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# Microstructural and antibacterial properties of silver nanoparticle-decorated porous polyurethane surface for water purification

Marzieh Nadafan[a,*], Rasoul Malekfar[a], Ali Izadi-Darbandi[b], Zahra Dehghani[c]

[a]*Department of Physics, Tarbiat Modares University, P.O. Box 14115–175, Tehran, I.R. Iran, emails: m.nadafan@modares.ac.ir (M. Nadafan), malekfar@modares.ac.ir (R. Malekfar)*
[b]*Department of Agronomy and Plant Breeding Sciences, College of Aburaihan, University of Tehran, Postal code 3391653775, Tehran, I.R. Iran, email: aizady@ut.ac.ir*
[c]*Faculty of Basic Sciences, Department of Physics, University of Neyshabur, Neyshabur, I.R. Iran, email: z_dehghani2004@yahoo.com*

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## ABSTRACT

Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy, and optical micrograph studies on silver nanoparticle-decorated polyurethane confirmed that silver nanoparticles were not washed away by repeated washing or immersion in an ultrasonic bath and keeping the treated foams for several weeks at the room temperature. Morphology of the foam did not change after coating with silver colloidal solution. According to the FTIR spectra, the nanoparticle binding is due to the interaction of silver atoms on the surface of the nanoparticles with the nitrogen atom at polyurethane foam. Highly antibacterial effects of polyurethane foams coated with silver nanoparticles were characterized through growth curve studies and colony counting of *Escherichia coli* on the LB (Luria Bertani) broth and LB-Agar media, consequently. Considering the low cost and effectiveness in prohibiting the growth of *E. coli*, this technology may have large implications for decontamination of liquid or solid environments.

*Keywords:* Antibacterial; Silver nanoparticle; Polyurethane; *E. coli*

## 1. Introduction

In recent years, incorporation or deposition of various particles in/on various inorganic host matrices on polymer-based composite materials field is being vastly noticed in research due to the reinforced properties and potential applications in optics, energy storage, catalysis, sensors, biological labeling, and environmental remediation [1–5].

Several metal or metal oxide particles like Au, Ag, and ZnO have been incorporated in various polymeric matrices. Among these, the antibacterial properties of metallic silver (Ag) have been known for centuries with the ancient Greek silver pots and spoons, in which dissolving of silver ions from the surface of the bulk silver has occurred [1,6].

As it was known, the bactericidal effect of bulk silver is long-lasting and stable [6]. Recently, compared with the silver bulk, utilizing silver nanoparticles as antimicrobial agents is more effective and their applications has increased in the plastics, health, textile and

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*Corresponding author.

paint industries [7–12]. Moreover, the application of bulk silver is not economical; especially in industrial or domestic applications because of its high price and low ion release rate. Therefore, nanoparticles are expected to play a crucial role in antimicrobial industry, the same as other industries.

Some researchers have studied the properties of silver-enhanced polymer composites in various polymer matrices, including polyethylene, polyvinyl alcohol, polyacrylonitrile, nylon, and polystyrene [11,13–19]. Polyurethane is a commonly used polymer with vast applications in different forms such as elastomers, fibers, and foams. Actually, the shape memory properties using polyurethane block copolymer have been interestingly noticed by tailoring their structure and properties because of controlled combination of hard and soft segments of polyurethane [13,20–22]. A few studies have tried the combination of silver nanoparticles in a polyurethane matrix to enable antimicrobial effects and further enhance their functionality in this field [23].

Water is the common breeding ground for several bacteria, viruses, etc. The removal and inactivation of pathogenic microorganisms are the last step in the treatment of drinking water [23]. Currently, available detection methods do not allow for the routine analysis of all microorganisms. The presence of *Escherichia coli* in drinking water would indicate fecal contamination of the water. There are many treatment methods such as chemical (chlorine, iodine, etc.), physical (ultraviolet light, ozone, radiation) or polymer films or synthetic and natural zeolites [23]. 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 [23].

Compared to other water treatment materials, polyurethane with high porosity does not distort during operation. Their long lifetime, high flexibility, low fabrication cost, and resistance to high pressure and corrosive solutions make them a very cost-effective and economical water treatment material [24].

