, then washed and air-dried at room temperature. The prepared silver colloidal solutions and silver-coated PU materials were characterized by several techniques including TEM, FESEM/EDS, UV-VIS, ICP-AAS, and Raman spectroscopy. The TEM images showed that the size of silver nanoparticles in colloidal solutions varies from 6 to 12nm. The Raman, FE-SEM/EDS and ICP-AAS data illustrated that silver nanoparticles were stable on the PU foam and were not washed away by water. Furthermore, the microbiological tests (tube tests and flow test) were carried out on silver-coated PU materials with the Coliforms, *E. coli*, and *B. subtilis*. The obtained results showed that the bacteria was killed completely with antibacterial efficiency of 100% being observed. Our research suggests that silver-coated polyurethane foams can be used as excellent antibacterial water filters and would have several applications in other sectors.

**Keywords:** Silver nanoparticles, polyurethane, *E. coli*, water filter

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**1. Introduction**

Water is the common breeding ground for many pathogens because it contains several bacteria, viruses, etc. The removal and inactivation of pathogenic microorganisms are the last step in the treatment of drinking water [1]. Currently available detection methods do not allow for the routine analysis of all microorganisms that could be present in inadequately treated drinking water. Instead, microbiology quality is determined by testing drinking water for total Coliforms and *Escherichia coli*, a bacterium that is always present in the intestines of humans and other animals. The presence of *E. coli* in drinking water would indicate faecal contamination of the water [1]. According to WHO, the maximum acceptable concentration of *E. coli* in drinking water is none detectable per 100mL [1, 2]. There are many treatment methods such as chemical (chlorine, iodine, etc), physical (ultraviolet light, ozone, radiation) or polymer films or synthetic and natural zeolites, etc [1-3]. During the past few years, advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly ameliorated using nanosorbents, nanocatalysis, etc and nanoparticles enhanced filtration resulting from the development of nanotechnology [4]. Flexible polyurethane (PU) foams have been extensively used in various applications because of their excellent biocompatibility and mechanical properties [6-8]. In 2004, Prashant Jain *et al.* [2] synthesized the silver colloidal solution by reduction AgNO\(_3\) using NaBH\(_4\), which is expensive and a toxic chemical,
and their microbiological test (flow test) on Ag-coated polyurethane were carried out with false water (purified water loaded \( E. \text{coli} \)). In this paper, we synthesized Ag colloids by reduction of silver nitrate using polyvinyl pyrrolidone as the capping agent. Microwave irradiation has been used as it offers several advantages over conventional heating. The main advantages of the method include (i) rapid initial heating process, (ii) uniform heat transfer to the solution, and (iii) significant reaction rate enhancement.

2. Experimental

2.1. Synthesis of silver colloidal solutions
Polyvinyl pyrrolidone (PVP, \( M_w \approx 1,000,000 \), China, 99%) and ethylene glycol (Merk, 99.9%) was poured into a 100mL pyrex becher. After the complete dissolution of PVP, silver nitrate \( \text{AgNO}_3 \) was added into the solution and stirred until the \( \text{AgNO}_3 \) was dissolved completely. The solutions were heated in a microwave oven (800W) for various concentrations of \( \text{AgNO}_3 \). Solutions at various \( \text{AgNO}_3 \) concentrations were heated in a domestic microwave oven at 800W.

2.2. Fabrication of silver-coated polyurethane foams
Polyurethane (PU) foams 50x50x6mm was washed by deionized water, dried and then soaked in silver colloidal solutions within 10 h. The sheets were washed repeatedly with water to remove any adsorbed chemical like PVP or ethylenglycol.

2.3. Characterization
The synthesized silver colloidal solutions and silver-coated polyurethane were characterized by analytical techniques such as UV-VIS Spectroscopy (Cary 100 Conc, Varian), TEM (JEM-1400), FESEM with EDS analyzer (JSM 7401F); Raman Scattering Spectroscopy (Horiba Jobin Yvon, Excition laser of 632.81 nm).

2.4. Microbiological tests
**Tube Test:** \( E. \text{coli} \) (Gram-negative bacteria) and \( B. \text{subtilis} \) (Gram-positive bacteria) were supplied by Faculty of Biology, University of Natural Sciences, VNU-HCMC. Antibacterial effects of the Ag colloidal solutions and Ag-coated polyurethane were studied by Colony Count Test Method [1]. The effect of bacterial strains was calculated, following the relation:

\[
\eta = \frac{N_2 - N_1}{N_1} \times 100\%
\]

where \( \eta \) is the percentage of bacterial reduction, \( N_1 \) is the number of surviving bacterial colonies from the control sample, and \( N_2 \) is the number of surviving colonies from test samples.

