FABRICATION OF ANTIBACTERIAL WATER FILTER BY COATING SILVER NANOPARTICLES ON FLEXIBLE POLYURETHANE FOAMS

Nguyen Thi Phuong Phong, Ngo Vo Ke Thanh, Phan Hue Phuong
Laboratory for Nanotechnology, VNU-HCM
(Manuscript Received on December 19th, 2008, Manuscript Revised February 10th, 2008)

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 10hrs, 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, FE-SEM/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. subtillis. The obtained results showed that the bacteria were killed completely with antibacterial efficiency of 100% being observed. Our research suggests that silver-coated polyurethane foams can be used as excellent good antibacterial water filters and would have several applications in other sectors.*

Keywords: *Silver nanoparticles, Polyurethane, E.coli, Water filter*

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 presence 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[1,2,3]. 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 [6,7,8]. In 2004, Prashant Jain et al. [2] synthesized the silver colloidal solution by reduction $AgNO_3$ using $NaBH_4$, which is expensive and toxic chemical, and their microbiological test (flow test) on Ag-coated polyurethane were carried out with false water (purified water loaded *E. coli*). In this paper, we synthesized Ag colloids by reduction of silver nitrate using polyvinyl pyrolidone as the capping agent. Microwave irradiation has been used as it offers many 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

Synthesis of silver colloidal solutions: Polyvinyl pyrrolidone (PVP, *Mw* ≈ 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 $AgNO_3$ was added into the solution and stirred until the $AgNO_3$ was dissolved completely. The solutions were heated in a microwave oven (800W) for various concentrations of $AgNO_3$. Solutions at various $AgNO_3$ concentrations were heated in a common microwave oven at 800W.

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

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

Microbiological tests

Tube Test: *E. coli* (Gram-negative bacteria) and *B. 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:

$$\eta = \frac{N1 - N2}{N1} \times 100\%$$

Where η 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. coli* were determinated by Most Probable Number (MPN) Method [1]:

Total Coliforms

* For each sample to be tested add the following amounts:

5x10ml to10ml 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 Brillant Green Lastose Bile Salt (BGBL) media. Incubate at 37°C

* Examine for: Growth – turbidity; Acid production - a yellow coloration; Gas - trapped in Durham tube. Those tubes that produce acid and gas were scored **positive.**

* Derive the McCarty index and calculate the MPN/100mL.

E.Coli

* The tube that produces gas in LSB media was selected and was grown it into EC media. Incubate at 45°C in 24hrs.

* The tube that produces gas in EC media was selected and was grown it 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 DISCUSSIONS

Synthesis and characterization of Ag Colloidal solutions

Four Ag colloidal solutions were synthesized by microwave irradiation (Table 1). The results of UV-Vis in Table 1 showed that silver nanoparticles were presented in solutions. The size and the shape of nanoparticles were illustrated clearly via TEM images (Fig1, Fig.2, Fig.3, Fig.4). It was observed that the nanoparticles had spherical shape and their major size were essential from 7 – 11nm (P1); 7 - 14nm (P2); 6 – 11nm (P3); 6 – 12nm (P4). These shape and size are suitable for killing bacteria, virus, and fungus. Indeed, these colloidal solutions exhibit highly efficient antibacterial property (antibacterial efficiency of 100%) at very low concentration (Table 2, Table 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].

Table 1. The UV-Vis absorbance peak of nano Ag colloidal solutions

Samples	Ethylene glycol(ml)	PVP(g)	$AgNO_3$(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

