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EXTRACTION OF COPPER NANOPARTICLES FROM COPPER SULFATE COMPOSITION BY CHEMICAL PRECIPITATION METHOD

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Annotatsiya. *Bu maqolada mis nanozarrachalarining yirik ishlab chiqaruvchi davlatlari (masalan, Xitoy, Rossiya, Yaponiya) va korxonalari (masalan, Norilsk Nickel) tahlillari keltirilgan. Bu davlatlar va korxonalarning texnologiyalari, kimyoviy cho'ktirish, elektroliz, sementatsiya kabi usullar orqali mis nanozarrachalarini ishlab chiqarish texnologiyalari o'rganilgan. Maqola mis nanozarrachalarini qo'llash sohalariga taalluqli, masalan, elektronika, sensorlar, antibakterial qoplamalar, katalizatorlar kabi sohalarda ularning foydalanishini metodlari ko'rsatilgan. Ishlab chiqarishning optimal parametrlari, masalan, harorat, konsentratsiya, vaqt, maydalik kabi faktorlar aniqlangan. Shuningdek, laboratoriya sharoitida amalga oshirilgan ishlar uchun texnik tizim va tajriba olish shartlari ham taqqoslanib olingan. Olingan namunalarning zamonaviy tahlili natijalari, masalan, SEM, TEM, EDS, XRF kabi tahlillar taqqoslanib olingan. Barcha tahlillar mis nanozarrachalarining sohalarda foydalanish mumkinligini ko'rsatmoqda.*

Kalit so'zlar: *mis nanozarrachalari, kimyoviy qaytarish, SEM, TEM, EDS, XRF, UV-Vis spektrometri.*

Аннотация. *В статье представлен обзор анализа ведущих производителей наноматериалов, таких как Китай, Россия, Япония, а также ключевых компаний, таких как Норильский никель. Она описывает технологии и производственные марки, используемые в производстве наноматериалов, такие как химическое осаждение, электролиз и цементация. Кроме того, подчеркивается область применения наноматериалов, включая электронику, сенсоры, антибактериальные покрытия и катализаторы, а также указываются оптимальные параметры для производства. Обсуждаются технические системы и экспериментальные условия в лабораторных условиях, включая такие факторы, как температура, концентрация, время и чистота. Представлены современные результаты анализа испытаний образцов, такие как SEM, TEM, EDS и XRF, что помогает понять эффективное использование наноматериалов в различных областях.*

Ключевые слова: *наночастицы меди, химическое восстановление, SEM, TEM, EDS, XRF, УФ-видовая спектрометрия.*

Abstract. *The article provides an overview of the analysis of leading producers of nanomaterials, such as China, Russia, Japan, and key companies like Norilsk Nickel. It outlines the technologies and manufacturing brands involved in nanomaterial production, such as chemical precipitation, electrolysis, and cementation. Additionally, it highlights the areas of application for nanomaterials, including electronics, sensors, antibacterial coatings, and catalysts, along with specifying optimal parameters for production. Furthermore, it discusses the technical systems and experimental conditions under laboratory settings, including factors like temperature, concentration, time, and purity. The modern analysis results of sample testing, such as SEM, TEM, EDS, and XRF, are presented, aiding in understanding the effective utilization of nanomaterials in various fields.*

Keywords: *copper nanoparticles, chemical reduction, SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy), EDS (Energy-Dispersive X-ray Spectroscopy), XRF (X-ray Fluorescence Spectrometry), UV-Visible spectrometry.*

Introduction

In recent years, great attention has been paid by researchers to the development of new methods for synthesizing and modifying the structure of ultrafine particles of Ultra Dispers Particle (UDP) and nanoscale structures of various materials. For example, it has been shown that the physicochemical properties of metal UDPs smaller than 100 nm differ from bulk metal made of the same atoms. The novel properties of UDP and nanoscale structures are of great practical interest in their use as antibacterial coatings, their applications in pharmaceuticals and textiles, and in photocatalysis [1], biochemical sensors [2] and their oxidation reactions [3] in order to change the surface properties of other materials and [4], are widely used in fields such as cosmetic pigments [5].