**Flow test:** Water (from a well at Thanh Long Company, Binh Chanh District, Ho Chi Minh City), flow rate of 50mL/min. Total Coliforms and \( E. \text{coli} \) were determinate by Most Probable Number (MPN) Method [1]:

**Total Coliforms**
* For each sample to be tested add the following amounts:
  5x10ml to 10ml double strength lauryl sulphate broth (LSB)
  5x1ml to 5 bottles single strength LSB
  5x0.1ml to 5 bottles single strength LSB
* Ensure Durham tubes were completely filled. Incubate at 37°C.
* The tube that produces gas in LSB media was selected and was grown it into Brilliant Green Lastose Bile Salt (BGBL) media. Incubate at 37°C
* Examine for: Growth – turbidity; Acid production - a yellow coloration; Gas - trapped in Durham tube. Tubes that produce acid and gas were positive scored.
* Derive the McCarty index and calculate the MPN/100mL. \( E. \text{coli} \)
* The tube that produced gas in LSB media was selected and was grown into EC media. Incubate at
45°C in 24 h.
* The tube that produce gas in EC media was selected and was grown into EMB media agar Petri dish.
* Purple colonies with gas ⟷ presumptive E. coli ⟷ IMViC test (Indol, Methyl Red, Vogues-Prokaure, Citrate) ⟷ If Indol (+), Methyl red (+), Vogues- Prokaure (-), Citrate (-) ⟷ E. coli (+)
* Derive the McCarty index and calculate the MPN/100mL.

3. Results and discussion

3.1. Synthesis and characterization of Ag colloidal solutions
Four Ag colloidal solutions were synthesized by microwave irradiation (table 1). The results of UV-VIS measurements in table 1 showed that silver nanoparticles were presented in solutions. The size and the shape of nanoparticles were illustrated clearly via TEM images (figure 1, figure 2, figure 3 and figure 4). It was observed that the nanoparticles had spherical shape and their major size were essential from 7 – 11 nm (P1); 7 – 14 nm (P2); 6 – 11 nm (P3); 6 – 12 nm (P4). These shapes and sizes are suitable for killing bacteria, virus, and fungus. Indeed, these colloidal solutions exhibit highly efficient antibacterial properties (antibacterial efficiency of 100%) at very low concentration (table 2 and 3). The differences between gram-positive (B. subtilis) and gram-negative (E. coli) anti-bacteria efficiency were shown clearly (at concentration of 50ppm, antibacterial efficiency of gram-positive is 99.79% and of gram-negative is 100%). These differences could be explained based on the structure of their cell walls. The gram-negative bacteria have a layer of lipopolysaccharide at the exterior, followed underneath by a thin (about 7–8 nm) layer of peptidoglycan. Although the lipopolysaccharides are composed of covalently linked lipids and polysaccharides, they lack strength and rigidity. Negative charges on the lipopolysaccharides are attracted towards weak positive charges available on silver nanoparticles. On the other hand, the cell wall in gram-positive bacteria is principally composed of a thick layer (about 20–80 nm) of peptidoglycan, consisting of linear polysaccharide chains cross-linked by short peptides to form a three dimensional rigid structure. The rigidity and extended cross-linking not only endow the cell walls with fewer anchoring sites for the silver nanoparticles but also make them difficult to penetrate [9].

| Samples | Ethylene glycol (ml) | PVP (g) | AgNO₃ (g) | Absorbance peak of UV-VIS (nm) |
|---------|---------------------|---------|-----------|-----------------|
| P0      | 50                  | 0.0752  | 0         |                 |
| P1      | 50                  | 0.0752  | 0.015     | 406             |
| P2      | 50                  | 0.0752  | 0.051     | 407             |
| P3      | 50                  | 0.0752  | 0.071     | 408             |
| P4      | 50                  | 0.0752  | 0.121     | 410             |

Figure 1. TEM image (magnification of 200 nm) and size distribution of Ag nanoparticles in P1 solution.

Figure 2. TEM image (magnification of 50 nm) and size distribution of Ag nanoparticles in P2 solution.
3. Fabrication and characterization of Ag-coated polyurethane

Four Ag-coated polyurethane foams were fabricated by soaking in four different Ag colloidal solutions. The results of FESEM/EDS and ICP-AAS proved clearly the presence of Ag nanoparticles in polyurethane foam sheets (figure 5 and table 4). Moreover, Raman spectroscopy of polyurethane (M0) and Ag-coated polyurethane (M1, M2, M3) showed that linkages of Ag-coated polyurethane samples changed very strongly in comparison with uncoated sample (figure 6, figure 7, figure 8, figure 9). The Raman spectroscopy of uncoated polyurethane (M0) matched that of polyurethane in the research works of J. W. Cho [5], and C.C Wei [6, 7]. The Raman peaks of M0 are 1450, 2750, 2900 cm\(^{-1}\) (O=C=N-); 1100, 1650 cm\(^{-1}\) (C=O); 1185 cm\(^{-1}\) (N-H). In Raman spectroscopy of M1, M2, M3, these Raman peaks disappear. This could explain the interaction between the nitrogen (of the N-H bond), oxygen (of the C=O or N=C=O bond) and silver nanoparticles.

