Synthesis of copper-containing nanoparticles and their potential application as biocidal agents

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Abstract. The paper presents the results of a study on the possibility of obtaining Cu nanoparticles stabilized with various polymers using chemical reduction method. The following stabilizer-reductant pairs were used for nanoparticles synthesis: gelatin - ascorbic acid, polyvinylpyrrolidone - tert-butylamine borane, polyethylene oxide - hydrazine borane. The formation of Cu nanoparticles was confirmed by electron spectroscopy. All the samples studied showed an absorbance maximum in the region of 580 nm, in agreement with the literature data on the phenomenon of localized plasmon resonance of copper nanoparticles. Transmission electron microscopy showed that the nanoparticles are spherical with an average diameter of 6 nm. The stability of the synthesis products was evaluated by long-term incubation in test tubes under normal conditions. Nanoparticles obtained in the presence of gelatin were stable for 15 days, polyvinylpyrrolidone - 6 weeks, and polyethylene oxide - 2 weeks. The potential application of the obtained nanoparticles as biocidal agents was considered. It was found that the synergistic effect of the presence of the polymer can enhance the biocidal properties of the system. The synthesized products were found to have applications in agriculture, environmental protection, medicine, and as components of antibacterial coatings for public transportation and healthcare facilities.

1 Introduction

Nanostructured materials are one of the hot spots of recent research due to the presence of special properties based on the dimensional factor [1]. At the same time, the properties of such materials are influenced by both their size, structural organization and morphology. These special properties make nanomaterials attractive for use in various industries [2].

One of the most common types of nanomaterials used in industry are nanoparticles. For example, metal nanoparticles have found applications in catalytic systems for environmental protection and as reagents in agriculture. Metal nanoparticles are known to be used as biocidal agents for the treatment of food packaging (protection of stored products from insect pests and pathogens) [3], soils (protection from fungal and bacterial contamination, enhancement of fertility) [4], and plants (control of diseases and pests, enhancement of resistance to environmental factors, stimulation of growth and yield) [5]. In addition, they

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are actively used in medicine as antibacterial agents [6]. Some studies show that metal nanoparticles can solve the problem of neutralizing antibiotic-resistant strains of Staphylococcus aureus [7, 8]. At the same time, the substitution of noble metals by less expensive base metals continues to be relevant.

Among many methods of nanoparticle production (electrochemical reduction, physical methods, etc.), chemical reduction of metal salts stands out. This method is promising due to its simplicity and cost effectiveness [9].

To obtain metal nanoparticles by chemical reduction, various stabilizers are usually used to control the growth of particles and their stability [10]. Polymers and other matrix-like structures act as stabilizers. Among the various polymers used, those that are water-soluble, which are distinguished by their superior environmental safety, warrant particular attention. [11]. Furthermore, the use of water-soluble polymers eliminates the necessity for more expensive and less safe solvents.

Therefore, the aim of this study is to evaluate the possibilities of obtaining copper nanoparticles in the presence of different stabilizers. In addition, different aspects of their application as biocidal agents are discussed.

2 Materials and methods

Copper-containing nanoparticles were obtained by chemical reduction of copper ions in an aqueous solution of a stabilizer [10]. The following stabilizer–reducing agent pairs were utilized in this study: gelatin-ascorbic acid, poly-N-vinylpyrrolidone (PVP) - tert-butylamine borane, and polyethylene oxide (PEO) - hydrazine borane.

To synthesize nanoparticles in the presence of gelatin, copper sulfate pentahydrate was added to an aqueous solution of the stabilizer. The resulting solution was brought to the boiling point by microwave irradiation at a power of 600 W, which allowed rapid and uniform heating of the solution to the required temperature. The copper ions were reduced by the addition of ascorbic acid as a reducing agent. NaOH solution was used to control the pH during the synthesis. The maintained pH was equal to 10.

The synthesis of nanoparticles in the presence of PVP (Mw = 60000) was carried out at 22°C. Copper sulfate pentahydrate was added to the aqueous solution of the polymer. The copper ions were reduced by tert-butylamine borane. The synthesis was carried out at pH = 7.

The reduction reaction of copper ions in the presence of PEO (Mw = 200000) was carried out under normal conditions. Copper sulfate pentahydrate was added to the aqueous solution of PEO. Hydrazine borane ($N_2H_4 \cdot BH_3$) was used as a reducing agent. NaOH or HCl solutions were added to change the pH of the system.

