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SILVER-CONTAINING NANOCOMPOSITE BASED ON GUAR GUM AS A CATALYST FOR THE REDUCTION OF 4-NITROPHENOL

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Guar gum, silver nanoparticles, catalysis, reduction, 4-nitrophenol

Abstract. *A silver nanocomposite on a matrix of the natural polysaccharide guar gum cross-linked with borate bridges was obtained. Metallic nanoparticles were synthesised by the reduction of silver ions under the action of the polysaccharide. The formation of the nanocomposites was confirmed by UV and IR spectroscopy and X-ray diffraction analysis. The resulting polymeric nanocomposite shows catalytic activity in the reduction of 4-nitrophenol with sodium borohydride under mild conditions.*

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Introduction

Nitroaromatic compounds in wastewater from chemical industry plants is a threat to aquatic flora, fauna, and humans, even at low concentrations. 4-Nitrophenol is a hazard class 2 substance with a maximum permissible concentration (MPC) of 0.02 mg/l in water for domestic, drinking, and municipal and amenity water use. Removing this and other nitroaromatic compounds from wastewater is an urgent task. In turn, the reduction of 4-nitrophenol yields 4-aminophenol. It is used as a component in fur dyes and as an intermediate in the production of various reducing agents and sulfur dyes.

Nowadays, the use of metal nanoparticles as catalysts for reduction has been developed. Their high specific surface area approximates catalysis closer to the homogeneous type. Moreover, the significantly higher proportion of metal atoms on the nanoparticle surface compared to conventional heterogeneous catalysts. Therefore, the term "nanocatalysis" has been introduced, regarded as a unique "bridge" between heterogeneous and homogeneous catalysis [1].

Nanoparticles of Rh, Pt, and Au have been used as reduction catalysts [2, 3]. However, the use of Ag nanoparticles is preferred [4] due to their relative affordability, catalytic activity, selectivity, stability, and potential for reuse. Initially, there were attempts to catalyse reactions

using colloidal solutions of silver nanoparticles [5]. However, those were unstable and degraded within 20–30 days. To stabilise the nanoparticles, inorganic matrices of Cu [6], iron metallogel [7], TiO_2 [8], and CeO_2 [9] have been applied.

The use of polymer nanoparticles as matrices for stabilising colloidal silver is more promising. Copolymers of *N*-isopropylacrylamide [10-12], styrene [12, 13], and pyrrole [14] obtained via emulsion polymerisation have been applied as such matrices. The reduction reaction of 4-nitrophenol occurs in an aqueous medium. Indeed, it is logical to utilise hydrophilic natural polysaccharides as carriers for silver nanoparticles. Reported examples include agar, pectin, and carboxymethylcellulose [15], extract from leaves of the tropical plant *Cucumis maderaspatanus* [16], polyaminocyclodextrin [17], and a graft copolymer of chitosan with *N*-isopropylacrylamide and acrylic acid [18]. An advantage of using this class of polymers is the reduction of Ag^+ ions to Ag^0 without the reducing agent (typically $NaBH_4$), by the functional groups of the polysaccharide itself only [15, 16, 19]. One of the most common polysaccharides is guar gum (GG). It refers to the group of galactomannans and consists of (1-4)-β-D-mannopyranose units linked at every second cycle to α-D-galactose units [20]. Guar gum is widely used in oil extraction, medical chemistry, water treatment systems, paper, textile, cosmetic, food, agricultural industries, etc. [21].

The purpose of this work is to study the feasibility of using silver nanoparticles on a guar gum matrix as a catalyst for the reduction of 4-nitrophenol.

Experimental part

UV spectra were recorded on a W&J UV1600PC spectrophotometer using LEKI ScanPro software. Measurements were performed in the wavelength range of 200 to 500 nm.

IR spectra were recorded on a Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer equipped with a Platinum ATR accessory and a diamond prism (4000-400 cm^{-1}, resolution 2 cm^{-1}).