The aim of this article was to evaluate the antibacterial properties of the polyurethane foam coated with silver nanoparticles. The same mechanism of antibacterial effect of Ag with waterborne polyurethane (elastomer), Ag with ceramic, and Ag with polyurethane foam have been reported in the literature [7,23,25,26]. Our study was carried out precisely under conditions similar to the real situation. For instance, the bacterial growth medium contained high nutrition level. In this type of medium, the activation of bacteria could be controlled and decreased at the lowest cost.

The experiments showed that the treated *E. coli* cells were damaged owing to immersion of polyurethane plates in silver colloidal solution. The –N (H) COO– (carbamate) group of polyurethane is expected to bind with the surface of the nanoparticles and to lead to reduced bacterial activity [23]. *E. coli*, as the indicator of fecal contamination, was chosen in this study.

The results obtained could have great potential applications in rural communities and in the developing countries as well as in the industries related to polyurethane. Here, we report on the structural properties of PU, loaded with Ag nanoparticles, along with resultant antimicrobial activity that can be applicable in water filtration.

## 2. Experimental

### 2.1. Materials

The polyurethane foam material composed of two commercially available reactants: components A and B; polyisocyanate and polyol, respectively, both of which are in the liquid form supplied by Exxon Panah Co., Iran (Semi Rigid Open Cell-SROC-polyurethane foam). The polyisocyanate employed was diphenylmethane diisocyanate (MDI, $\rho = 1.23\ \mathrm{g/cm^3}$), and component B was based on polyether polyol ($\rho = 1.1\ \mathrm{g/cm^3}$), the blowing agent (water), the catalyst and the surfactant. The perfect solvent for polyurethane, N,N-dimethylformamide (DMF), silver nitrate ($AgNO_3$), and trisodium citrate were purchased from Merck (Germany). We assume that for preparing of 1 $m^2$ foam, total price of all material will be 17 USD that can be used currently for water filtration.

### 2.2. Preparation of silver colloid

Colloidal silver nanoparticles were prepared in an aqueous solution by reduction of silver nitrate with sodium citrate according to the method reported by Lee and Meisel [27]. Thirty-six milligrams of silver nitrate was added into 200 ml distilled water. The solution was heated to boiling and 4 ml of 1% trisodium citrate solution was added. The solution was boiled for one and a half hours, and the gray silver colloid was obtained after cooling at the ambient temperature, which was stable for several days or weeks [28]. The concentration of silver nanoparticles in colloid is $1.04 \times 10^{-3}$ M.

### 2.3. Preparation of blank polyurethane

The one-step system is a common procedure for fabricating the polyurethane foam [29]. For blank polyurethane foam, two components (component A: polyisocyanate and component B: polyether polyol, the blowing agent, the catalyst, and the surfactant) mixed at a 1:1 ratio (1 cc for each component) at 2,000 rpm for about 10 s in an open cylindrical mold using MS2 minishaker (IKA, Germany) at the room temperature. No heating is necessary for mixing. The polymerization reaction begins to start and simultaneously foaming appears due to $CO_2$ gas generation [30]. For good sample preparation and emerging $CO_2$ gas during the reaction time, the container cover was taken off.

### 2.4. Surface functionalization of polyurethane plates with silver colloidal nanoparticles

The polyurethane foam with 2-mm thickness was soaked in a previously prepared colloidal silver solution at the room temperature overnight (8 h). For the saturated coating of cylindrical mold of polyurethane foams with 1-cm radius and 2-mm thickness, 60 cc of the nanoparticle solution was required, which leaded to saturation coverage. After 8 h of immersion, brownish-yellow colored samples obtained were taken out. The sheets were repeatedly washed with water to remove any adsorbed ions like citrate. Finally, the sheets were air-dried for further characterization and measurements. Ultraviolet-visible (UV–vis) spectra analysis was performed on the colloidal solution by picking 2 ml of the solution every 2 h after the immersion treatment. X-ray diffraction (XRD analysis) was done for the polyurethane samples immersed in the above solution after 2, 4, 6, and 8 h; which will be referred as PUAg2, PUAg4, PUAg6, and PUAg8, respectively. For some analysis purposes (scanning electron microscopy (SEM), XRD, optical micrograph, and Fourier transform infrared spectroscopy (FTIR)), all the samples synthesized were kept in the liquid nitrogen gas stream.

The UV–vis absorption data were collected on a UV–vis system, PG Instrument (UK) model T80+. The optical absorption spectrum was recorded in the range of 250–800 nm.