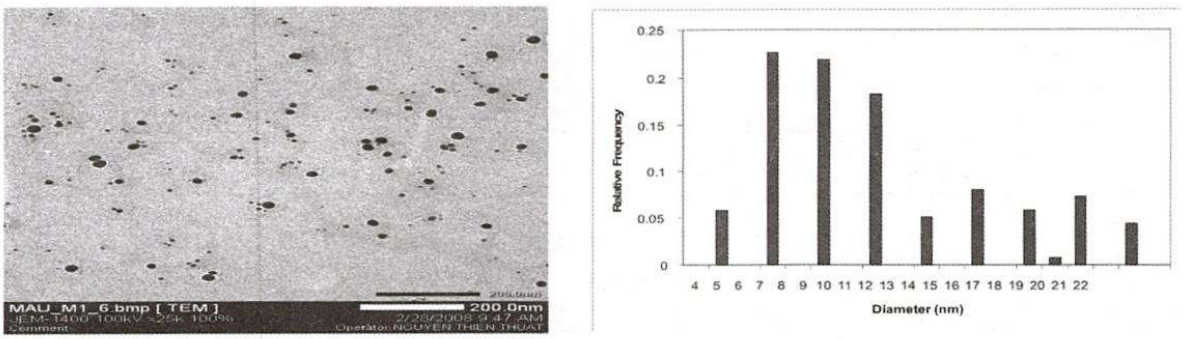

Fig 1. TEM image (magnification of 200nm) and size distribution of Ag nanoparticles in P1 solution

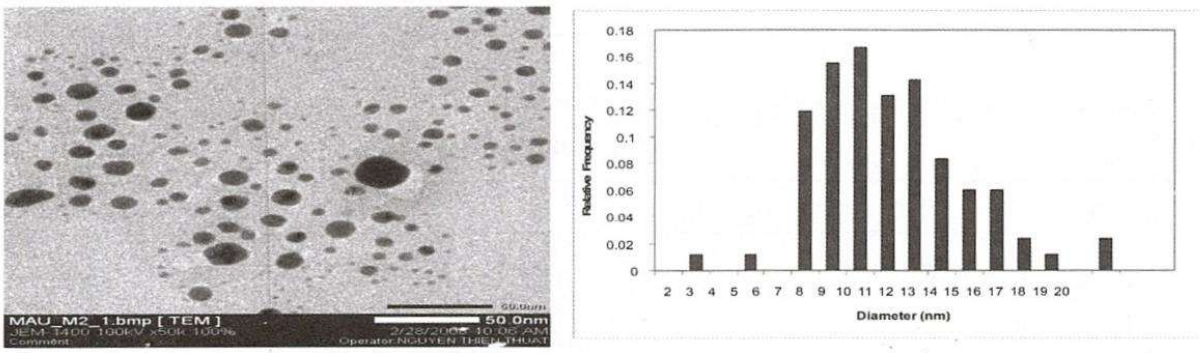

Fig 2. TEM image (magnification of 50nm) and size distribution of Ag nanoparticles in P2 solution

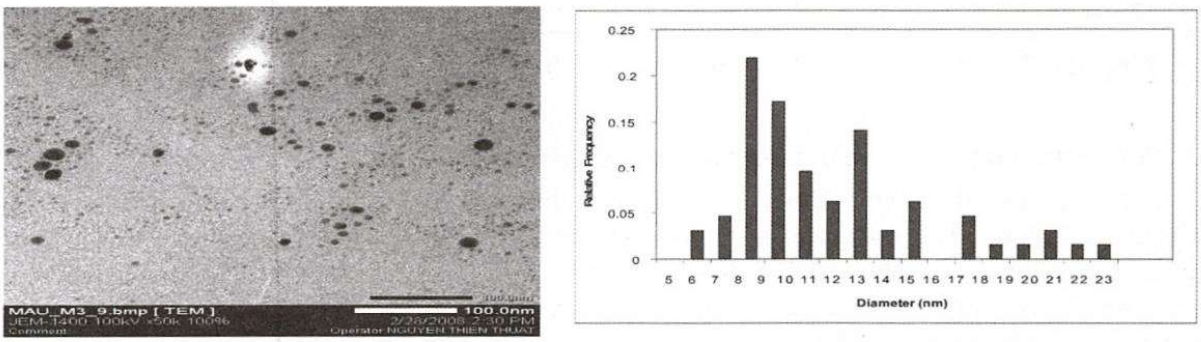

Fig 3. TEM image (magnification of 100nm) and size distribution of Ag nanoparticles in P3 solution

