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Surface characteristics and antibacterial activity of a silver-doped carbon monolith

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Abstract

A carbon monolith with a silver coating was prepared and its antimicrobial behaviour in a flow system was examined. The functional groups on the surface of the carbon monolith were determined by temperature-programmed desorption and Boehm's method, and the point of zero charge was determined by mass titration. The specific surface area was examined by N₂ adsorption using the Brunauer, Emmett and Teller (BET) method. As a test for the surface activity, the deposition of silver from an aqueous solution of a silver salt was used. The morphology and structure of the silver coatings were characterized by scanning electron microscopy and x-ray diffraction. The resistance to the attrition of the silver deposited on the carbon monolith was tested. The antimicrobial activity of the carbon monolith with a silver coating was determined using standard microbiological methods. Carbon monolith samples with a silver coating showed good antimicrobial activity against *Escherichia coli*, *Staphylococcus aureus* and *Candida albicans*, and are therefore suitable for water purification, particularly as personal disposable water filters with a limited capacity.

Keywords: carbon monolith, surface properties, silver, antimicrobial activity, water purifier

1. Introduction

In the last few years, there has been growing interest in the carbon monolith (CM) as an alternative to conventional carbon materials. CMs can be produced with the desired shape and morphology with controlled composition, structure and porosity. Several methods for producing CMs have been reported. In one of these methods, solid templates filled with carbon are used as a precursor [1–3]. After the carbonization and subsequent template removal, a porous CM is obtained. The size and shape of the CM can be easily tailored by controlling the size and shape of the template. However, the synthesis of the template for the monolith is complex. An alternative method of obtaining materials with a defined shape is powder pressing [4]. Tonanon *et al* [5] described a new method for preparing CMs by ultrasonic irradiation. CMs are attractive for applications in catalysis, biocatalysis, adsorption, as porous electrodes under a continuous flow condition and as chromatography columns. It was reported

that a CM in the shape of a parallelepiped with longitudinal parallel channels has been used for the adsorption of toluene, a volatile organic compound [6]. Also, cylindrical CMs with square channels obtained from polyfurfuryl alcohol with Pt and Pd deposits were used for the removal of volatile organic compounds in a catalytic combustion process [7].

We are interested in the potential of using a cylindrical CM with longitudinal capillary channels as a filter for water purification. The CM surface was characterized, then the material was modified by silver deposition. The antimicrobial activity of the modified CM against *Escherichia coli* (*E. coli*), one of the more frequent species inhabiting water, as well as *Staphylococcus aureus* (*S. aureus*) and *Candida albicans* (*C. albicans*) was tested.

Silver-coated carbon materials act as an efficient filter for the removal of bacteria from polluted water [8–11]. Silver is well known for its antibacterial properties [12–15]. Silver ions are highly toxic to microorganisms, and have a strong biocidal effect on many bacteria species. The mechanism of

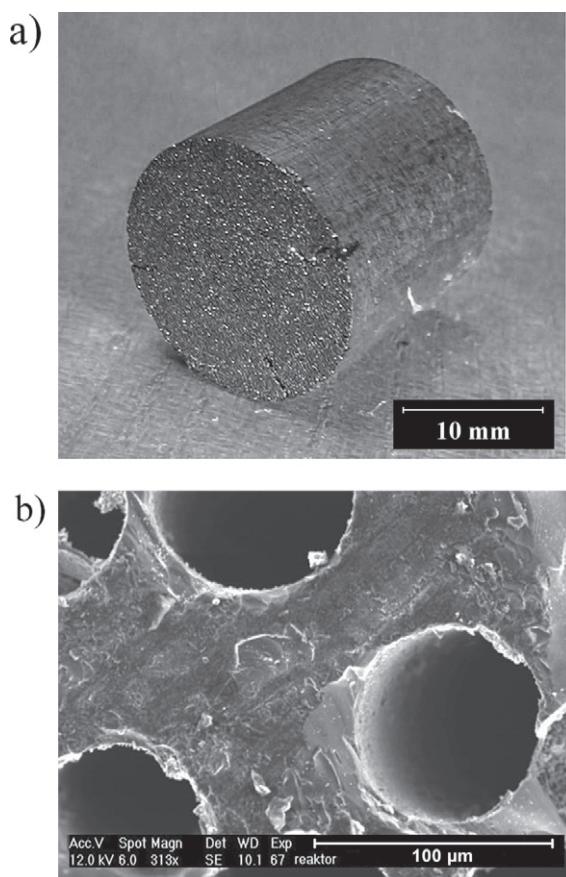


Figure 1. Carbon monolith (CM): (a) optical photograph, and (b) SEM image of the cross section.

the antimicrobial effect of silver is still not fully understood. It is believed that DNA loses its replication ability and cellular proteins become inactivated upon treatment with silver ions. In addition, it has also been shown that silver ions bind to the functional groups of proteins, resulting in protein denaturation [15–17].