The chemical and physical properties of copper have made it a highly sought-after metal for various purposes. Additionally, copper, being a highly versatile metal, possesses outstanding electrical and thermal conductivity, ductility, corrosion resistance, and other desirable properties, such as:

Electronic industry: for the generation, transmission, and distribution of electricity. [6] Construction and architecture: used in automotive wiring, connections, and various electrical components for the construction of ships, airplanes, and trains. [7-8] Industrial machinery and equipment: utilized in engines, generators, pumps, compressors, and heat exchangers. [9] Renewable energy: serves as an important component in solar panels, wind turbines, and energy storage systems. Coins and currencies: employed in the production of coins, especially those with low denominations. [10] Medical devices: used in medical devices and equipment, including surgical instruments, imaging systems, touch surfaces, and hospital equipment, to help reduce the spread of infection.

During the synthesis process, hydrazine hydrate ($N_2H_4 \cdot H_2O$) is used as a reducing agent. This is because hydrazine yields favorable results as a substance capable of being controlled with specific properties. The oxidation of hydrazine results in the release of nitrogen gas, which does not oxidize the collected metal, thereby ensuring the quality of the synthesized copper nanoparticles.

The utilization of sodium dodecyl sulfate as a stabilizer helps maintain the stability of the nanoparticles and prevents their agglomeration during the synthesis process.

The reduction of copper by hydrazine follows the reaction:

$$2Cu^{2+} + N_2H_4 + 4OH^- = 2Cu + N_2 + 4H_2O$$

Currently, several methods for obtaining copper nanopowders have been developed. The methods for obtaining nanopowders are divided into physico-chemical and mechanical methods. Mechanical methods involve producing nanoparticles without altering their chemical composition. The physico-chemical method allows for obtaining nanoparticles through chemical precipitation. The main advantage of this method is the ability to control the structure and properties of the particles by changing the parameters of electrolytic deposition and electrolyte composition. This enables control over the structure, size, shape, and chemical composition of the nanoparticles. [11-12].

In particular, the introduction of chemically active compounds (complexing agents, stabilizers and surfactants) into the electrolyte results in improved technological properties and a more stable one with the required particle size. allows you to get powders [13].

Chemical methods of obtaining copper nanoparticles are summarized and analyzed. The main types of processes leading to the production of copper nanoparticles are identified: thermal destruction of copper compounds; targeted selection of ligands to reduce redox potentials of copper complexes; application of various spatially confined systems as nanoreactors. The most important factors affecting the morphology and stability of the obtained copper nanoparticles (redox potential of copper complexes, reducing agent, stabilizers, pH, etc.) are shown [14-15].

Nanotechnology has opened up great opportunities in the field of materials science, and to better understand its properties, it was necessary to include other fields such as photochemistry and electrochemistry [16]. Easy size adjustment of UD materials [17] allows to improve and change their properties in a wide range; therefore, their optical and electrical properties are also modified [18]. Copper UDPs (Cu UDP) have been targeted for use in health-related processes due to their antibacterial properties and antifungal activity, as well as catalytic, optical, and electrical properties [19]. UDP Cu is often synthesized via dispersible polymers [20] and solvent evaporation [21]; Some methods have been proposed to obtain smaller nanometer-sized particles, such as ultrasonic or organic separation and the use of solvents for extraction-evaporation or diffusion [22]. In recent years, the implementation of low-cost ecological systems for the synthesis of Cu UDP has been difficult due to the difficulty of obtaining metal UDP instead of metal oxide [23]. The development of Cu UDP synthesis technology is in continuous growth and development [24].

Materials and experimental

The necessary chemical materials for this research are copper sulfate pentahydrate ($CuSO_4 * 5H_2O$) crystals and iron pieces, as well as distilled water.

Preparation of the solution for precipitation: A solution with a concentration of 0.02M $CuSO_4 * 5H_2O$ is prepared by adding it to distilled water.

Reducing agent: Iron (Fe).

Experiment: Initially, 40 ml of 0.02M $CuSO_4 * 5H_2O$ solution is poured into a flask and heated to a temperature between 80-90 °C. Then, iron pieces are added, and the solution's color changes to green. At the end of the process, the solution turns completely green. After the reaction is complete, the solution is filtered, and the particles are covered with aluminum foil to prevent oxidation. Experimental samples are collected at various time intervals for analysis.