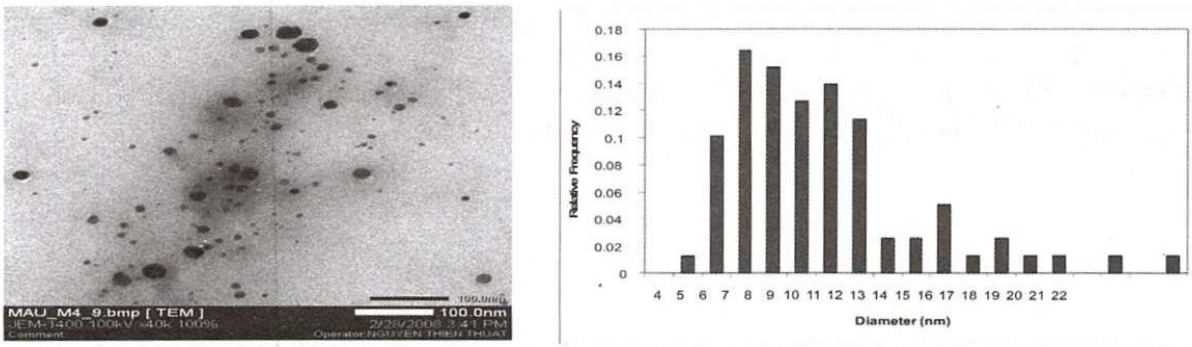

Fig 4. TEM image (magnification of 100nm) and size distribution of Ag nanoparticles in P4 solution

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

Samples	M_i (CFU/ml)			η (%)		
	15mins	5hrs	24hrs	15mins	5hrs	24hrs
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.Sutilis) antibacterial efficiency of nanoAg colloidal solutions

Samples	M_i (CFU/ml)			η (%)		
	15min	5hrs	24hrs	15min	5hrs	24hrs
Control samle	$1.95.10^5$	$2.41.10^7$	$1.42.10^9$			
N_1 (10ppm)	$1.96.10^4$	$1.29.10^2$	0	89.95	99.99	100
N_2 (20ppm)	$9.0.10^3$	$7.7.10^1$	0	95.85	99.99	100
N_3 (50ppm)	$4,45* 10^2$	0	0	99.79	100	100

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 FE-SEM/EDS and ICP-AAS proved clearly the presence of Ag nanoparticles in polyurethane foam sheets (Fig.5 and Table 4). Moreover, Raman spectroscopy of polyurethane (M_0) and Ag-coated polyurethane (M_1, M_2, M_3) showed that linkages of Ag-coated polyurethane samples changed very strongly in comparison with uncoated sample (Fig. 6, Fig.7, Fig.8, Fig.9). The Raman spectroscopy of uncoated polyurethane (M_0) matched that of polyurethane in the research works of J.W.Cho [5], and C.C Wei [6,7]. The Raman peaks of M_0 are 1450, 2750, 2900 cm^{-1} (O=C=N-); 1100, 1650 cm^{-1} (C=O); 1185 cm^{-1} (N-H). In Raman spectroscopy of M_1, M_2, M_3, these Raman peaks disappear. This could be explained the interaction between the nitrogen (of the N-H bond), oxygen (of the C=O or N=C=O bond) and silver nanoparticles.

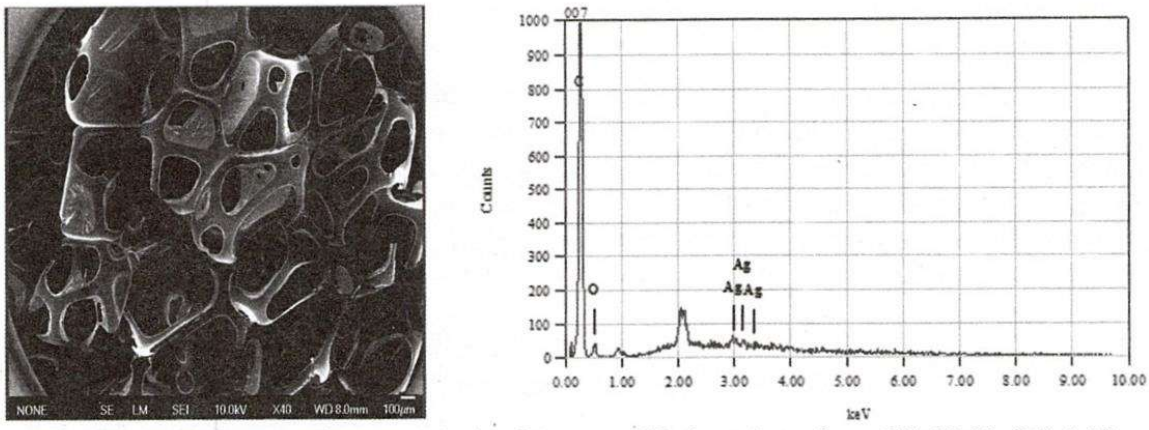

Fig. 5. FE-SEM image and EDS analysis of Ag-coated Polyurethane foam C%:92.32; O%:1.39; Ag%:6.29