2. Experimental

2.1. Materials

Cylindrical CM (length 3.0 cm, diameter 1.8 cm) with 8600 capillary channels (each 80 μm in diameter) inside the material were purchased from Fractal Carbon (UK). The design and structure of the CMs used are shown in figure 1. The monolith is a composite material, consisting of a glassy carbon bed and an activated carbon layer on the inner capillary walls. The adsorption characteristics of the CM depend on the adsorption capacity of the activated carbon layer.

2.2. Surface characterization

The surface area of the CM was determined by nitrogen adsorption at the temperature of liquid nitrogen using an accelerated surface area and porosity analyser (Micromeritics ASAP 2020 MP, USA). Nitrogen adsorption isotherms were

analysed using the Brunauer, Emmett and Teller (BET) method [18].

The functional groups on the surface of the CM were determined by Boehm's method [19, 20]. Acidic sites were determined by mixing small quantities (0.1 g) of the CM with 10 cm^3 of different bases (0.1 M NaOH, 0.1 M NaHCO_3 and 0.05 M NaHCO_3) in 25 cm^3 beakers. Beakers were sealed and shaken for 24 h. The solutions were then filtered and titrated with 0.05 M H_2SO_4 . Basic sites were determined in the same way, by mixing 0.1 g of the CM with 10 cm^3 of 0.1 M HCl. After the filtration, the solution was titrated with 0.1 M NaOH.

Temperature-programmed desorption (TPD) in combination with mass spectrometry was used to investigate the nature and thermal stability of CM surface oxygen groups. The TPD profiles were obtained using a custom-built set-up consisting of a quartz tube placed inside an electrical furnace. A CM sample was outgassed in the quartz tube and subjected to TPD at a constant rate of heating of 10 K min^{-1} to 1173 K under high vacuum. The amounts of CO and CO_2 released from the carbon sample (0.1 g) were monitored using an Extorr 3000 quadrupole mass spectrometer (Extorr Inc, USA). TPD plots were deconvoluted using OriginPro 6.1 (OriginLab Corporation, USA). A multiple Gaussian function was used to fit each of the TPD curves, taking the position of the peak centre as the initial estimate [21].

The point of zero charge (PZC) of the CM was determined by mass titration by placing various amounts (0.05, 0.1, 0.5, 1 and 10% by weight) of the CM in 10 cm^3 of 0.1 M KCl solution (prepared using preboiled water to eliminate CO_2). The beakers were held in Ar atmosphere to eliminate any contact with air. They were then placed in a thermostat shaker overnight. The equilibrium pH values of the mixtures were then measured. The limiting pH value was taken as the PZC [22].

The rate of silver deposition at the material surface was examined as a function of the initial concentration of AgNO_3 solution (0.23, 0.46, 0.70, 0.93 and 1.16 mmol dm^{-3}), and the contact time between the CM surface and the AgNO_3 solution (0.70 mmol dm^{-3}). Silver deposition at the CM surface was observed by measuring the decrease in silver concentration in the solutions using a Pye Unicam SP9 atomic absorption spectrometer (Pye Unicam Ltd, UK).

A JEOL-T20 scanning electron microscope (SEM) (JEOL Ltd, Japan), was used for examining the morphology of silver deposited at the CM surface. A Philips 1050 x-ray diffractometer was used to verify the composition of the silver deposit. Diffraction lines were measured using Ni-filtered $\text{CuK}\alpha_{1,2}$ radiation.