Diffraction patterns were obtained using a Thermo ARL X'TRA diffractometer with Cu-K_α radiation (K_α=1.54443 Å). A current of 35 mA and a voltage of 45 kV were applied. Diffraction intensity was measured at a scanning rate of 2°/min; the measured 2θ values ranged from 10 to 80°.

Synthesis of the guar gum/silver nanocomposite (GG/Ag)

196 ml of distilled water was equilibrated at room temperature under constant mechanical stirring (500 rpm); then 4 g of a commercial guar gum sample (India) was added to the water. After 30 minutes of stirring, 1.36 g of $AgNO_3$ was added to the polysaccharide solution to achieve a final concentration of 40 mmol/l, followed by stirring for 30 minutes at 500 rpm.

After 24 hours of storage in the darkness, a colour change from colourless to dark brown was observed. 50 ml of this solution was thieved and diluted with 50 ml of water to achieve a homogeneous consistency.

Using a syringe, 5 ml of the homogenized mixture was dropwise added to a beaker containing 100 ml of acetone, resulting in the formation of spherical granules with a diameter of 2-4 mm. The granules were placed in acetone for 2 hours.

The granules were then filtered from acetone, air-dried for 1 hour, and transferred to 100 ml of a 1% aqueous sodium tetraborate solution. They were stored for 4 hours to achieve sufficient cross-linking between the gum and borate ions.

The granules were filtered, washed with distilled water and acetone until a neutral pH (as indicated by pH test), and dried at room temperature. The dried granules shrank to half their original size.

Catalytic reduction of 4-nitrophenol

In a spectrophotometer cuvette with a 1 cm optical path length containing 3 mL of an aqueous 4-nitrophenol solution (concentration 10 mg/L), 10 mg of catalyst particles and a weighed sample of $NaBH_4$ were added to achieve a final reducing agent concentration of 20 mmol/L. The mixture was immediately stirred and placed in the spectrophotometer cuvette compartment. The progress of the reaction was monitored by periodically scanning the reaction mixture in the 200-500 nm range.

Main body

The construction of silver nanocomposites based on guar gum was conducted according to the *"bottom-up" nanotechnology* principle, involving the reduction of silver ions to particles with a size of about 10 nm using primary hydroxyl and aldehyde groups of the polysaccharide.

The formation of silver nanoparticles (prior to the cross-linking stage with borate ions) is confirmed by objective data, specifically surface plasmon resonance. It leads to the appearance of an absorption maximum in the UV spectrum. Silver nanoparticles typically exhibit a distinct absorption peak between 390 and 420 nm. According to Fig. 1, a broad absorption maximum at 428 nm indicates variations in particle size, shape, or composition. Most likely, the shift to the longer-wavelength region is due to deviations from the sphericity of the formed particles rather than an increase in their size [22].

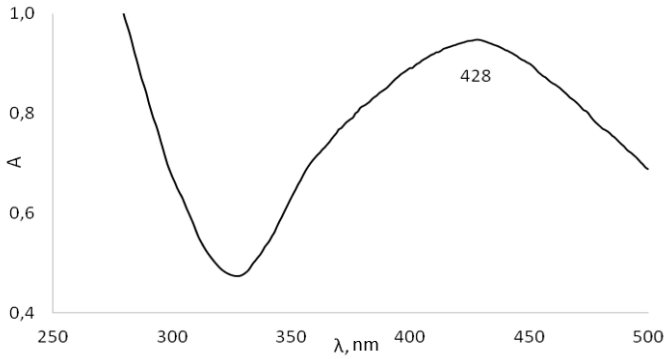

Fig. 1. UV spectrum of the guar gum solution with silver nanoparticles

For the powdered sample obtained after drying, an X-ray diffraction spectrum was recorded. The spectrum of the initial guar gum sample (Fig. 2) exhibits a bimodal amorphous halo with a distinct reflex at $2\theta = 20.5°$. A similar spectrum is provided in the literature [23].