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

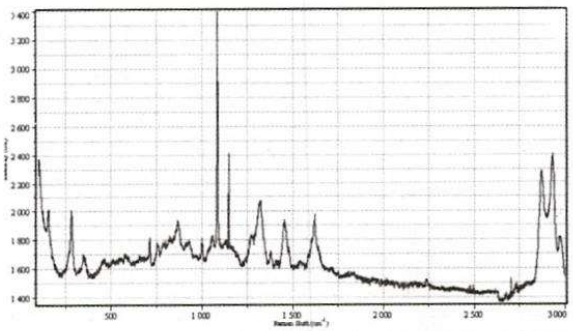

Fig. 6. Raman spestrocopy of polyurethane foam

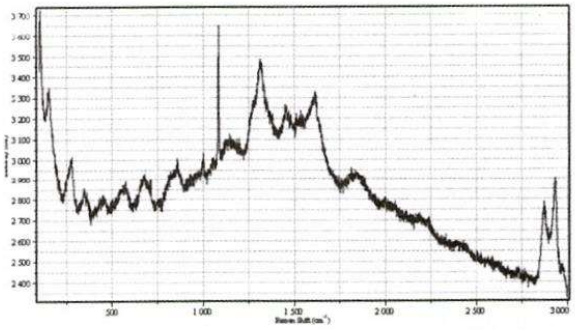

Fig. 7. Raman spectroscopy of Ag-coated polyurethane foam (M1)

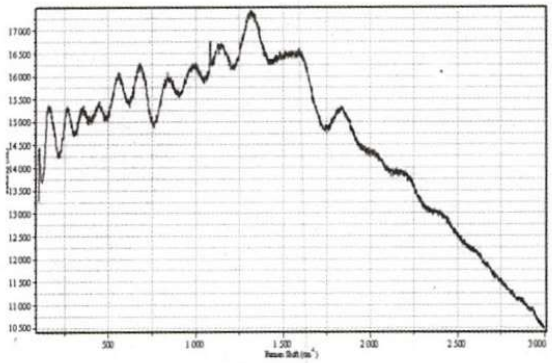

Fig. 8. Raman spectroscopy of Ag-coated polyurethane foam (M2

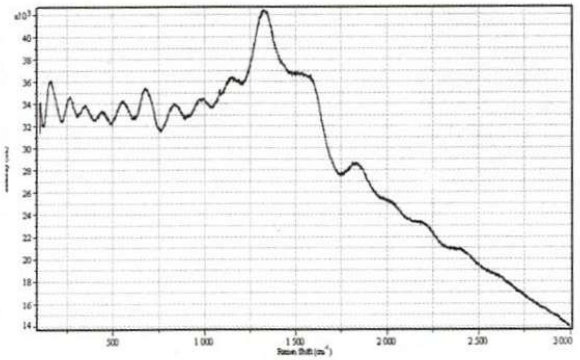

Fig. 9. Raman spectroscopy of Ag-coated polyurethane foam (M3)

Microbiological test on Ag-coated polyurethane

Tube test

The results of microbiological test in tube test condition were presented in Table 5. The *E.coli* was killed after 15min with the antibacterial efficiency of over 95% being observed, and were killed completely after 5hrs for all Ag-coated polyurethane sheets. Contrary to Ag-coated polyurethane sheets, it was found that colony density of uncoated polyurethane sample (M_0) increase significantly to soaking time (from $2.45.10^5$ after 15mins to $1.43.10^6$ after 5hrs and to $2.43.10^9$ after 24hrs).

Table 5. Colony density and Gram-negative (E.coli) antibacterial efficiency of Ag-coated polyurethane foam

Samples	M_i (CFU/ml)			η (%)		
	15min	5 hrs	24hrs	15min	5 hrs	24 hrs
M_0	$2.45.10^5$	$1.43.10^6$	$2.43.10^9$			
M_1	$1.20.10^3$	0	0	95.10	100	100
M_2	$7.65.10^2$	0	0	96.88	100	100
M_3	$5.95.10^2$	0	0	97.57	100	100
M_4	<10	0	0	99.99	100	100

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/100mL, *E.coli* density of 30 MPN/100ml (Sample1) and coliforms density of 110 MNP/100mL, *E.coli* density of 70 MPN/100mL (Sample 2) (Fig.10, Fig.11, Table 6). After testing two samples, it was found that no bacteria were detected.