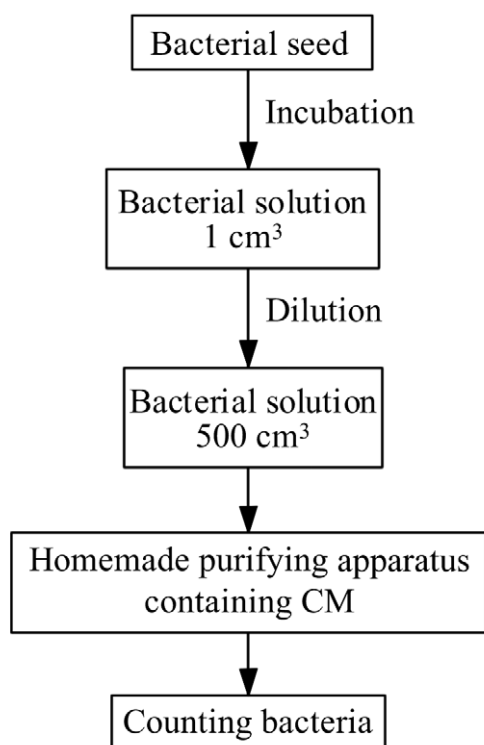
The resistance to attrition of the CM samples impregnated with silver (CM/Ag) was determined by a washing test. A CM/Ag sample was exposed to the flow of distilled water at a flow rate of 6 $\text{cm}^3 \text{min}^{-1}$. Effluent increments of 25 cm^3 were tested for silver attrition by atomic absorption spectrometry.

2.3. Antibacterial activity

CM/Ag samples were obtained by silver adsorption on the inner capillary walls of the CM. A constant flow of AgNO_3

Table 1. Surface characteristics of CM: surface area by N₂ adsorption, acid and basic functional group content and PZC.

BET (m ² g ⁻¹)	Basic functional groups (mmol g ⁻¹)	Acid functional groups (mmol g ⁻¹)	Carboxyl (mmol g ⁻¹)	Lactone (mmol g ⁻¹)	Phenol (mmol g ⁻¹)	PZC
150	0.776	0.388	0.228	0.050	0.110	9.47

**Figure 2.** Flow chart for the antibacterial test.

solution (concentration 0.93 mmol dm⁻³) through the CM tube was used as the source of silver ions. The amount of silver deposited was 3.42 mg Ag g⁻¹. This amount was chosen so that the silver attrition remained under the concentration limit allowed in drinking water and to achieve satisfactory antibacterial activity simultaneously.

The antibacterial properties of top and bottom cross sections of the CM tube were tested by the diffusion method using an agar plate. Each cross section was placed on an agar plate seeded with *E. coli*. A clear zone on both plates confirmed the uniform antibacterial effect throughout the whole monolith.

The antibacterial activity of the CM/Ag sample was determined using standard microbiological methods. Tests against *E. coli* were conducted using homemade water-purifying apparatus. The steps in the antibacterial test are shown in figure 2. 500 cm³ of water polluted with *E. coli* was discharged through the CM/Ag tube. After each 100 cm³ of the water had passed through the CM/Ag tube, samples of 1 cm³ of the purified water were collected. Each water sample was poured onto a sterile culture plate that contained agar. The culture plates were incubated for 24 h at 37 °C. After incubation, the number of bacteria was

determined by counting. The antibacterial activity of CM/Ag was determined by comparing the number of bacteria in the original solution with the number in the purified solution.

Also, the antimicrobial activity of CM and CM/Ag samples for a mixture of bacteria (*E. coli* and *S. aureus*) and fungus (*C. albicans*) was tested.

3. Results and discussion

3.1. Surface characteristics

Nitrogen adsorption isotherms were analysed using the BET method to determine the surface area of the CM sample (table 1). The surface oxygen complexes on the CM have acidic as well as basic properties and can be conveniently determined by Boehm's titration method and by mass titration (PZC). The results obtained are presented in table 1. The results obtained by Boehm's method showed that the amount of basic groups is twofold higher than the amount of acidic groups. The PZC value obtained indicates that the CM surface has a basic character, as expected from the results of Boehm's titration method (table 1).

It has been shown in TPD experiments that surface groups on carbon material decompose by releasing CO and CO₂. According to the literature [21, 23–25], TPD peaks can be assigned to specific surface groups. The CO₂ profile results from carboxylic acids at low temperatures and lactones at higher temperatures; carboxylic anhydrides are the origin of both CO and CO₂ peaks; phenols, ethers and carbonyls are the origin of the CO peak.