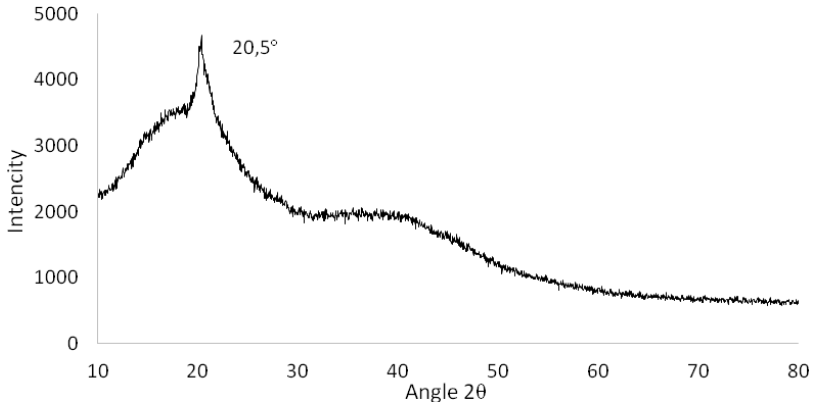

Fig. 2. Diffractogram of the initial guar gum

The spectrum of the polysaccharide (Fig. 3) containing silver nanoparticles confirms their presence in the sample. Thus, the distinct reflex at 2θ = 39.3° corresponds to the (111) plane of the face-centered cubic lattice. The reflex at 2θ = 46.4° corresponds to the (200) plane. The values are overestimated compared to the classical values (38.1° and 44.3°, respectively). However, as for the UV spectra, it can be explained by distortions of the crystal lattice caused by its incomplete formation and deviations from the ideal shape. The reflexes at 2θ = 21.5° and 23.8° are attributed to the crystalline structures of guar gum.

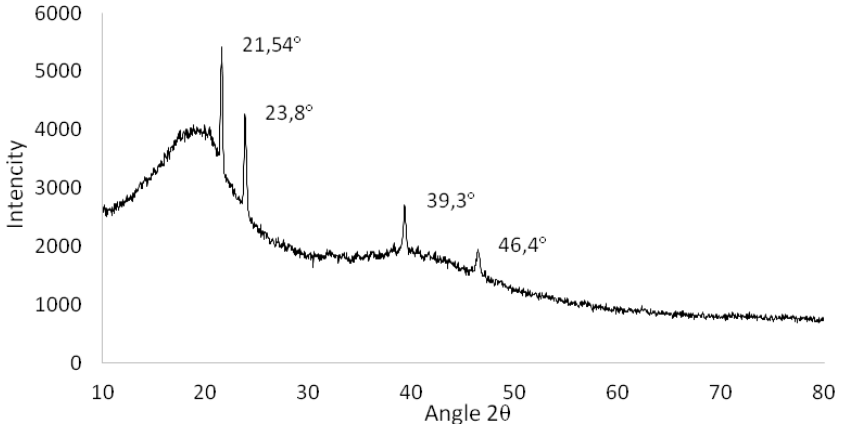

Fig. 3. Diffractogram of guar gum with silver nanoparticles

The IR spectrum of the gum with silver nanoparticles shows no significant differences from the spectrum of the initial guar gum. However, differences appear after treating the granules with a sodium tetraborate solution. In the IR spectra of polysaccharides, the most informative and sensitive to structural changes is the range from 1200 to 1000 cm^{-1}. It exhibits absorption bands at 1148 cm^{-1} (C–O stretching vibrations in the CH_2OH fragment), 1059 cm^{-1} (asymmetric C_6–O–C_1 stretching vibrations), and 1015 cm^{-1} (–CH_2– twisting vibrations). When comparing the spectra of the gum before and after treatment with $Na_2B_4O_7$ (Fig. 4), a noticeable change in the intensity of the absorption bands in this range is observed. A shift to the longer-wavelength region occurs for the absorption bands at 1015 cm^{-1} (to 1030 cm^{-1}) and 1059 cm^{-1} (to 1070 cm^{-1}).