### Table 2. Colony density and Gram-negative (E. coli) antibacterial efficiency of nano Ag colloidal solutions.

| Samples       | M\(_i\) (CFU/ml) | \(\eta\) (%) |
|---------------|------------------|--------------|
|               | 15 min. | 5 h     | 24 h     | 15 min. | 5 h     | 24 h     |
| Control sample| 2.25.10\(^5\)  | 2.29.10\(^7\) | 2.31.10\(^9\) |          |          |          |
| 10ppm         | 2.90.10\(^4\)  | 6.20.10\(^2\) | 0       | 87.11   | 99.99   | 100      |
| 20ppm         | 4.65.10\(^3\)  | 0       | 0       | 97.93   | 100     | 100      |
| 50ppm         | 0       | 0       | 0       | 100     | 100     | 100      |

### Table 3. Colony density and Gram-positive (B. subtilis) antibacterial efficiency of nano Ag colloidal solutions.

| Samples       | M\(_i\) (CFU/ml) | \(\eta\) (%) |
|---------------|------------------|--------------|
|               | 15 min. | 5 h     | 24 h     | 15 min. | 5 h     | 24 h     |
| Control sample| 1.95.10\(^5\)  | 2.41.10\(^7\) | 1.42.10\(^9\) |          |          |          |
| N\(_1\) (10 ppm) | 1.96.10\(^4\)  | 1.29.10\(^2\) | 0       | 89.95   | 99.99   | 100      |
| N\(_2\) (20 ppm) | 9.0.10\(^3\)   | 7.7.10\(^1\)  | 0       | 95.85   | 99.99   | 100      |
| N\(_3\) (50 ppm) | 4.45* 10\(^2\) | 0       | 0       | 99.79   | 100     | 100      |
Figure 5. FESEM image and EDS analysis of Ag-coated Polyurethane foam C%:92.32; O%:1.39; Ag%:6.29.

Table 4. The ICP-AAS results of Ag nanoparticles content of polyurethane sheets.

| Samples | Ag nanoparticles content (g) of polyurethane sheets (kg) |
|---------|---------------------------------------------------------|
| M1      | 0.25                                                    |
| M2      | 0.72                                                    |
| M3      | 0.96                                                    |
| M4      | 2.80                                                    |

3.3. Microbiological test on Ag-coated polyurethane

3.3.1. Tube test
The results of microbiological test in tube test conditions were presented in table 5. The E. coli was killed after 15 min. with the antibacterial efficiency of over 95% being observed, and were killed completely after 5 h for all Ag-coated polyurethane sheets. Contrary to Ag-coated polyurethane sheets, it was found that colony density of uncoated polyurethane sample (M_o) increase significantly to soaking time (from 2.45.10^5 after 15 min. to 1.43.10^6 after 5 h and to 2.43.10^9 after 24 h).

Figure 6. Raman spectroscopy of polyurethane foam. Figure 7. Raman spectroscopy of Ag-coated polyurethane foam (M1).
Table 5. Colony density and Gram-negative (E. coli) antibacterial efficiency of Ag-coated polyurethane foam.

| Samples | $M_i$ (CFU/ml) | 15 min. | 5 h | 24 h | 15 min. | 5 h | 24 h |
|---------|----------------|---------|-----|------|---------|-----|------|
| M0      | 2.45.10^5      | 1.43.10^6 | 2.43.10^9 |
| M1      | 1.20.10^3      | 0       | 0   | 95.10 | 100    | 100 |
| M2      | 7.65.10^2      | 0       | 0   | 96.88 | 100    | 100 |
| M3      | 5.95.10^2      | 0       | 0   | 97.57 | 100    | 100 |
| M4      | <10            | 0       | 0   | 99.99 | 100    | 100 |

3.3.2. Flow test
The results of the microbiological test on Ag-coated polyurethane in flow test condition confirmed the antibacterial property of these materials. Input water samples, which were received from a well at Binh Chanh District, had total coliforms of 45 MPN/100 ml, E. coli density of 30 MPN/100 ml (sample 1) and coliforms density of 110 MNP/100 ml, E. coli density of 70 MPN/100 ml (sample 2) (figure 10, figure 11, table 6). After testing two samples, it was found that no bacteria were detected.

Figure 10. Anti-Coliforms ability of water filter containing Ag-coated polyurethane.
4. Conclusions

Silver colloidal solutions were synthesized rapidly by using microwave irradiation. The UV-VIS measurements showed that these as-synthesized samples have absorbance peak at 406-410 nm. The major size of silver nanoparticles was about 6-12 nm via TEM images. These colloidal solutions had highly efficient gram-negative (E. coli) and gram-positive (B. subtilis) antibacterial property at very low concentration. The antibacterial efficiency increased when increasing the concentration of silver solutions and the exposure time.
The Ag-coated polyurethane foams were fabricated successfully. The results of Raman, FE-SEM/EDS and ICP-AAS demonstrated that silver nanoparticles strongly immobilized to the polyurethane foams sheet by the chemical linkage. The results of the microbiological test on Ag-coated polyurethane in tube test conditions showed that these materials exhibited highly efficient gram-negative antibacterial property.

The results of the microbiological test on Ag-coated polyurethane in flow test condition confirmed the antibacterial property of these materials. Using input water received from a well at Binh Chanh, it was found that no bacteria were detected. Our research suggests that silver-coated polyurethane foams can be used as excellent antibacterial water filters and could offer several applications in other sectors with simple treatment systems (figure 12).

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