The decomposition temperature is related to the strength of each specific oxygen-containing group. Thus, the amount of oxygen-containing species released corresponds to the quantity of oxygen groups. To determine the amounts of the several different oxygen groups, TPD plots were deconvoluted. The deconvolution of the CO and CO₂ desorption plots for the CM sample are presented in figure 3 and the corresponding quantitative values are specified in table 2.

The CO₂ TPD profile reaches its first maximum at a low temperature, 620 K, due to the decomposition of carboxylic and lactone groups. The second maximum at 870 K, with a small shoulder near 1000 K, originates from more stable anhydrides and/or lactone groups.

The CO TPD profile for the CM has a local maximum at 620 K. This is a very low temperature for CO evolution, and according to the literature [22] it may originate from carboxyl anhydride. Since the CO₂ profile also has a peak at 620 K, evolution of CO at this temperature may originate from CO₂ reduction on the CM surface [26]. The maximum at approximately 1150 K suggests the existence of anhydride,

Table 2. Results of TPD obtained by deconvolution.

Temperature (K)	CO ₂ (mmol g ⁻¹)	Total CO ₂ (mmol g ⁻¹)	Temperature (K)	CO (mmol g ⁻¹)	Total CO (mmol g ⁻¹)
620	0.430	0.982	620	0.058	2.005
870	0.497		~1150	1.947	
1020	0.055				

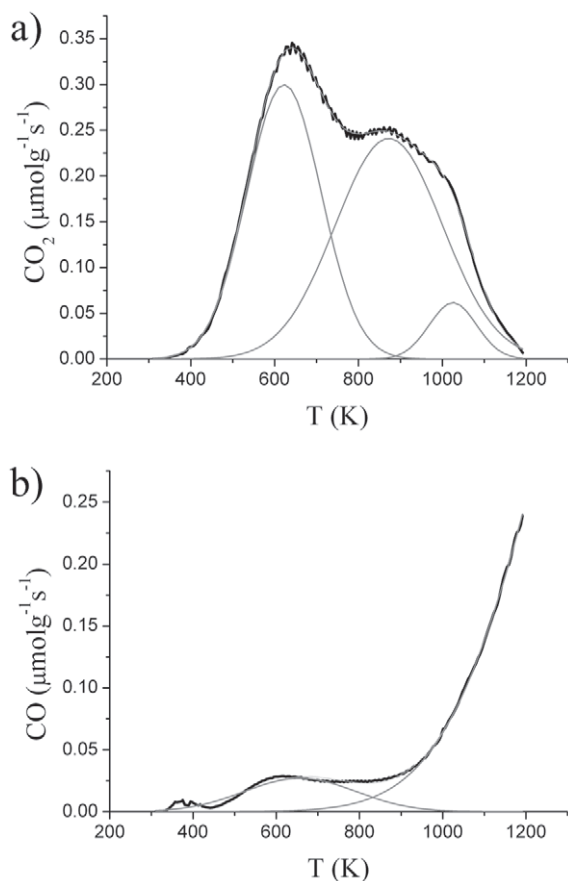


Figure 3. Deconvolution of TPD spectra of CM sample: (a) CO₂ evolution and (b) CO evolution.

although, it may also be attributed to phenols, ethers, carbonyls or quinones.

The total amount of groups obtained by TPD is higher than that obtained by Boehm's method. The discrepancy between these results is either due to the difficulty the solution has in accessing the porous structure of the inner capillary walls of the CM or due to the limitations of Boehm's titration method. Boehm's method provides a method of detecting acidic (in the form of carboxyl groups, lactones and phenols) and basic surface groups, while TPD detects CO and CO₂ obtained by the decomposition of all surface species.

The rate of silver deposition on carbon materials depends on the specific surface area as well as on the quality and quantity of functional groups that can act as initial active sites [27]. We studied the rates of silver deposition on CM samples as a function of contact time and the concentration of AgNO₃ solution (figure 4).