The XRD pattern was recorded with an automated Philips X'Pert X-ray diffractometer with Cu Kα radiation (40 kV and 30 mA) for $2\theta$ values over 5–80˚.

The FTIR absorption spectra of the synthesized samples as powder-pressed KBr pellets were collected using a Thermo Nicolet Nexus 760 (USA) FTIR spectrometer system with 4 $cm^{-1}$ resolution and in the spectral region from 4,000 to 2,000 $cm^{-1}$ at the room temperature.

### 2.5. Antibacterial test

Bacterial inactivation test was carried out in a batch set-up. Gram-negative *E. coli* DH5α strain was used as the model microorganism. A single colony of *E. coli* was taken out from the original stock in an agar plate and was cultured into 15 ml of LB medium containing the appropriate selective agent and grown for ~72 h at 37˚C, 200 rpm using a shaking incubator. After coating with silver colloidal nanoparticles, the polyurethane foams with 1-cm radius and 2-mm thickness were put in the testing tubes, seven pieces in each test tube. The same treatment was done with uncoated polyurethane foams as the control sample. In real condition before pumping of water to pipelines of city for end use, there are stock buildings, so we can put this filter in the direction of water flow or on the surface of water storage building and make circulation in it.

Growth curve of *E. coli* were depicted by measuring the solution OD at 600 nm after 0, 8, 15, 22, and 28 h. The coated (PUAg8) and uncoated foam pieces were saturated by adding 3 ml of the bacterium in a load of ~$10^5$ colony-forming units (CFU)/ml from each of the above sterilized flasks and incubated for 20 min under aseptic conditions. The foam samples were squeezed to get the treated solution. Plating was done with these treated solutions by the serial dilution method for $10^4$ dilutions with LB Broth medium. After the final dilution, 40 μL of the solution was plated. Plating was done by the pour plate method. The plates were incubated at 37˚C for 24 h. Each of bacteria culture (inoculation and plating) was done in a completely randomized design experiment with three replications.

## 3. Results and discussion

### 3.1. Morphology

Color of the polyurethane foam turned from white into brownish-yellow by its immersion in silver nanoparticle solution overnight. A brownish-yellow color appears because of the saturated binding of nanoparticles on polyurethane. As polyurethane is a porous material, the color of polyurethane immersed in silver nanoparticles results from the light absorption by silver nanoparticles attached to the channel walls of the porous polyurethane. After washing with distilled water for several times (6 times), ultrasonic irradiation for 20 min, performing the drying operation in an oven (40˚C for 24 h), and keeping the treated samples for several months in a closed environment, the color of treated foams remained stable. This indicates that silver nanoparticles are attached tightly to polyurethane components.

Optical images of polyurethane and polyurethane coated with silver nanoparticles show incorporation of silver nanoparticles as brownish-yellow contours in the film (Fig. 1). The film morphology showed no obvious change as a result of nanoparticle incorporation. This claim has been confirmed by other researchers as well [23].

Polyurethane samples immersed in silver colloidal solution after 2, 4, 6, and 8 h; which will be referred herein as PUAg2, PUAg4, PUAg6, and PUAg8, respectively. The SEM images of coated overnight (PUAg8) and uncoated polyurethane are shown in Fig. 2. As illustrated in Fig. 2(a) and (b), the polyurethane maintained its morphology upon coating with silver nanoparticles. It can be supposed that the nanoparticle binding is on the surface. In the next section, it is shown that the binding is due to the interaction between nitrogen of the –N (H–) bond of polyurethane and silver nanoparticles. At much higher magnifications, it can be observed that silver nanoparticles can be spread homogenously in the channels walls of polyurethane (Fig. 2(d)). The aggregation of silver nanoparticles affects on the size of porous into polyurethane [31]. Since based on our SEM results in treatment of foams with Ag colloidal solution, there was not any detectable agglomeration of silver nanoparticles on foam so total size and the porosity of foam was constant before and after treatment.

### 3.2. Spectroscopy

Silver nanoparticles absorb radiation in the 380- to 450-nm regions of the electromagnetic spectrum due to the excitation of surface plasmon resonances. This is responsible for the striking yellow-brown color of silver nanoparticles in various media [17].