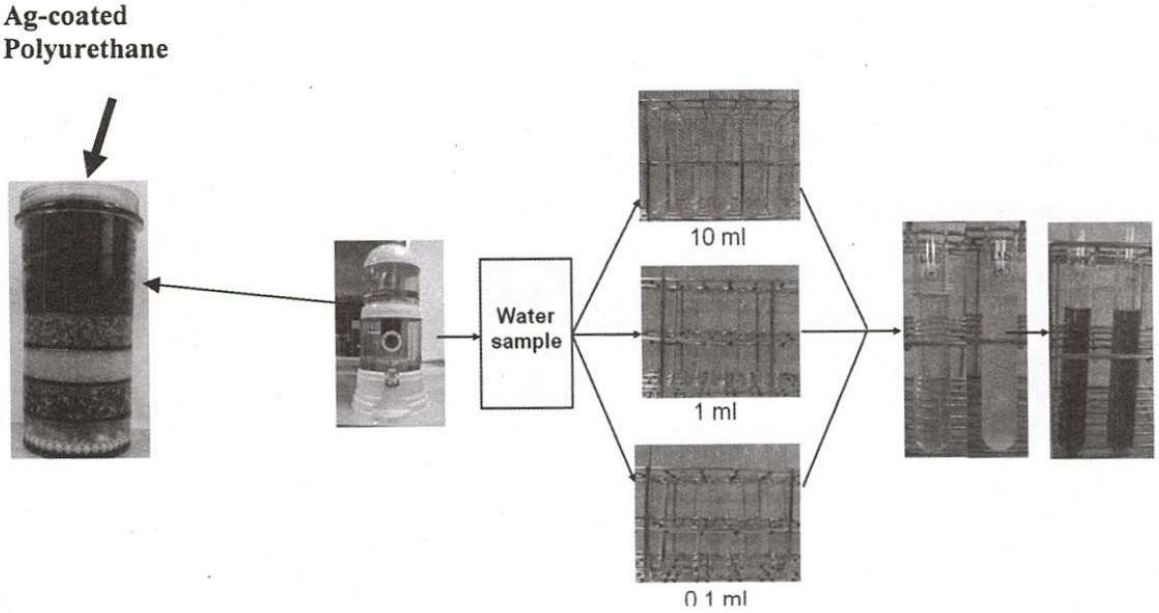

Fig 10. Anti-Coliforms ability of water filter containing Ag-coated polyurethane

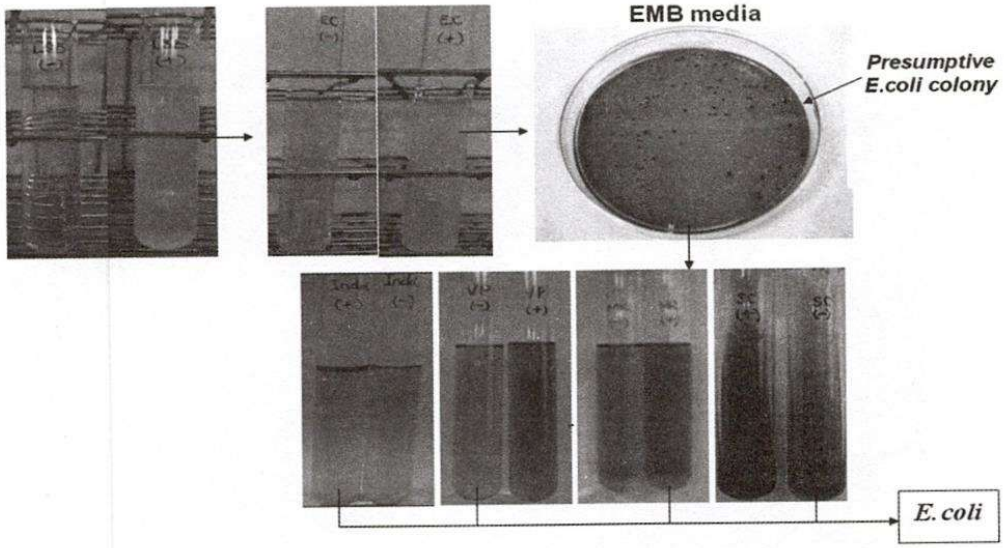

Fig. 11. Anti-E.coli ability of water filter containing Ag-coated polyurethane

Table 6. The Coliforms and E. coli density results of water treated with Ag-coated and uncoated polyurethane water filter