The deposition of silver on a CM is a relatively slow process. The silver deposition rate is reasonably high during

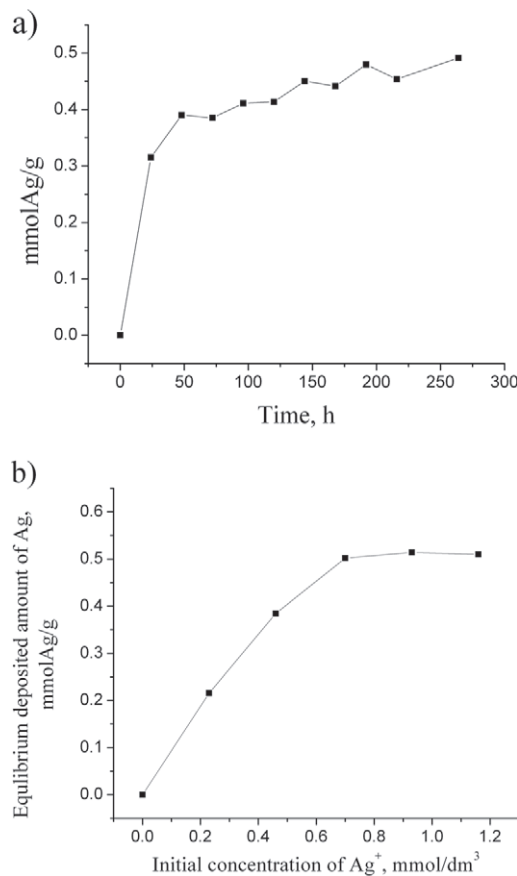


Figure 4. Silver deposition as a function of (a) time and (b) initial concentration.

the first day (figure 4(a)) but subsequently becomes very low; thus, equilibrium is not reached even after two weeks.

The initial concentration of AgNO₃ solution has a considerable effect on the total silver content deposited on carbon materials, as reported in the literature [11, 27]. The silver content deposited on the CM increases with the initial concentration of AgNO₃ solution up to a concentration of 0.70 mmol Ag⁺/dm⁻³, as shown in figure 4(b). Further increases in concentration have no effect on the amount of silver deposited. The maximum amount deposited was approximately 0.5 mmol Ag g⁻¹ CM.

The composition and crystallinity of silver deposits were examined by x-ray diffraction. The x-ray diffraction patterns display diffraction peaks of metallic silver on the CM/Ag surface (figure 5(a)). Diffraction patterns at 2θ values of approximately 38°, 44°, 64.2° and 77.2° corresponding to (111), (200), (220) and (311) planes of silver metal, respectively, are deposited as a face-centred-cubic (FCC) Ag structure [28]. Sharp peaks, corresponding to the diffraction

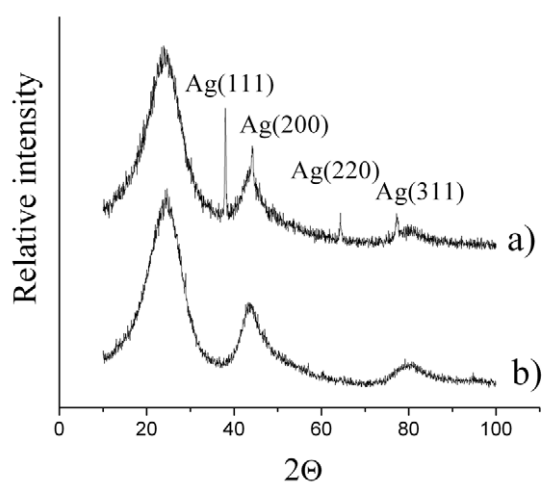


Figure 5. X-ray diffraction patterns of (a) CM/Ag and (b) CM.

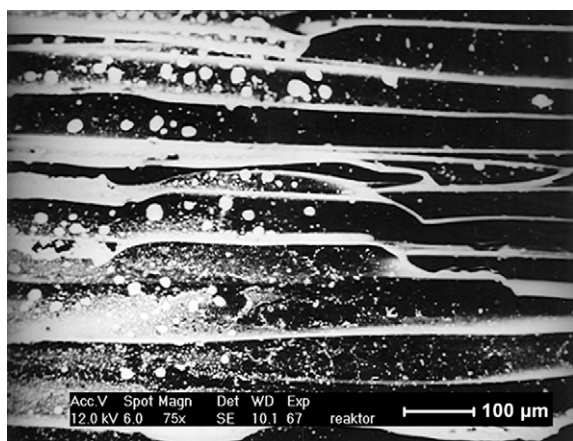


Figure 6. Morphology of silver deposit at the surface of CM cross section.

profiles of the Ag metal lattice, are superimposed on the broad profile typical of a disordered carbon structure [29]. The x-ray diffraction pattern of the CM without the Ag deposit is shown in figure 5(b) for comparison.