Methods

In the mentioned scientific study, analyses were conducted on samples using titration, physico-chemical, and chemical methods, such as SEM-EDS, XRF, TEM, spectral, X-ray, and photometric analysis.Computer-controlled BRA-135 energy-dispersive X-ray fluorescence universal spectrometer (Russia) and Rigaku XRF (Japan) X-ray fluorescence spectrometers were used for quantitative and qualitative analysis of experimental results (liquid and solid products) and identification of samples based on diffractograms. Using chemical methods of analysis (titration), the amount of main metals in the product of scientific research was determined. Quantitative and qualitative analysis of research results was carried out on a Perkin Elmer 3100 atomic absorption spectrometer. Microscopic analysis of powdered and precipitated samples obtained from experiments was carried out using SEM EVO MA (10) Zeiss (Germany) scanning electron microscope equipped with X-act X-ray detector and JSM-IT500 (Japan) analytical multifunction electron microscope. The microscope measures the length of the projection of geometric distances on the horizontal plane, that is, the distance between the points corresponding to the horizontal directed plane relative to the surface of the object.

Results and Discussion

The formation of copper nanoparticles follows a series of color changes which are related to the chemical reactions.

The result of the analysis of the sample is presented in Fig. 1. Small metal nanoparticles on the surface of the sample show absorption of visible electromagnetic waves due to collective vibrations of electrons. This phenomenon is called surface plasmon resonance effect. This phenomenon can be studied with a simple UV-visible spectrometer. The size dependence of plasmon resonance is a complex phenomenon for particles smaller than 20 nm. One of the interesting features is the increase of the resonance line with the decrease in the size of the powder particles due to the increased electron scattering on the surface. Thus, resonance shift and resonance line shift are important parameters for the characterization of metallic nanoparticles.

Using UV diffuse reflectance spectroscopy, absorption lines were identified in the initial spectra of copper sulfate, at 250, 320-370 nm (charge transport lines of O-Cu-O and Cu-O-Cu complexes), at 620-850 nm (d-d transitions in Cu^{2+} ions) (Fig. 1).

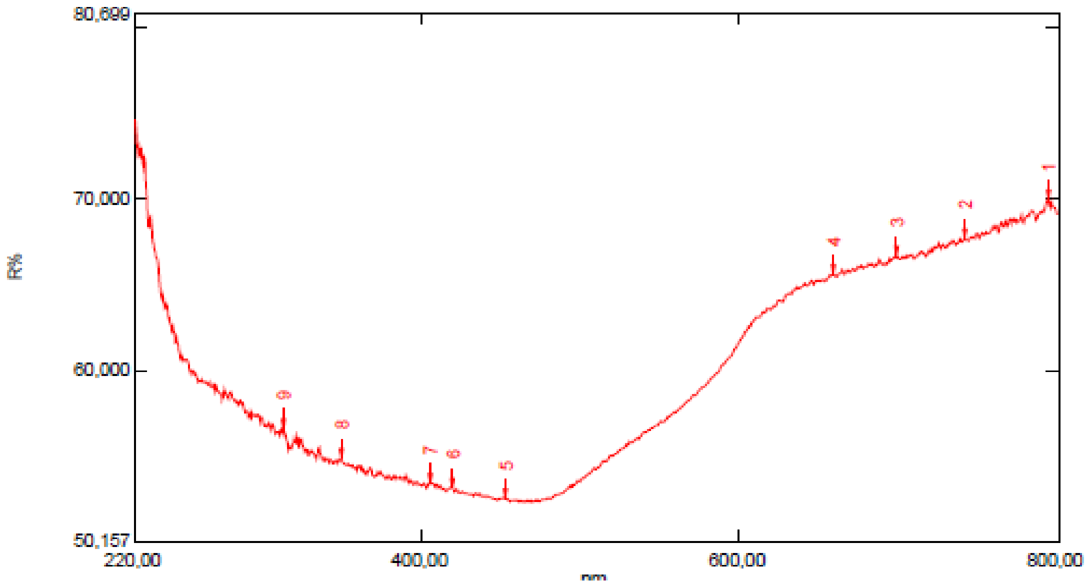


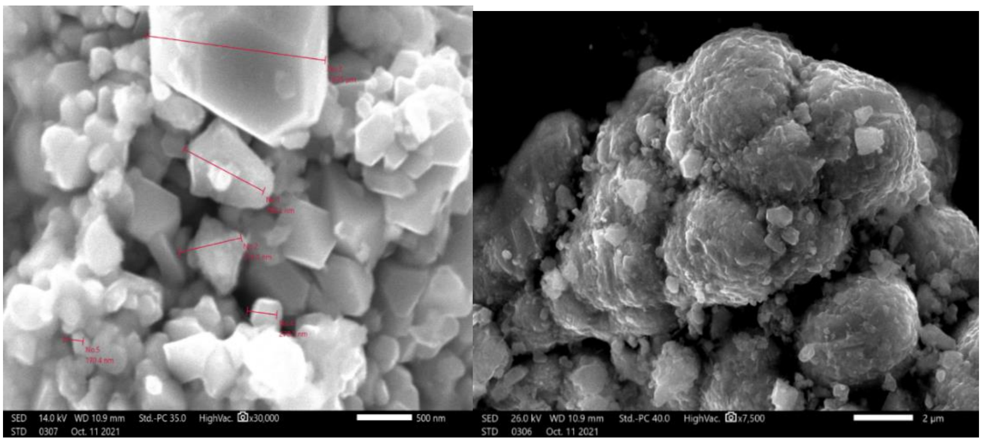
Fig. 1. UV-diffuse reflectance spectra of copper nanopowder.