The absorption spectrum measurements during 8 h are shown in Fig. 3. The silver colloidal solution suspending polyurethane was evaluated under UV–vis spectrometer after 2, 4, 6, and 8 h. As illustrated in the UV–vis spectra (Fig. 3), a strong surface Plasmon resonance was centered at approximately 386 nm, which is consistent with the established absorbance wavelength of silver nanoparticles suspension. In other words, as the time of soaking polyurethane increased, the intensity of peak decreased. It occurs because of decreasing

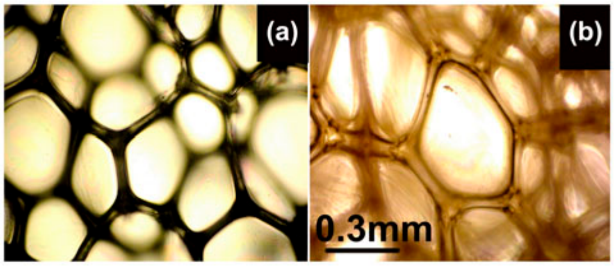

Fig. 1. Optical microscopic images of pure polyurethane (a) and polyurethane coated with silver nanoparticles overnight (b).

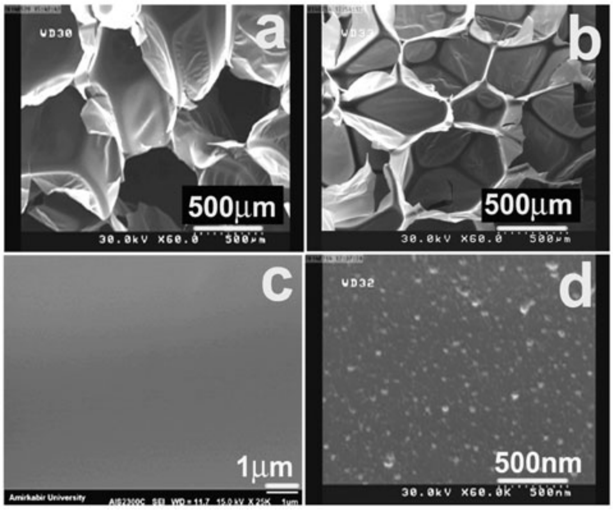

Fig. 2. SEM images of pure polyurethane (a and c), and polyurethane coated with silver nanoparticles overnight (b and d) at different magnifications.

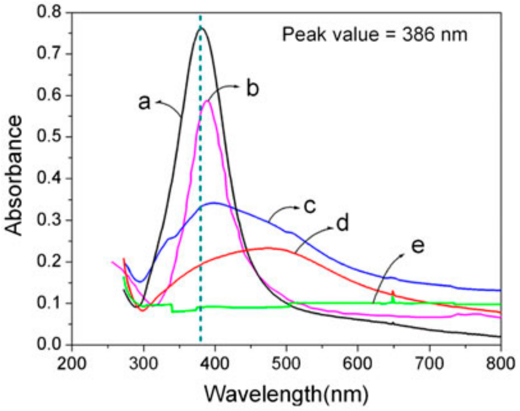

Fig. 3. UV–vis absorption spectra of the aqueous silver colloid (a), UV–vis absorption spectra of the colloidal solution after 2 h (b), 4 h (c), 6 h (d), and 8 h (e) of immersion treatment.

the number of silver nanoparticle in the solution. After 8 h, the coating of polyurethane with silver nanoparticle was approximately complete. The UV–vis spectrum of the last sample (Fig. 3(e)) is in favor of this claim. Furthermore, according to followed research, by passing time the peaks of absorption may be shifted to higher wavelength because of partial agglomeration of silver nanoparticles that was expected [32].

The XRD pattern of silver nanoparticles powder is shown in Fig. 4. The pattern exhibits peaks at 2$\theta$ angles of 38.4°, 44.2°, 64.1°, and 76.8° that correspond to (1 1 1), (2 0 0), (2 2 0), and (3 1 1) crystal planes of face-centered cubic lattice structure of silver nanoparticles, respectively [18]. These peaks are evidence of silver nanoparticles forms from the salts as reported by other researches [33–35].

From the full-width at half-maximum of the diffraction peaks, the average size of the silver nanoparticles was calculated using the Debye–Scherrer equation [19,20]. The calculated average size of silver nanoparticles was around 25 nm.

