

# Nanocomposite carbon material – silver nanoparticles: Preparation and antibacterial activity

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## Abstract

Silver nanoparticles (AgNPs) are suitable component for preparation of nanocomposite materials with an antibacterial activity. The preparation of such materials was realized by the adsorption of AgNPs from the aqueous dispersion. Carbon based materials, namely active carbon, carbon nanotubes and carbon aerogels, were used as adsorbents. Firstly were these carbon adsorbents used in pure form, secondly were used in oxidized state and thirdly in form modified by polyethylenimine. Oxidation was handled by boiling in 5 mol·dm<sup>-3</sup> HNO<sub>3</sub>, addition of polyethylenimine was done through the adsorption from the solution. These steps should lead to the better adsorption of AgNPs because of their higher affinity to the oxygen and especially to the nitrogen. There was also studied an antibacterial activity of nanocomposites that was created by adsorption high amount of AgNPs and which did not cause the aggregation of AgNPs.

**Key words:** Silver nanoparticles; Adsorption; Carbon materials; Oxidation; Antimicrobial activity

## Introduction

Carbon materials have important and irreplaceable position among all adsorbents. Firstly, the most of carbon materials provides high specific surface area volume and good porosity. Secondly, they are often very cheap and available for many laboratories. Thirdly, every organic substance is made of carbon, so that the danger which could cause these adsorbents to the environment is minimal. Carbon adsorbents are already used for adsorption of heavy metals<sup>1</sup> or for purification of waste waters<sup>2</sup>. These materials can be doped or impregnated with substances to improve their current properties or even to develop a new one. For example silver impregnated materials are used for removal of cyanide from aqueous solution<sup>3</sup> or for capturing the mercury<sup>4</sup>. Very interesting could be the modification of these carbon adsorbents with AgNPs providing antibacterial activity especially against *Staphylococcus aureus*<sup>5</sup>, *Escherichia coli* and *Pseudomonas aeruginosa*<sup>6</sup>. This combination can lead to the very promising materials with antibacterial activity which could be used for water purification and disinfection or for medical purposes.

## Experimental

The preparation of AgNPs was based on modified Tollens method<sup>7</sup> where the complex cation [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> was reduced by maltose. Such prepared nanoparticles had size range 24 – 33 nm and were used for adsorption after a day in order to avoid the creation of new nanoparticles during the adsorption.

Used carbon materials can be divided into two groups: to the first group belong active carbon (CXV) and multi-walled carbon nanotubes (MWCNT) which were bought as commercial adsorbents. To the second group belong three

types of carbon aerogels: RFA, RFA X and RFB which were prepared in the laboratory. The preparation of RFA and RFA X was based on article by M. Reuß and L. Ratke<sup>8</sup>. The ratio of resorcinol to formaldehyde was 1:1 and the reaction was catalyzed with 0.23 mol·dm<sup>-3</sup> HCl. The difference between RFA and RFA X is in the drying part of the preparation. While the RFA was after the addition of the catalyst 24 hours at room temperature, the RFA X was put for 1 hour into the autoclave at 110°C. Then were both materials for 24 hours in oven at 70°C and after that they were pyrolyzed. The preparation of RFB aerogel was based on article by M. Wiener<sup>9</sup>. The ratio of resorcinol to formaldehyde was 1:2 and the reaction was catalyzed with 0.035% solution of NaHCO<sub>3</sub>. Then it was dried in the oven at 70°C for 48 hours and after that was that material pyrolyzed.

The oxidation of all adsorbents was done by boiling 4.5 g of chosen adsorbent in 100 ml 5 mol·dm<sup>-3</sup> HNO<sub>3</sub> for three hours. After boiling, the materials were washed in water to the neutral pH. These materials were characterized with IR spectrometry. The polyethylenimine was added through the adsorption from the solution. 0.5 g of oxidized material was shaken with 150 ml of 0.01% polyethylenimine for 2 hours and then for 1 hour in distilled water.

The adsorption of AgNPs from aqueous dispersion proceeded as follows: the 0.25 g of carbon adsorbent was shaken in the 75 ml of solution of AgNPs of six different concentrations for three hours and then was the solution filtered and an adsorbent dried at the room temperature. The amount of adsorbed nanoparticles was determined through the UV/Vis spectrometry from Lambert-Beer law.

