NANOCOMPOSITES ON THE BASES OF SILICATE MATERIALS AND SILVER NANOPARTICLES

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Abstract

High application potential of nanocomposite materials is coming from the combination of unique properties of their individual components into one final material. Frequently, it can be formed by a bulk matrix in the form of microparticles and active nanostructured material that is anchored into the matrix to form the composite. This combination of micro- and nanostructured materials results into improvement of e.g. mechanical properties and makes the manipulation with the nanoparticles (NPs) easier. Silicate materials, such as clay minerals or zeolites, are frequently used as the inert support for metal NPs. Therefore, this study is aimed on the preparation of the composite materials based on silicate materials and incorporated silver NPs. Aqueous dispersion of silver NPs, with the average diameter of approx. 30 nm, was prepared using a modified Tollens process. These silver NPs were adsorbed from the primarily prepared aqueous dispersion on the montmorillonite and several types of synthetic zeolites. Antibacterial activity of the prepared nanocomposites was tested using a micro-dilution method. The obtained results showed that the antibacterial activity of the silver NP containing composite is only slightly influenced by their adsorption on this type of an inert support. However, adsorption of the silver NPs on these silicate materials is rather weak as approx. 10-30% of the adsorbed silver could be released just by the performed washing of the as-prepared composites in distilled water.

Keywords: silver nanoparticles, zeolites, montmorillonite

1. INTRODUCTION

Nanomaterials have become a common part of human life in the 21\textsuperscript{st} century because their unique properties are more and more frequently used in products of everyday usage that are commonly available on the market. Chemical approaches to the synthesis of nanomaterials already left the research laboratories and have entered the industrial operations. It can be illustrated by the production of e.g. nanoparticles of titanium dioxide, which enabled their mass-usage building materials, where they contribute to the retained cleanliness of facades due to their photocatalytic activity. Additionally they contribute to purification of the exhalations of the surrounding environment. [1] Nanoparticles (NPs) of zinc oxides can be found in colours or cosmetics, where they are used as the UV-irradiation absorber. [2] Silver NPs can be found in such products where antibacterial effect is required as e.g. textile materials, [3] cosmetics, [4] antibacterial surfaces of home appliances as e.g. refrigerators or washing machines. [5]

Although the preparations of silver NPs dispersion, based on the reduction process, represents already well-established processes (e.g. citrate method [6] or modified Tollens method [7]), which can be considered well-reproducible, their application in practice can be limited by a possible toxicity of the NPs if they were evolved into the environment. These problems are also encountered with the composite materials (e.g. textile fibres coated by silver NPs) because several mechanical and chemical processes, like washing, can release the NPs from the solid surface. The improvement can be approached by the composite nanomaterials, where the silver NPs are fixed to any inert carrier of microscopic or macroscopic diameters and where also the
unique characteristics of the NPs, also involving the antibacterial activity, are retained. From the inert carriers, aluminium oxide [8] or silicon oxide [9] can be mentioned. Additional profitable characteristics of a composite material can be achieved when the carrier is represented by iron oxides because then the composite, on the basis inert carrier-silver NP (nanoAg@inert carrier), can be manipulated using magnetic field. [10] However, also silicate materials, such as clays or zeolites, can be used as inert carriers of silver NPs. [11,12] The usage of such natural materials, as the inert carriers forming the nanocomposites, bring advantages not only from the economical point of view (low-cost material) but also because of their physicochemical properties such as large surface area (i.e. high adsorption capacity) and non-toxicity from the chemical point of view.

Composition materials consisting of surface anchored silver NPs, as the active part, and inert carrier of silicate character, represent an interesting material from the technological point of view. This kind of nanomaterial can find application especially in the field of disinfection either for antibacterial coating of surfaces like textile fibres or plastics or for disinfection of drinking water. Therefore this work is aimed on the preparation of such materials and their tests of antibacterial effect of the resulting nanocomposite of the nanoAg@inert carrier composition. The fundamental procedure of the material preparation is based on a pure adsorption of the silver NPs, from their aqueous dispersion, on silicate materials both of natural (montmorillonite) and synthetic (zeolite) origin.

2. EXPERIMENTAL PART

The silver NPs were prepared following modified Tollens reaction [7], which is based on the reduction of 1mM solution of AgNO<sub>3</sub> (Tamda, ČL 2009) with 10mM solution of D-maltose (Sigma-Aldrich) in the presence of 5mM solution of ammonium (Lach-Ner, p.a.), which forms complex cation [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. The reduction was carried out at pH equal to 12.5, which was maintained by the solution of NaOH. The as-prepared silver particles were of the following characteristics: average particle diameter was 28 nm and the value of polydispersity was 0.09. These values were obtained from DLS measurements performed at Zeta Potential Analyzer Zeta Plus (Brookhaven Instr. Co., USA) and they were confirmed by the transmission electron microscopy JEM 2010 (Jeol Ltd., Japan). The nanodimensional character was additionally checked by UV-Vis spectroscopy (spectrophotometer Specol S600, Analytic Jena AG, Germany) through the significant absorption maximum around the wavelength 415 nm, which corresponds with the existence of surface plasmon specific to the silver NPs in the diameter of several tens of nanometers. All the solutions were prepared with demineralised water obtained from AQUAL 29 (0.05 µS/cm).

