

Antibacterial properties of argentum nanoparticles deposited on different carriers



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Introduction

Nowadays Ag nanoparticles (AgNPs) are becoming more and more wide used materials. They have especially been employed as antibacterial, antifungal, and antioxidant materials in agriculture and medicine. With the development of new knowledge in nanotechnology and related sciences, it becomes possible to expend their using in the role of sorbents or catalysts, in which they can be deposited on the carriers. The zeolites in the role of carrier for AgNPs has not been enough investigated yet.

Therefore, the aim of this study was to obtain promising nanoscale silver-containing antibacterial sorbents based on different carriers such as natural zeolite, aluminum oxide, and activated carbon as well as to compare their efficiency.

Experimental

The original carriers were gamma-alumina, activated birch charcoal BAU, and dealuminated Ukrainian clinoptilolite. The samples were doped with 1 wt% of silver using silver nitrate. "Green" reduction with glucose solution were utilized for AgNPs obtaining. For this purpose samples were put into flat bottom glass flasks and poured with distilled water. Obtained suspension was heated (up to 100 °C) and stirred (160 rpm) on the magnetic stirrer, then glucose solution was slightly given by syringe pump with rate of 240 cm³/h. After full dose addition the reaction system was stirred for 1 h. Weight silver-to-glucose ratio was 1:7 and solid-to-liquid ratio was 1:10. Samples were filtered on paper filter and watered. As the result Ag-Al₂O₃, Ag-BAU, and Ag-zeolite samples were obtained.

Total viable count (TVC) determination was used to compare the antibacterial properties of the samples. Methodological instructions "Sanitary and microbiological control of drinking water" (Order of the Ministry of Health of Ukraine No. 60 of the 02.03.2005). All colonies, including microorganisms that grew at 36 °C for 24 hours and could be seen at a 2–5 times magnification, were considered.

Results

N₂ adsorption. All Ag-containing samples were subjected to low-temperature nitrogen adsorption/desorption. The results of the calculations are shown in Table 1. As we can see from the results, two samples (based on zeolite and alumina) are micro-mesoporous ones, but alumina is a predominantly mesoporous sample, whereas the BAU-based sample is practically a microporous one. It is interesting that modification with silver slightly influences the porous properties of alumina and coal samples. In the case of the zeolite sample, silver had a more significant influence on the porous properties. The volume of micropores dropped twice, but the total volume of pores remained unchanged. It seems that the macropore volume increases, which is indicated by a sharp increase in the end of the isotherm. According to the **X-ray fluorescence analysis** data, the contents of silver in the samples synthesized were 1.0 wt % for zeolite and BAU samples as well as 1.2 % for alumina sample.

Table 1. Porous properties of samples synthesized

Sample	S _{BET}	St	St _{micro}	Vt _{micro}	ΣV	Vt _{micro} /ΣV	Rdft	Rbgh (ads)	Rbgh (des)	R
	m ² /g	m ² /g	m ² /g	cc/g	cc/g	%	nm	nm	nm	nm
Zeol	88,2	10,47	78,1	0,036	0,061	59,02	0,974	1,517	1,977	1,38
Ag-zeol	50,71	21,60	29,11	0,015	0,065	23	0,74	1,63	1,82	2,57
Al ₂ O ₃	221,64	214,5	7,14	0,010	0,651	1,54	1,81	1,95	1,83	5,87
Ag-Al ₂ O ₃	235,1	233,1	2,01	0,001	0,660	0,15	1,9	1,63	1,97	5,66
BAU	941	31	910	0,469	0,516	90,9	0,74	1,63	1,54	1,10
Ag-BAU	940	36	904	0,474	0,532	89,1	0,74	1,62	1,55	1,13

Antibacterial activity. Early water samples of three Kyiv's lakes were compared by us due to total viable count. The worst characteristics last summer had water sample from Lake Sonyachne. TVC was 1500-3000 colony-forming units per cm³ (CFUs/cm³). In this research we wanted to compare the antibacterial properties of AgNPs on the different carriers.

Figure 1 shows some of photos for the deep inoculation of water samples into nutrient peptone-yeast agar in the presence of 0.1 g of a zeolite sample with silver (right) and without it (left). The expansion of colonies is considerably slowed. There is no evidence of overgrowth in particular.

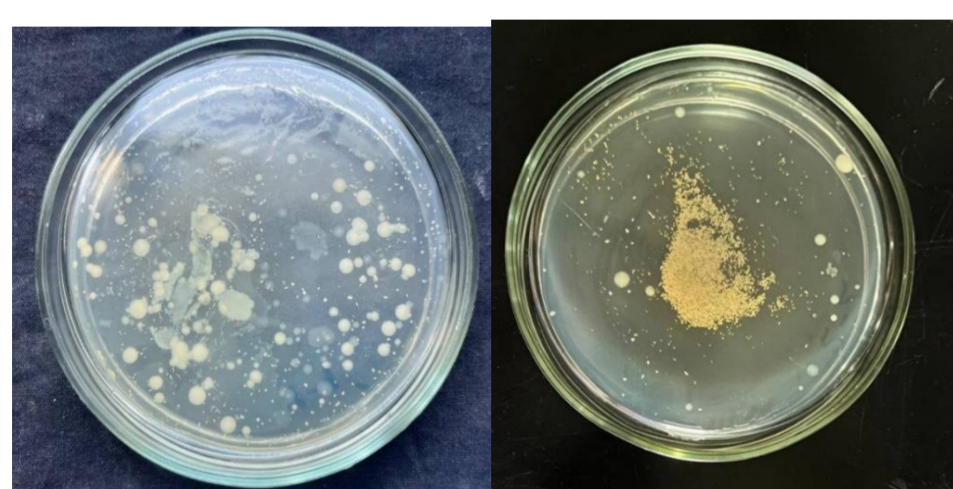


Fig. 1 Photos of sowing of water samples into nutrient agar in the presence of silver-containing zeolite (right) and without sample (left)