Samples	Coliforms Density (MPN/100ml)		*E.coli* Density (MPN/100ml)	
	Uncoated PU	Ag-coated PU	Uncoated PU	Ag-coated PU
Number 1	45	0	30	0
Number 2	110	0	70	0

4.CONCLUSIONS

1.Silver colloidal solutions were synthesized rapidly by using microwave irradiation. The UV-Vis showed that these as-synthesized samples have absorbance peak at 406-410nm. The major size of silver nanoparticles was about 6-12nm 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 sliver solutions and the exposure time.

2.The Ag-coated polyurethane foams was 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 condition showed that these materials exhibited highly efficient Gram-negative antibacterial property.

3. The results of the microbiological test on Ag-coated polyurethane in flow test condition confirmed the antibacterial property of these materials. Using input water receives 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 simply treatment system (Fig. 12)

Fig. 12. Bacteria contaminated drinking water treatment system by Ag-coated polyurethane foams

CHẾ TẠO VẬT LIỆU NANO BẠC MANG TRÊN MÚT XỐP POLYURETHAN ỨNG DỤNG LỌC NƯỚC UỐNG NHIỄM KHUẨN

Nguyễn Thị Phương Phong, Ngô Võ Kế Thành, Phan Huệ Phương
Phòng Thí nghiệm Công nghệ Nano, ĐHQG-HCM

TÓM TẮT: *Trong bài báo này chúng tôi chế tạo vật liệu mút xốp polyurethane mang các hạt nano bạc (PU@Ag) sử dụng lọc nước uống nhiễm khuẩn. Polyurethane được ngâm với dung dịch keo nano bạc trong thời gian 10 giờ. Các phương pháp phân tích hóa lý hiện đại như TEM, FE-SEM/EDS, UV-Vis, ICP-AAS và Raman được sử dụng để xác định các tính chất lý hóa của dung dịch keo nano bạc và vật liệu PU@Ag đã điều chế được. Ảnh TEM và kết quả UV-Vis cho thấy hạt nano bạc trong dung dịch keo có kích thước từ 6 đến 12nm. Những kết quả phân tích trên phổ Raman, FE-SEM/EDS and ICP-AAS cho thấy các hạt nano bạc bám chặt vào trong nền polyurethan. Các thử nghiệm vi sinh được thực hiện trên vật liệu lọc PU@Ag với Coliforms, E. coli, B. subtillis trong điều kiện tĩnh (trong ống nghiệm) và động (mô hình dòng chảy). Các kết quả cho thấy các vi khuẩn trên bị tiêu diệt hoàn toàn và phân tích không phát hiện bạc trong nguồn nước, nước được xác nhận là uống được.*

Từ khóa*: Silver nanoparticles, Polyurethane, E.coli, Water filter*

REFERENCES

[1]. E. Greenberg, L. S.Clesceri, Andrew D. Eaton, *Standard Methods 18th Edition 1992, for examination of water and wastewater.*

[2]. P. Jain, T. Pradeep, *Biotechnology and bioengineering*, Vol.90, No.1, (2005).

[3]. Y Chen., L.Wang, S Jiang., *Journal of Polymer Materials 20:279-284*, (2003).

[4]. N.Savage, M.S. Diallo, *Journal of Nanoparticle Resarch 7:331-342*, (2005).

[5]. Jae Whane Cho, Jung Hyun So, *Materials Letter 60*, 2653-2656, (2003).

[6]. C.Chih-Wei, H. Shan-hui et al., *Polymer Degration and Stability No. 91*, 1017-1024, (2006).

[7]. U.Samuel, J.P.*Guggenbicher International Journal of Antimicrobial Agents* 23S1, S75-S78, (2004).

[8]. H.Shan-Hui, C.Chei-Wei, *Polymer Degration and Stability No. 85*, 675-680 (2006).

[9]. S.Siddhartha, B. Tanmay, *Nanotechnology 18,* 225103 (9pp.), (2007).

[10]. P.Shane, K.Min, M. Cakmak, Polymer 44, pp.5137-5144, (2003).