The amount of silver deposited depends on the surface area and the quantity of acidic functional groups that can act as initial active sites for adsorption. A possible mechanism of silver adsorption is through an ion-exchange reaction between silver ions and carboxylic groups [30]. However, in the case of the CM, the amount of silver deposited is different from the amount of carboxylic groups; thus, not only carboxylic groups affect silver deposition. Another possible mechanism of silver adsorption is redox adsorption [30], which is confirmed by x-ray and SEM results. The x-ray pattern indicates that Ag^+ was reduced to Ag^0 crystals. Silver metal is an electrical conductor; thus, crystals can grow by Ag^+ reduction at a silver crystallite surface. An SEM photograph (figure 6) shows that the deposited silver forms bulky, separate islands.

If CM/Ag is to be used to purify drinking water, the attrition rate of silver is an important parameter. The concentration of Ag in the effluent should not exceed the maximum allowed concentration in drinking water

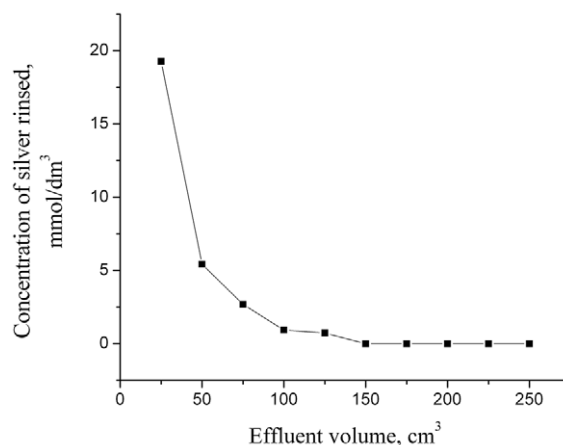


Figure 7. Ag attrition test for CM/Ag.

($0.05 \text{ mg Ag dm}^{-3}$). The concentration of silver rinsed from the CM/Ag sample containing $3.42 \text{ mg Ag gCM}^{-1}$ as a function of effluent volume is given in figure 7. The silver concentration decreases rapidly at first. The initial high concentration values are probably due to the residue of AgNO_3 in the porous capillary channels or due to the dissolved surface Ag oxide layer, previously formed upon contact between the dry surface of deposited Ag and air [17, 31, 32]. However, after rinsing the CM with 150 cm^3 of distilled water, the attrition rate becomes negligible and the concentration of Ag in the effluent remains two times lower than the maximum allowed concentration in drinking water. From the results obtained, the total amount of silver rinsed from CM/Ag was calculated. The initial silver content of 3.42 mg g^{-1} decreased to 93% of its initial value then remained virtually constant.

3.2. Antibacterial activity

The diffusion method using an agar plate was used to evaluate the antibacterial properties of the CM/Ag tube. Two disks sliced from the top and bottom of the tube were placed on agar plates seeded with *E. coli*. Results obtained by the diffusion method are shown in figure 8. Clear zones under both disks confirmed a uniform antibacterial effect throughout the whole monolith. From these results, it can be concluded that silver was evenly deposited throughout the CM tube.

The results of the antibacterial test against *E. coli* are shown in figure 9. The initial number of *E. coli* bacteria in 1 cm^3 of water was approximately 10^4 CFU (colony-forming units). The polluted water was purified through the CM/Ag tube at flow rates of 6 and $12 \text{ cm}^3 \text{ min}^{-1}$. After purification, the number of bacteria was reduced by 25–50%. For the lower flow rate, greater purification efficiency was observed due to the increased contact time between the polluted water and CM/Ag.

Water polluted with a mixture of bacteria and fungus was purified through both the CM and the CM/Ag tube at the flow rate lower than $6 \text{ cm}^3 \text{ min}^{-1}$ (table 3). The initial number of each species was approximately 10^4 CFU cm^{-3} . During the purification using the CM the number of bacteria