Polyurethane coated with silver nanoparticles at different time coverage was evaluated by XRD diffractometer. By focusing on Fig. 4(a)–(d), the intensity of silver nanoparticles becomes more obvious by increasing the time of polyurethane coating, which clearly indicates higher presence of silver nanoparticles on the polyurethane surface. Furthermore, the weak diffraction peak near $2\theta = 22^\circ$ in all coated samples is due to the hard segment of polyurethane, in which its intensity is associated with the hard segment content.

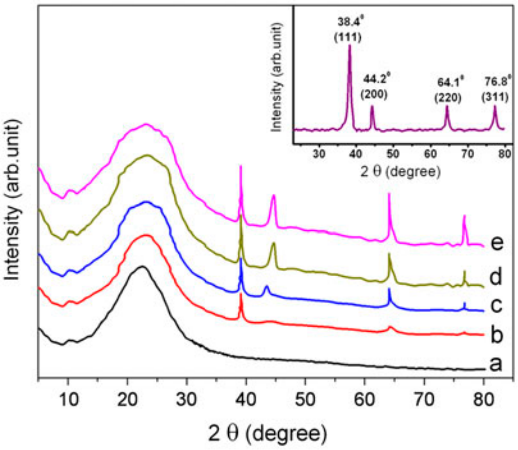

Fig. 4. XRD pattern of neat polyurethane (a), PUAg2 (b), PUAg4 (c), PUAg6 (d), PUAg8 (e), and silver nanoparticles (inset).

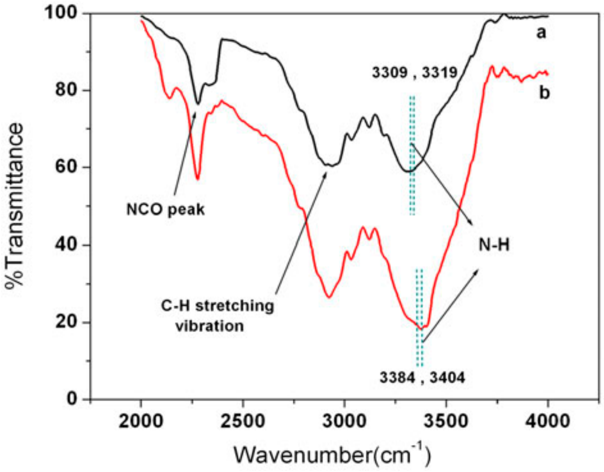

Fig. 5. FTIR spectra of uncoated (a) and coated (b) polyurethane.

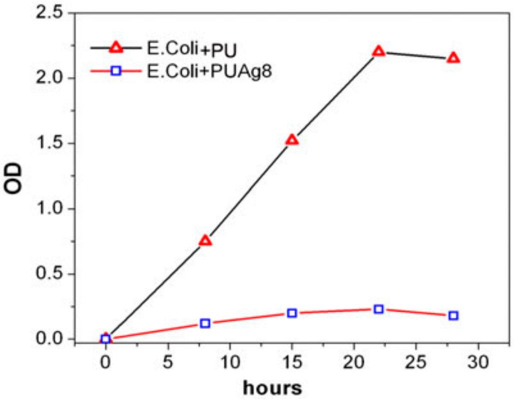

Fig. 6. Bacterial inactivation efficiency of neat polyurethane and polyurethane coated by silver nanoparticles for overnight incubation.

The connection between polyurethane and silver nanoparticles was confirmed by the FTIR measurements. Fig. 5 shows the FTIR spectra of pure polyurethane and polyurethane coordinated with silver nanoparticles (PUAg8) in the region of relevance. Furthermore, the N–H stretching vibrations correspond to weak broad band at 3,319 $\text{cm}^{-1}$ in Fig. 5(a) [7]. As for polyurethane cross-linked silver nanoparticles, this broad band is gradually shifted and its intensity increased, due to the interaction between the nitrogen of the –N (H)-bond of polyurethane and silver nanoparticles and the formation of N–Ag coordinate bonds [7]. The crucial shift observed is about 85 $\text{cm}^{-1}$ but usually there is no shifting of –N–(H)–bond [23,31]. The –CH group asymmetric and symmetric stretching vibrations are related to the broad peaks at 2,850–2,900 $\text{cm}^{-1}$ [7]. Formation of the –CH group caused by the interaction between the $NH_2$ at the head of the carbon chain and the silver nanoparticles caused that these peaks are slightly shifted and its intensity increased [7,23]. Therefore, the coordination between the nitrogen of the $–NH_2$ group of polyurethane and silver nanoparticles is demonstrated.