The composite nanoAg@silicate was prepared using simple adsorption of the silver NPs from their aqueous dispersion on the surface of the silicate, which stirred with the dispersion for the period of 3 hours (the time when a stable concentration of the silver NPs was adsorbed on surface of the inert carrier). The adsorption was always performed with the silver NP dispersion in the volume of 40 mL in different silver concentrations (from 10.8 to 108 mg Ag/L) and 0.2g of the particular silicate. After the mentioned period of time, the as-prepared nanocomposite was filtrated from the remaining aqueous dispersion and consequently dried at 105°C for two hours. The amount of the trapped silver NPs was determined from the decrease in the absorbance at the maximum of the specific absorption at the wavelength of 415 nm, which could be done because the specific absorbance is linearly dependent on the concentration of the particles in the dispersion. A check of the silver content was also performed by AAS at atomic absorption spectrometer Perkin Elmer 3300 after the extraction of silver from the nanocomposite by 30% solution of HNO<sub>3</sub> (Lach-Ner, p.a.). The following substances were used as the inert silicate carrier: Ca-montmorillonite (Ca-MMT, Institute of geonics AV ČR in Ostrava) consisting of (in weight percentage): SiO<sub>2</sub>: 70.1; Al<sub>2</sub>O<sub>3</sub>: 16.0; TiO<sub>2</sub>: 0.22; Fe<sub>2</sub>O<sub>3</sub>: 0.65; FeO: 0.15; MnO: 0.009; MgO: 3.69; CaO: 1.59; Na<sub>2</sub>O: 0.27; K<sub>2</sub>O: 0.078; F: 0.084; P<sub>2</sub>O<sub>5</sub>: 0.026; S: 0.04 and having specific surface area 96 m<sup>2</sup>/g; synthetic zeolite Ammonium Y (Sigma Aldrich) having the specific surface area 266 m<sup>2</sup>/g; Sodium Y (Sigma Aldrich) with specific surface area 655 m<sup>2</sup>/g and zeolite 13X (BDH) with specific surface area 586 m<sup>2</sup>/g. The specific surface areas of the used materials were determined due to the method of static adsorption of inert gas using Sorptomatic 1990 (Thermo Scientific).
The antibacterial activity of the prepared composite nanomaterials was tested using a standard dilution micro-method, which enables to determine minimal inhibition concentration (MIC). Determination of the inhibition concentration was performed in micro-titration plates, when the samples of the as-prepared nanocomposite (0.1g of the composite was dispersed in 3 mL of distilled water) were consequently diluted twice, four-times, eight-times, sixteen-times, thirty two-times, sixty four-times and a hundred twenty eight – times with Mueller-Hinton cultivation broth. The plates were inoculated by a standard amount of microorganism at the concentration about 105 CFU/mL. Minimal inhibition concentration of the composite nanomaterial was read after 24-hour incubation at 37°C.

Fig. 1: Dependency of the amount of silver NPs adsorbed on the surface of inert carrier on the amount of silver present in the as-prepared aqueous dispersion for the following silicate materials: (a) zeolite Sodium Y, (b) zeolite Ammonium Y, (c) zeolite 13X, and (d) Ca-MMT.

3. RESULTS AND DISCUSSION

The preparation of the nanoAg@silicate nanocomposite was performed via a simple adsorption of silver NPs from their aqueous dispersion on the particular silicate material. These experiments were carried out in the system containing 0.2 g of the silicate material in 40 mL of the NP dispersion with the growing concentration of silver, in the form of the NPs, in the range from 10.8 to 108 mg Ag/L in the dispersion. After the establishment of the equilibrium, the as-prepared composite was filtered from the dispersion and the content of silver was indirectly determined through the decrease of the amount of silver NPs in the filtered dispersion, which was determined due to the changes in absorbance of the surface plasmon. The obtained values of the silver NPs adsorbed on the surface of the inert silicate carrier were consequently recalculated for 1g of the inert carrier. In all studied cases the dependencies of the silver NPs amount, adsorbed on the surface of the inert silicate carrier, on the amount of silver NPs originally present in the dispersion (Fig. 1) revealed typical tendencies corresponding to the model of Langmuir adsorption isotherm with a characteristic limitation of the adsorbed amount of the silver NPs at their higher concentrations in the dispersion. Based on the presented graphs, using mathematical expression of the Langmuir adsorption isotherm, the limit values of possible
adsorption of the silver NPs on the carrier surface were determined. For zeolite Sodium Y, the value was 8.60 mg Ag per 1g of zeolite, for zeolite Ammonium Y it was 6.65 mg Ag per 1g of zeolite, and for zeolite 13X 8.42 mg Ag per 1g of zeolite. The obtained values point out at the fact that zeolite Sodium Y and 13X (both of them being typical sodium zeolites) proved to have comparable values of maximal amount of silver NPs, which can be adsorbed on their surfaces. Additionally these values are nearly one third higher in comparison with Ammonium Y. These results correlate really well with the experimentally determined value of the silicate specific surface areas (655 m²/g and 586 m²/g for Sodium Y and zeolite 13X, respectively). In both cases the surface area is more than twice higher in contrast to Ammonium Y, which has the specific surface area equal to 266 m²/g. In the case of the Ca-MMT, the amount of maximally adsorbed amount of silver NPs is significantly lower than in the case of the zeolites and has the value of only 5.4 mg Ag per 1g of Ca-MMT. This effect can be simply explained by the value of the specific surface area, which is equal to 96 m²/g.