The components and synthesis conditions of the systems studied are summarized in Table 1.

Table 1. Summary of nanoparticle synthesis conditions

N	Stabilizer	Reducing agent	Synthesis condition
1	Gelatin	Ascorbic acid	Heating until boiling is reached. pH = 10.
2	PVP	Tert-butylamine borane	Normal conditions. pH = 7.
3	PEO	Hydrazine borane	Normal conditions. pH = 8.

Distilled water was used for the preparation of all the solutions.

During synthesis, the pH was monitored using a Mettler-Toledo FiveGo FG2 pH meter.

To obtain data on the ansorbance of the synthesis products, an Ecros PE-5400VI spectrophotometer (spectral range = 315-1000 nm, spectral slit width - 4 nm) was used in photometer mode, as well as a Specord 210 Plus spectrophotometer ("Analytik Jena AG"). The absorbance values were obtained for the interval between 530-630 nm with a step of 5 nm.

The study of particle morphology was carried out by electron microscopy. A transmission electron microscope (TEM) EM-1011 ("Jeol", Japan) with a digital camera "Gatan" (USA) operating under the control of "Digital micrograph" program was used. Manual calculation was used to determine the particle size.

The stability of the obtained colloidal systems was evaluated visually during prolonged exposure in test tubes under normal conditions.

3 Results and discussion

3.1 Copper nanoparticles synthesis and characterization

The chemical reduction of metal ions results in the formation of particles of these metals. The process of particle growth involves mutual recognition between the particles and the stabilizer introduced into the system. As a result of this process, particle growth is limited by the stabilizer [12]. This mechanism is illustrated in Fig. 1.

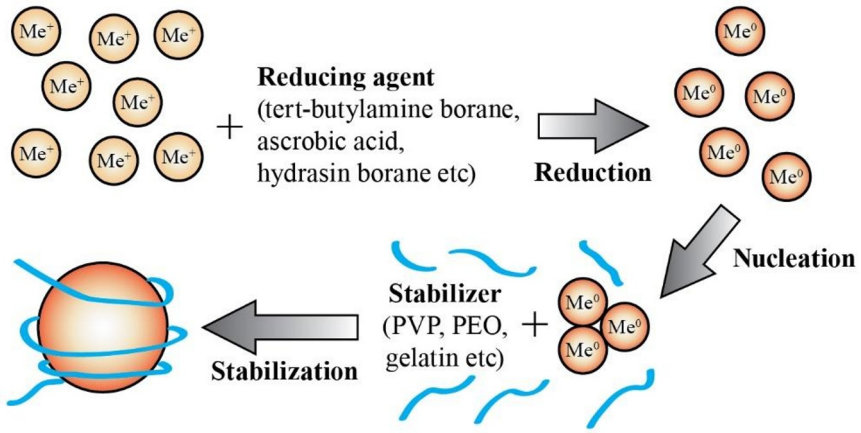

Fig. 1. Mechanism of copper nanoparticles formation in the presence of stabilizer

The successful result of the synthesis can be traced visually. The color of the solution changes during the formation of nanoparticles. In the case of copper nanoparticles, the solution becomes red-brown [13]. Thus, the concentrations of reducing agent and nanoparticle precursor were selected experimentally and considered acceptable when the color of the solution changes.

Electron spectroscopy was used to confirm the formation of nanosized copper particles (Fig. 2). As a result of nanoparticle formation, characteristic maximum appears in the spectra, indicating the manifestation of the localized plasmon resonance (LPR) effect. For Cu nanoparticles, the maximum values typical for LPR are observed in the region of 580 nm [14]. It is noted that the maxima corresponding to the LPR of copper nanoparticles can shift in the range between 570 and 610 nm [15].

The data presented in Fig. 2 show that copper nanoparticles were obtained with all the stabilizers under study. At the same time, the location of the maximum was slightly different.

It was at 585 nm in the presence of gelatin and at 575 nm in the presence of PEO and PVP. The synthesis products also differed in the value of absorbance, which is due to the differences in the components of the polymer-reducing agent systems, as well as insignificant differences in the synthesis products and the peculiarities of sample preparation.