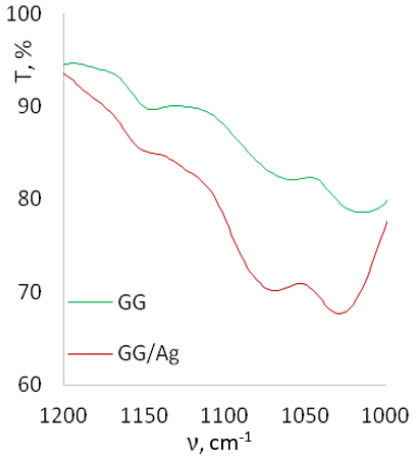

Fig. 4. IR spectra of the initial and modified gum

To catalyze, it was necessary to form special catalyst particles for their conveniently introduction into the reaction mixture, recovery, and reuse. Guar gum, while being a water-soluble polymer, is insoluble in a number of water-miscible solvents (ethanol, methanol, acetone). We utilised this property to obtain the subsequently convenient polymer granules to use them in catalytic reduction reactions. A solution of the polymer loaded with silver nanoparticles at various concentrations was introduced using a medical syringe into a beaker containing acetone; the spherical granules with a diameter of 2-4 mm rapidly were formed in the solution. A 1% gum solution proved to be the most convenient for the formation of isolated granules. In this case, individual granules resistant to agglomeration were formed. When using a 2% solution, the flow through the nozzle of the medical syringe was very slow, resulting in the formation of elongated particles. The structure of the formed granules was fixed by strong covalent intermolecular bonds formed by borate ions.

The obtained catalyst granules were used for the reduction of 4-nitrophenol. The reduction reaction of 4-nitrophenol is thermodynamically favorable. However, it proceeds very slowly in the absence of a catalyst. Without the addition of the catalyst, the optical density in the cuvette remains almost unchanged (Fig. 5).

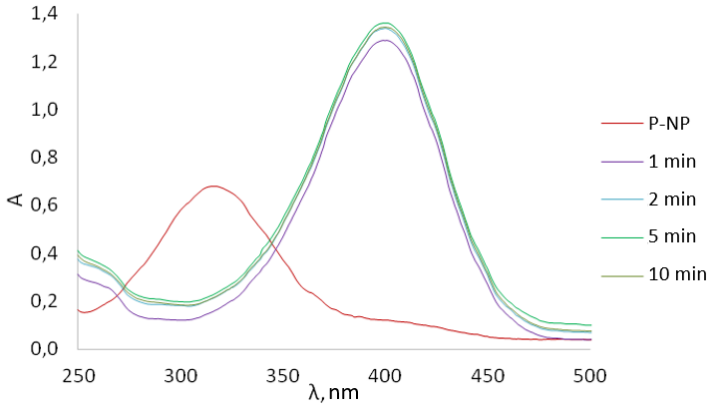

Fig. 5. UV spectra of 4-nitrophenol in the absence and presence of sodium borohydride

The initial spectrum of 4-nitrophenol is characterized by an absorption maximum at 316 nm. However, in the presence of sodium borohydride, a bathochromic shift occurs; the absorption maximum shifts to the 400 nm range. After the addition of sodium borohydride, a

gradual decrease in absorption at 400 nm and a corresponding increase in optical density at 300 nm are observed (Fig. 6). It is associated with an increase in the concentration of 4-aminophenol. During this process, hydrogen generated from $NaBH_4$ promotes solution mixing and removes air, preventing the oxidation of 4-aminophenol in air. However, the bubbles affect the accuracy of optical density measurements; in some cases, it makes them almost impossible.