Fig. 2: TEM figures of (a) pure calcium montmorillonite (Ca-MMT) and (b) nanocomposite nanoAg@Ca-MMT.

The presence of silver NPs adsorbed on the inert silicate carrier was proved indirectly on the bases of control determination of the silver content in the as-prepared composites after their rinsing in HNO₃ and subsequent determination of silver by AAS. Direct proof of the silver NP presence was obtained from TEM images, on which it can be clearly seen that the silver NPs gathered on the surface of the microparticulate silicate material (Fig. 2). Because of the structure of the pores in the silicate carrier (microporous material) one cannot expect that the silver NPs, having the average diameter of 28 nm, would be able to penetrate into the structure of pores of the used silicate materials and therefore they are adsorbed only on the carrier surface. Thanks to this adjustment of the as-prepared nanocomposite, the particles can interact with their surrounding intensively, which is also necessary if we require retaining their antibacterial activity, which is according to the already published studies closely connected with the direct interaction of the silver NPs with the living organism. [13] The fact that the particles retain their antibacterial effect was, however, proved by the tests of the antibacterial activity of the as-prepared nanocomposites performed on a variety of both gram-positive and gram-negative bacteria. The nanocomposite proved inhibition effect, or eventually bactericidal effects, however, this activity is from one to two orders lower than the activity of independent silver nanoparticles in aqueous dispersion (Table 1). The subsequently performed tests, evaluating possible release of the silver NPs from the as-prepared nanocomposite, proved that the particles are bounded only weakly to the inert silicate carrier because they were release even when the composite was only rinsed in water. The composites nanoAg@zeolite proved to have a high decrease in the content of silver NPs (max. 26 %) in the rinsing process for the composite with zeolite Sodium Y. Zeolite 13X, as the carrier of the NPs, proved to release 23% of the silver NPs and Ammonium Y just 16% of them. The lowest decrease, in the rinsing process, was revealed to be in the case of the composite of the nanoAg@Ca-MMT composition, where the decrease was determined to be approx. 10%. Based on these results it can be assumed that the determined antibacterial activity of the as-prepared nanocomposite is most probably connected with the silver release from the composite into the cultivation broth. This assumption can be supported by the fact
that the values of MIC, for the tested nanocomposites, correspond to the trend of the released silver NPs from the nanocomposite in the process of rinsing.

**Table 1:** The values of antibacterial activity of the as-prepared nanocomposites (nanoAg@inert carrier) determined, using microdilution method, as minimal inhibition concentration (MIC) of the prepared nanocomposites for tested microorganisms.

<table>
<thead>
<tr>
<th>Tested bacterial strain</th>
<th>Minimal inhibition concentration (mg/mL) of nanocomposites</th>
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<tr>
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<td>z. Sodium Y</td>
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<tr>
<td>Enterococcus faecalis</td>
<td>13,3</td>
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<tr>
<td>Staphylococcus aureus</td>
<td>9,2</td>
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<tr>
<td>Pseudomonas aeruginosa</td>
<td>7,1</td>
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<tr>
<td>Staphylococcus epidermidis</td>
<td>9,2</td>
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<tr>
<td>Klebsiella pneumoniae</td>
<td>9,2</td>
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<tr>
<td>Escherichia coli</td>
<td>13,3</td>
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4. CONCLUSION

The experiments, aimed on the preparation of the nanocomposite materials of the composition nanoAg@inert carrier proved to be simple for preparation, when the primarily obtained particles are adsorbed on the surface of the carrier. The whole process proceeds according to model of Langmuir adsorption isotherm. The amount of the silver NPs adsorbed on the silicate material is dependent on the value of the specific surface area of the material. The as-prepared nanocomposites revealed also reasonably high antibacterial activity, which is undoubtedly connected with the silver NPs. However, it is necessary to admit that the particles are not strongly adsorbed on the carrier surface and their stability in aqueous medium is low. The particles can be released from the surface even when the material is rinsed or washed with water.

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