Table 2 The results of the inoculation of water into nutrient agar in the presence of AgNPs on the different carriers

Sample	Ag-Al ₂ O ₃	Ag-zeolite	Ag-BAU
The number of microorganisms, CFUs/cm ³	300	170	750

*The number of microorganisms for initial lake water was 3005 CFUs/cm³

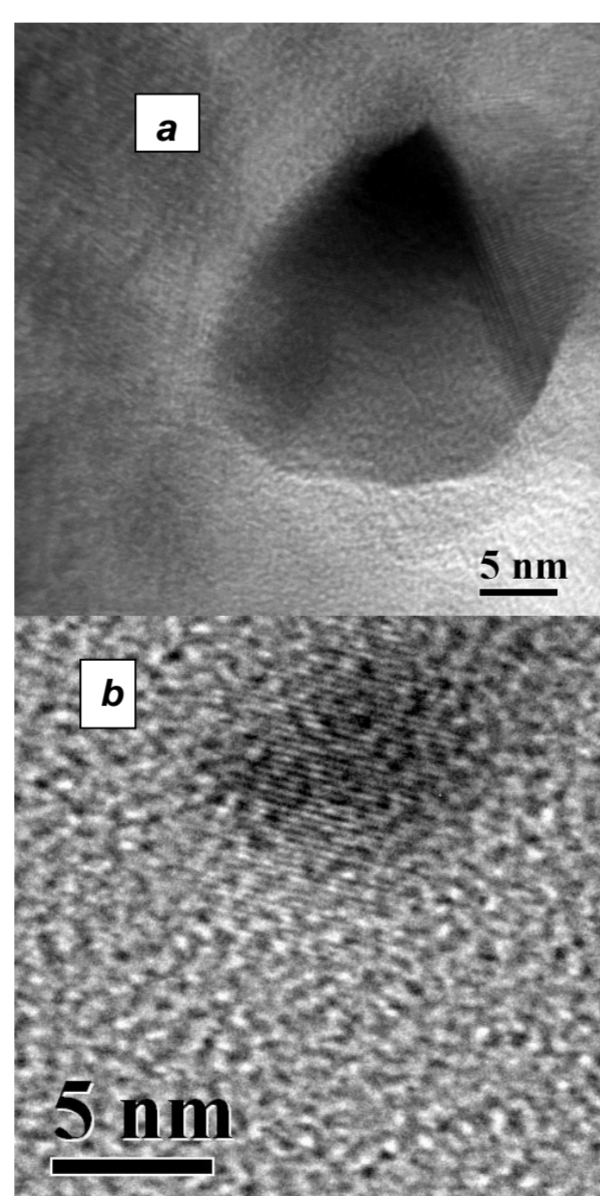


Fig. 2 TEM images of Ag-Al₂O₃ (a, b), Ag-zeolite (c, d), and Ag-BAU (e, f) samples

Fig. 3 High resolution TEM images of silver nanocrystals for Ag-Al₂O₃ (a) and Ag-zeolite (b)

Secondly, the role of the interaction of Ag with the zeolite matrix cannot be ignored. It is known that Si–O–Si groups are functional groups of clinoptilolite with which heavy metals interact [Argun M.E. J Hazard Mater. 2008. 150. 587]. This interaction may be similar to the interaction of Brønsted and Lewis acid centers in zeolites with metal particles, which contribute to the high acidity and activity of zeolites. It is possible that silver nanoparticles localized near the exchangeable cations of zeolites can be stabilized by cations, which further improves their antibacterial properties. It is known that the cations in zeolites of different types are localized in the cavities and channels. For clinoptilolite with three channel (A, B and C) structure the cations can be localized in the center of these channels depending on cation nature. As seen in the HR TEM image (Fig. 3), one silver nanoparticle of ~7 nm is localized over at least above 30 cavities. Therefore more than 30 different cations or acid sites can interact with one AgNP and stabilized it or improve its properties.

Conclusions

Therefore, AgNPs size distribution significantly depends on porous structure of the carrier used. AgNPs with preferable size of 5-10 nm have been obtained on zeolite with microporous and mesoporous structure. For mesoporous alumina carrier predominant size of AgNPs was - 10-20 nm with some bigger species of 30 nm. By the biggest particles of 10-20 nm with some bigger agglomerates characterized BAU-coal microporous sample. As a result the Ag-BAU sample with the biggest BET surface demonstrates the lowest antibacterial activity.

A significant decrease in the total viable count of lake water indicates a higher efficiency of using Ag-zeolite for water purification compared to Ag-Al₂O₃ or Ag-BAU samples. The latter can be caused, firstly, by the optimal size of silver particles, and, secondly, by the interaction of silver with cations or acid sites of zeolite.

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