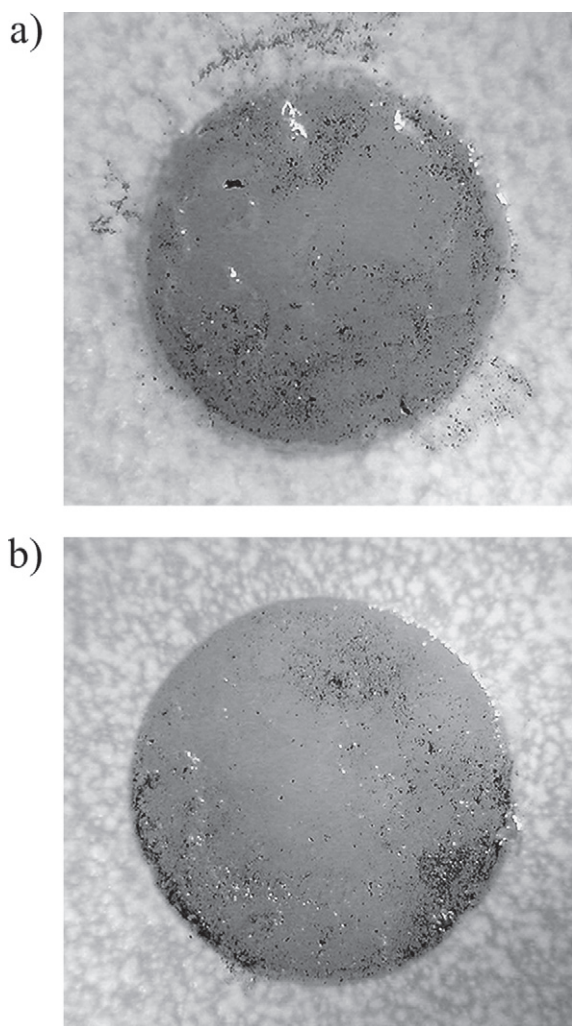


Figure 8. Clear zone on the agar plate placed below (a) top and (b) bottom cross-section of the CM tube.

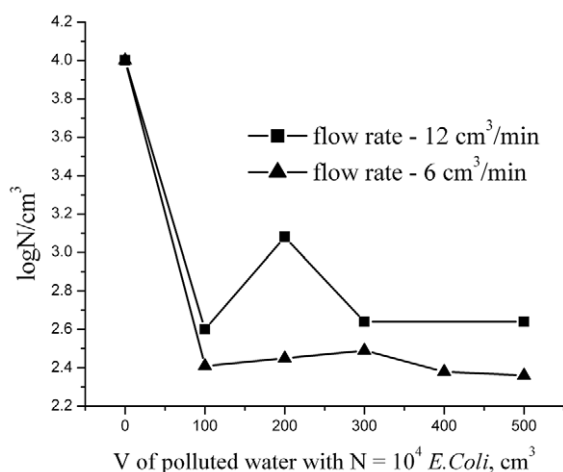


Figure 9. Antibacterial activity of CM/Ag against E. coli.

decreased by approximately 35%, probably due to the fact that bacteria adhere to the solid supports, which are made of carbon materials. Bacteria can breed on the carbon material surface; thus, the carbon material itself acts as a pollutant

Table 3. Antimicrobial activity for mixture of bacteria and fungus.

Material	Efficiency (%)		
	<i>E. coli</i>	<i>S. aureus</i>	<i>C. albicans</i>
CM	36.54	36.36	31.58
CM/Ag	99.90	97.36	96.49

[9, 11]. This can be avoided by impregnating the carbon material with silver as a bactericide. The obtained results showed that CM/Ag has strong antimicrobial activity against *E. coli*, *S. aureus* and *C. albicans*, removing more than 96% of each tested species.

Additionally, in an attempt to simulate real environmental conditions, water polluted with 10^2 CFU cm^{-3} of *E. coli* was prepared. As the result of purification through the CM/Ag tube, bacteria-free water was obtained.

4. Conclusions

A carbon monolith impregnated with silver, which combines the strong biocidal properties of silver with the adsorption properties of carbon materials, was used for the disinfection of water polluted with *E. coli*, *S. aureus* and *C. albicans*.

In highly polluted water (number of bacteria: approximately 10^4 CFU cm^{-3}) a purification rate of higher than 96% was achieved for all the microorganisms tested. Upon using a lower concentration (10^2 CFU cm^{-3}) of *E. coli*, closer to real environmental conditions, CM/Ag completely removed the bacteria from the polluted water.

Therefore, a carbon monolith impregnated with silver can be used for purifying water polluted with *E. coli*, *S. aureus* and *C. albicans*. Because of its specific shape, low silver attrition rate and good antibacterial activity, the impregnated monolith can be utilized as a personal disposable filter.

Acknowledgments

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