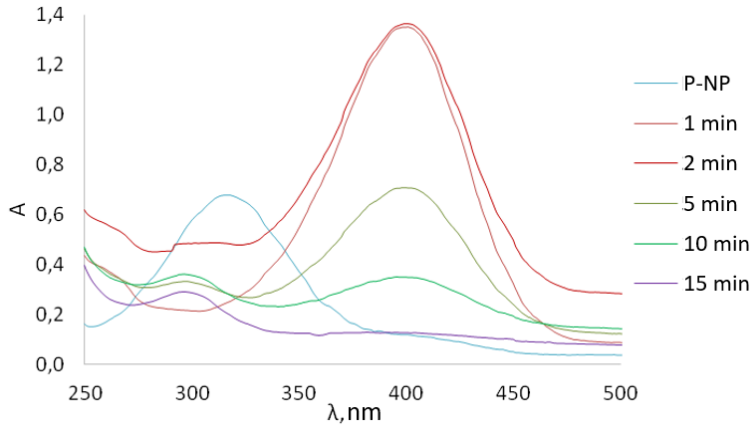

Fig. 6. UV spectra of 4-nitrophenol and its reduction products

Figs. 7 and 8 show the dependence of the optical density of 4-nitrophenol and 4-aminophenol for the borate-crosslinked catalyst at 400 and 300 nm. As a result, the reaction is completed within 15 minutes; it indicates the high efficiency of the catalyst used.

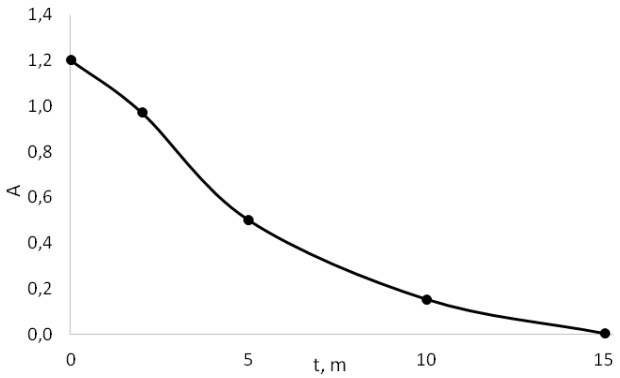

Fig. 7. Dependence of the optical density of 4-nitrophenol at 400 nm on the reduction time

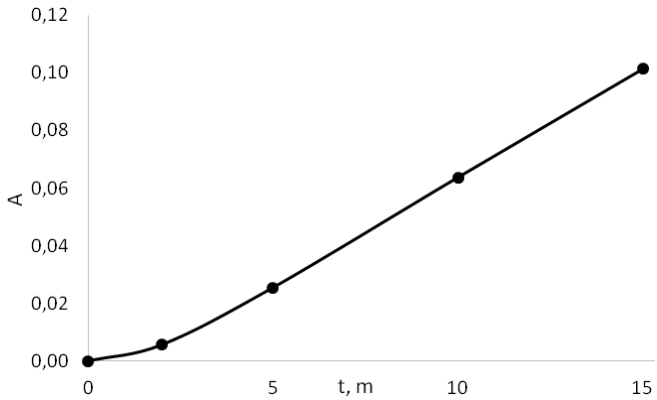

Fig. 8. Dependence of the optical density of 4-aminophenol at 300 nm on the reduction time

Conclusions

A silver nanocomposite on a matrix of the natural polysaccharide guar gum cross-linked with borate bridges was obtained. The silver nanoparticles were obtained through reduction of silver ions mediated by the functional groups of the polysaccharide. The formation of the nanocomposites was confirmed by UV and IR spectroscopy and X-ray diffraction analysis. The synthesized polymer nanocomposite demonstrates catalytic activity in the sodium borohydride reduction of 4-nitrophenol at room temperature, with the reaction proceeding on a minute timescale.

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