Plasmon absorption (562 nm) appears when the solution shifts to the red, that is, when small clusters or nanoparticles are formed. In the case of copper nanopowder, lines 520-580 (plasmon resonance) are observed in the form of a curved line (Fig.1), which indicates the presence of a small number of nanoparticles smaller than 20 nm.

At the same time, there are sulfur inclusions in the sample, which may be related to the adsorption of sulfate ions on the surface of nanoparticles.

Based on the SEM analysis results, the image depicts agglomerates of small grains alongside cubic-shaped copper particles. The EDS analysis of the sample further confirms the findings, aligning with the elemental analysis of the copper nanoparticles using energy dispersive X-ray spectroscopy (EDS).

Figure 2(a) displays the SEM image capturing the morphology of the copper nanoparticles. Meanwhile, Figure 2(b), (c), and (d) depict the corresponding EDS spectra of the nanoparticles. These spectra reveal the elemental composition of the nanoparticles, confirming the presence of copper as the primary constituent.



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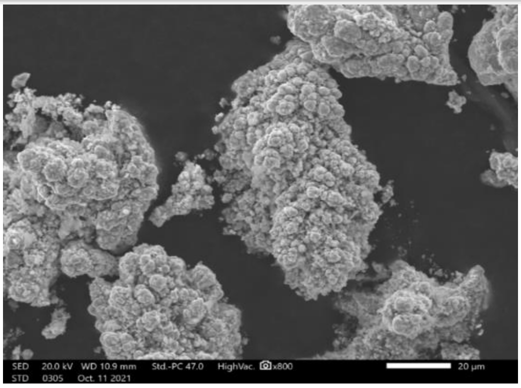

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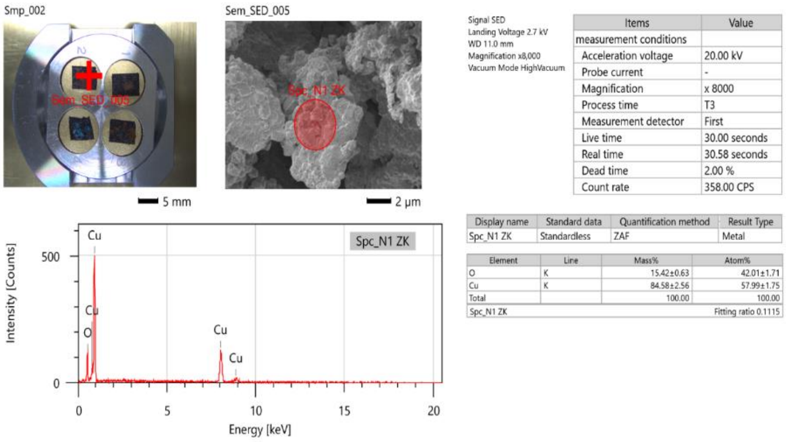

d

Figure 2. SEM-EDS image of the sample (nanopowder).

Conclusions

These scientific investigations are highly significant for the global scientific community as they contribute to the advancement of synthesis methods for copper nanoparticles. This is crucial because these nanoparticles possess antibacterial properties and offer potential for intermolecular interactions. Corporations producing copper nanoparticles in large quantities are expanding their exports, emphasizing the use of chemical precipitation and electrolysis as the primary methods for copper nanoparticle production. Moreover, it is emphasized that the price of cathode copper is significantly lower than that of copper nanoparticles, currently standing at less than $10/kg. The main challenge in manufacturing copper nanoparticles lies in preserving them from oxidation during filtration and drying processes. Various inorganic and organic materials are currently utilized to achieve this goal, and we have succeeded in obtaining nanoparticles smaller than 100 nm. The purity level exceeds 99%.

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