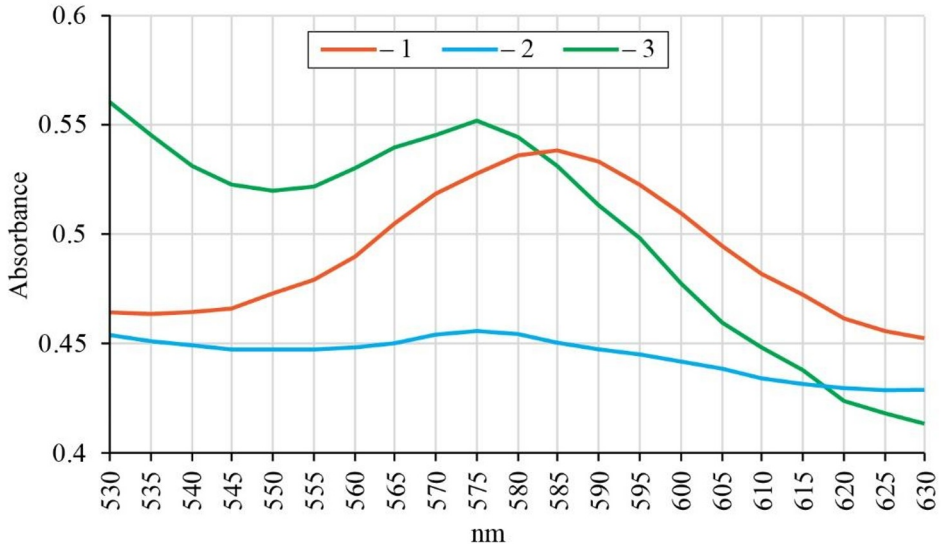

Fig. 2. Absorbance of copper-containing nanoparticles obtained in the presence of gelatin (1), PVP (2), and PEO (3).

The nanoparticles obtained in the presence of PEO were investigated using TEM methods (Fig. 3). Examination of microphotographs showed that nanoparticles have spherical shape. No signs of aggregation of nanoparticles were found. The particle sizes were in the range of 1 to 12 nm (Fig. 4). The average diameter of the majority of the particles was about 6 nm.

The stability of the synthesis products was evaluated during prolonged exposure in test tube under normal conditions. Colloidal systems with PEO and gelatin showed the lowest stability, retaining their properties for 15 (gelatin) and 14 (PEO) days. Nanoparticles obtained in the presence of PVP remained stable for 6 weeks or more.

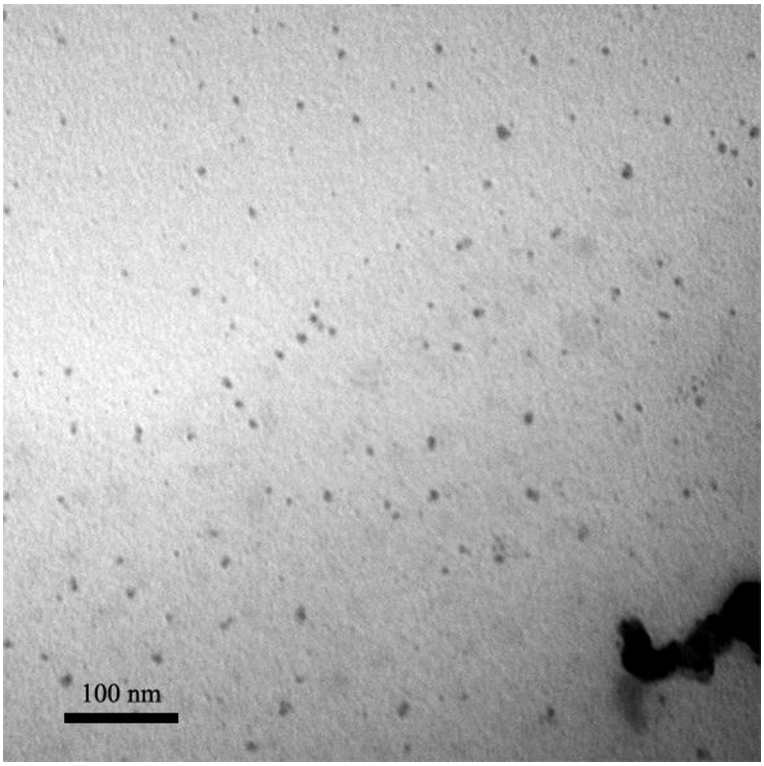

Fig. 3. TEM image of copper nanoparticles obtained in the presence of PEO.