## Results and discussions

Adsorption isotherms obtained from pure materials are showed at figure nr.1. The materials can be again divided into two groups – commercial available adsorbents which have adsorption limited by the maximum amount of AgNPs in the solutions (they adsorb 90-100%) and carbon aerogels which had quiet low adsorption ability. The low adsorption of carbon aerogels is probably caused by the size of their pores, which were measured to be around 2 – 10 nm where obviously AgNPs with size range 24 – 33 nm cannot fit. On the other hand, CXV and MWCNT created nanocomposites Ag@(carbon material) and their pictures from transmission electron microscopy (TEM) are showed at figures nr.2 and nr.3. Ag@CXV and Ag@MWCNT also exhibited good antimicrobial activity comparable with ionic silver or AgNPs. The oxidation had bad influence on adsorption abilities. All oxidized materials had worse results than pure ones and some of them did not adsorb at all. The modification with polyethylenimine again increased the adsorption of the materials, nevertheless there were observed some issues with desorption of polyethylenimine back to the solution which caused the adsorption of AgNPs also on the laboratory glass.

## Conclusions

From the five used carbon materials as adsorbents two were able to create nanocomposite with AgNPs. Ag@MWCNT and Ag@CXV had good antibacterial activity comparable with ionic silver or AgNPs. On the other hand, carbon aerogels are not suitable for this type of nanocomposite. At this stage of research, oxidation or any other modification did not improve the adsorption of AgNPs.

## Acknowledgements

This work was financed by project nr. CZ.1.07/2.2.00/28.0084.

I would also like to thank to the Mr. Ales Panacek and Dr. Vaclav Slovak for their help and cooperation.

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## Figures

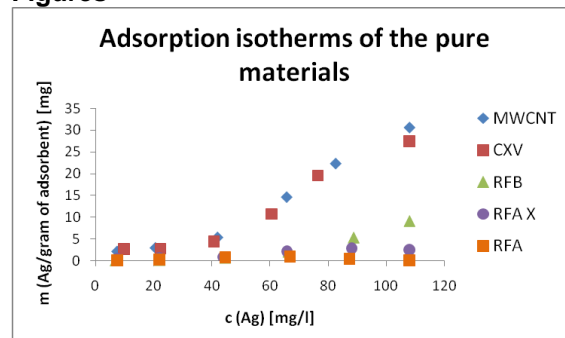


Figure nr.1: The comparison of adsorption abilities of pure materials.

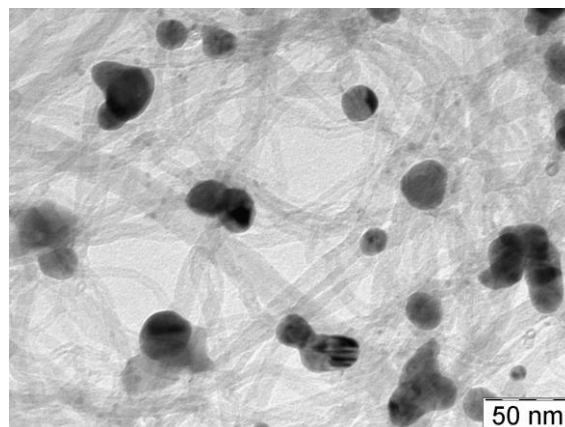


Figure nr.2: The TEM image of Ag@MWCNT.

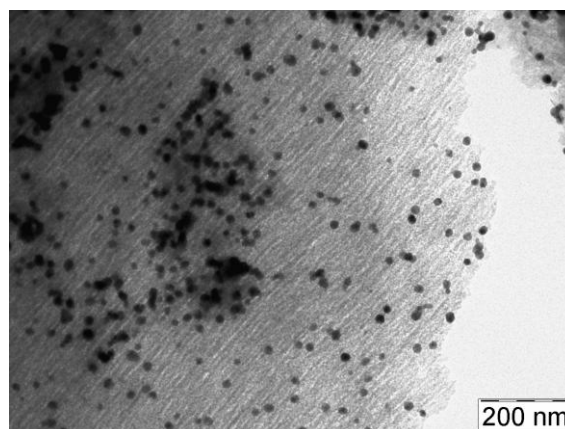


Figure nr.3: The TEM image of Ag@CXV.