### 3.3. Microbiological results

Analysis for growth curve of *E. coli* on LB media under polyurethane foam treated and untreated with silver nanoparticles confirmed the antimicrobial and decontamination effects for the coated polyurethane foams. It is very clear that the growth curve of *E. coli* in the control LB Broth medium had a hyperbolic trend and the ODs (optical density) of the bacterium increased exponentially from zero to 2.2. However, in the media containing polyurethane foams included silver nanoparticle, the bacterial growth curve was highly suppressed and the ultimate OD reached 0.23 (Fig. 6). These results have proved the antibacterial effects for polyurethane foams coated with silver nanoparticles. The trend lines of each growth curve in different conditions were estimated as well.

For bacterial load on foams in the saturated form, after a contact time of 20 min with polyurethane coated by silver nanoparticles, we deduced that a few bacteria have grown on the medium. This is while in the control experiment (pure polyurethane) a substantial growth of bacteria on the LB-agar was observed. These results confirm the antibacterial property for polyurethane coated with silver nanoparticles (Fig. 7). It should be mentioned that the *E. coli* cell cycle at the optimal condition is about 20 min; so, it is presumed that longer treatment time may lead to higher bacterial growth inhibition.

Based on the results obtained and considering other results reported, we can deduce that there are two possible antimicrobial mechanisms:

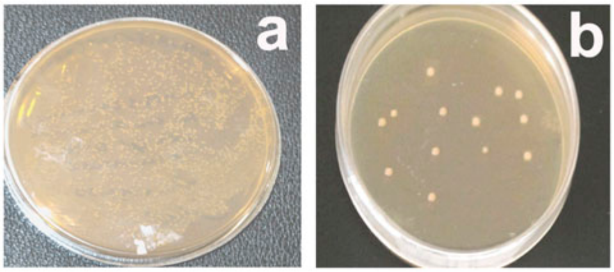

Fig. 7. Test tube results for *E. coli* ($10^5$ CFU/mL) (a) after exposure to pure polyurethane and (b) after exposure to nanoparticle-decorated polyurethane.

(1) Bactericidal effect: the bacteria are directly killed by the silver ions released from foams. It is suggested that silver positive ion adheres to the negatively charged cell wall of bacteria; this can induces cell lysis and death [7,36]. Silver positive ion can also damage the DNA replication mechanisms, cell membranes and outer cell layers of sensitive cells [37,38].

(2) Bacteriostatic effect: the silver ions interfere with the bacterial growth signaling pathways that produce putative peptide for cell viability and division [27]. The bacterial growth rate will decrease significantly on the LB-agar or broth media. Thus, disappearance of the bacteria may be due to the bactericidal or bacteriostatic effect of materials.

Our results are in correspondence with similar studies. However, it should be mentioned that we used enriched media instead of pure water that promoted bacterial growth. So, polyurethane foams coated with silver nanoparticle can be more effective for decontamination of real media with lower concentration, such as polluted water.

## 4. Conclusion

Silver nanoparticles can be coated durable and uniformity onto the polyurethane foams. However, this nanoparticle is stored for extended periods after washing, drying and ultrasonic irradiation. Polyurethane-coated silver nanoparticles were evaluated as an antibacterial water filter and shown to be strong sterilizers. The test tube and incubation tests for decontamination of *E. coli* confirmed the antibacterial properties of the composite material.

FTIR, SEM and optical micrograph investigations on silver nanoparticle-decorated polyurethane confirmed that they were not washed away by repeated washing or immersion in an ultrasonic bath and keeping the treated foams for several weeks at the room temperature. Accordingly, the nanoparticle binding is due to the interaction of silver atoms on the surface of the nanoparticles with the nitrogen atom at polyurethane foam.

The chemistry involved in the synthesis of foams and also nanoparticle-coated foams are available at low costs and are non-toxic. The experiments prove the potential of these materials in water treatment applications. Also, it can be offered with other nanoparticles to be used in air filtration, domestic and industrial air quality management, antibacterial packaging and so on. It is applicable to apply silver nanoparticle-decorated porous polyurethane in a pilot scale for removal of pathogenic bacteria; we can use a surface of foam with enough thickness infornt of water current and measure the results. However, we need to optimize the fold time of treatments.

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