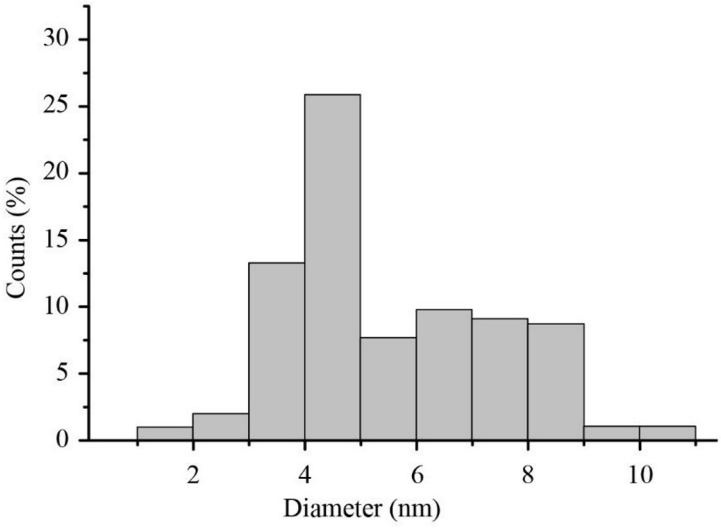

Fig. 4. Size distribution of particles obtained in the presence of PEO.

3.2 Application of copper nanoparticles as biocidal agents

Copper nanoparticles obtained by chemical reduction can be used as components of more complex materials and also as standalone materials. Such nanostructured objects have a high

potential for application in agriculture and medicine due to the ease of production and safety of the synthesis products.

The biocidal properties of both copper itself and its nanoparticles are well known. Copper is used for disinfection and has antiviral and antifungal activity [16]. Copper nanoparticles can be used in the production of anti-fungal and anti-bacterial drugs for the agricultural industry, materials for the control of algae pollution. In addition, recent studies show that copper nanoparticles are a promising material to combat antibiotic-resistant Staphylococcus aureus [17].

Materials based on copper nanoparticles can be used to control bacterial contamination of soil ecosystems. The effectiveness of their application was proved on the example of Bacillus subtilis and Pseudomonas fluorescens [18].

The experiments showed the insecticidal activity of copper nanoparticles. Materials based on such nanoparticles have proven effective for the elimination of Anopheles stephensi, Aedes aegypti, Culex quinquefasciatus, and Tenebrio molitor [19].

The potential for developing antibacterial coatings using copper nanoparticles to minimize the transmission of infectious diseases in public transportation and healthcare facilities has been demonstrated [20].

It should be noted that stabilizers used in the synthesis process (PEO, PVP) have their own biocidal activity [21]. It is assumed that the combination of such stabilizers and copper nanoparticles in one material will allow to achieve mutual enhancement of biocidal properties. In addition, it is known that the use of polymeric stabilizers makes it possible to control the release of ions from copper nanoparticles, which increases the efficiency of materials based on them [17].

Consequently, polymer-stabilized copper nanoparticles represent a promising universal biocidal agent, offering low cost, high efficiency, and a wide range of applications with minimal environmental risk.

4 Conclusion

In this work, copper nanoparticles were obtained by chemical reduction and characterized. The following stabilizers were used for the synthesis of nanoparticles: gelatin, PVP and PEO. The following reagents were used as reducing agents: ascorbic acid (gelatin), tert-butylamine borane (PVP), hydrazine borane (PEO).

The obtained nanoparticles were characterized by electron spectroscopy. Photometric data showed the presence of a localized plasmon resonance phenomenon with a maximum at 580 nm, confirming the formation of nanosized Cu particles. It is noted that the position of the maximum varied insignificantly.

TEM showed that the use of PEO as a stabilizer has resulted in the formation of spherical nanoparticles with an average diameter of 6 nm.

The stability of the synthesis products in the presence of gelatin was 15 days, in the presence of PVP it was 6 weeks, and in the presence of PEO it was 2 weeks.

The possible application of the obtained nanoparticles as biocidal agents is considered. It is established that the obtained nanoparticles can be potentially applied in agriculture, medicine, as well as a component of antibacterial coatings for public transport and health care facilities. It is shown that some stabilizers also have a biocidal effect. It is noted that the efficiency of biocidal properties of copper nanoparticles can be enhanced due to the synergistic effect of interaction with the stabilizer.

Further studies are required to obtain experimental confirmation of the biocidal properties of the nanoparticles produced.

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