ENRICHMENT OF COLLOIDAL SOLUTIONS BY NANOPARTICLES IN UNDERWATER SPARK DISCHARGE

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The underwater spark discharge between manganese granules was studied. Optical emission spectroscopy methods were used for diagnostics of such discharge plasma. The colloidal solution with manganese nanoparticles was produced by this discharge. The biological applications of this colloid were analyzed. The mechanism of metallic nanoparticle action and their transformation at interacting with biological objects were studied in Alternaria alternata culture.

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INTRODUCTION

There is a steady growth of nanomaterials applications in various fields of human life (industry, medicine, biology, etc.). Different kind of nanomaterials production methods were developed. Common problem for all these methods is obtaining of nanomaterials with predetermined and stable characteristics. Certainly, nanomaterials cannot be in an isolated state for a long time and finally they are consolidate.

One of the most promising methods for nanomaterials producing is spark erosion treatment of the material in water and formation of colloidal solutions with nanoparticles. A combination of intense heat and force action on the material during ultra-short time intervals in spark discharge gives possibility to obtain nanoparticles with non-equilibrium structure, increased level of free energy and spatial sizes of 20…100 nm.

Previous studies [1-9] of the underwater spark discharge showed the formation of metal nanoparticles in the form of colloidal solution. A physical model of nanoparticles formation at the discharge periphery was suggested [4, 6, 8].

Optical emission spectroscopy of the discharge between copper and silver granules was used to estimate the excitation temperatures in plasma [1, 2, 4-8]. Obtained colloidal solutions with metal nanoparticles were tested in different applications. Colloidal solution with aluminum nanoparticles showed good properties for metallurgy usage as effective deoxidant, increasing of structure dispersion, globulization and homogeneity [9]. Colloids, contained copper and silver, showed good properties for biological applications, namely for activation of antioxidant protective mechanisms of plants [1, 3]. These colloidal solutions showed also good antifungal and antibacterial features [5, 6, 9].

This paper is a continuation of such kind investigations with the aim to study the peculiarities of the underwater spark discharge between manganese granules and biological applications of the colloidal solutions with manganese nanoparticles which are produced by this discharge.

1. EXPERIMENTAL SETUP

Specially developed pulse power source was used to initiate a discharge between manganese granules immersed into the deionized water. Implementation of the low-voltage spark discharges was carried out on the experimental setup, which is shown in Fig. 1. It consists of a pulse generator 1, control unit 2, measuring and auxiliary devices: oscilloscope 3, Rogowsky coil 4, voltage divider 5; and discharge chamber 6.

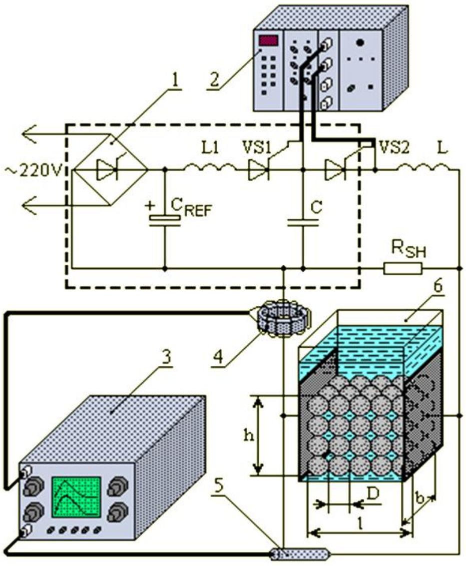


Fig. 1. Experimental arrangement

General view of the discharge is shown in Fig. 2. The voltage, applied to electrodes, caused a current flow along the chain of closely arranged granules in the stochastic switching mode. Investigation of the influence of process variables on dispersion and morphology of the products of metal granules erosion during the formation of local spark discharges was performed by varying of electrical parameters of the discharge circuit. Typical values of voltage were of 40…200 V, current was up to 150 A and pulse frequency was in the range of 0.2…2 kHz. As a result of a spark-erosion process, the formation of colloidal fraction was observed. Its morphology markedly differs from a micro fraction and is a common for metallurgical processes at low pressure, namely, the formation of a solid phase resulting from evaporation followed by condensation.

Fig. 2. General view of the discharge

2. SPECTROSCOPY INVESTIGATION

Optical emission spectroscopy methods were used in plasma diagnostics of underwater electric spark discharge between manganese granules.

Plasma emission of the spark discharge was registered by the diffraction spectrometer (600 gr/mm) coupled with CCD camera (3008x2000 pixels) [10]. Tungsten ribbon lamp as an etalon radiation source was used to define spectral sensitivity of the experimental apparatus.

The emission spectrum of the discharge between manganese granules is shown in Fig. 3. It consist mainly from Mn I spectral lines. Some merged Mn II spectral lines were also observed. In general, this manganese emission spectrum is very complicated due to the significant overlapping of atom and ions spectral lines.

Obviously, special technique must be developed at the next steps of investigation to provide diagnostics of such plasma. Nevertheless, the presence of ion manganese lines in the spectrum allow to affirm that plasma temperature is high enough to excite the electron energy levels up to 12 eV.

3. BIOLOGICAL APPLICATION

The influence of colloidal solutions with metal nanoparticles was investigated on Alternaria alternata culture. Colloids with manganese particles produced by underwater spark discharge were used in this study.

Fig. 4,a shows TEM image of manganese particles, which was registered by JEOL JEM-2100F microscope. Malvern Zetasizer Nano was also used to obtain size distribution of manganese particles (see Fig. 4,b). Combination of these techniques shows that average size distribution of manganese particles is in the range from 30 to 50 nm (see Fig. 4).

The colloidal solution with 10 mg/l concentration of manganese solid phase was prepared for further biological experiments. This solution was added into the suspension, which contained Alternaria alternata culture. The influence of colloidal solution with manganese nanoparticles on micromycetes was studied after 1 and 19 hours exposition. After that, micromycetes were removed from the suspension, fixed and cut by Ultratome. Obtained cut samples were studied by TEM microscope (Fig. 5).

Fig. 5,a shows incorporation of metal nanoparticles into the membrane of a unicellular organism. Moreover, penetration of the nanoparticles through the membrane and their further dissolvent in the cellular volume were also observed.

Such behavior of biogenic manganese nanoparticles allow assuming that they are involved in general metabolism of a unicellular organism. Increasing of the exposure time up to 19 hours leads to accumulation of the nanoparticles on the membrane surface and increasing of the particles amount entered into the cell (see Fig. 5,b).

It must be mentioned that average size of the nanoparticles, entered into the cell, decreases with increasing of the exposure time. Namely, the manganese particles are dissolving.

Dissolution of the nanoparticles in the cell and the extracellular space occurs primarily for such metals, which have a biological functionality. Moreover, such nanoparticles must have corresponding structural and phase composition and morphology. It also explains the absence of materials degradation that have no physiological values for biological objects, or such materials have biologically unacceptable form (graphite nanotubes, natural and synthetic polymers, complex minerals, chromium-nickel steel etc.). Therefore, when such materials enters the body, they cause chronic toxicity and pathology of the target organs.

Electron diffraction of the manganese nanoparticles was studied before (Fig. 6,a) and after 19 hours of interaction with suspension, which contained Alternaria alternata culture (see Fig. 6,b). One can conclude by comparing these figures that interaction with micromycetes leads to the destruction of polycrystalline structure of the manganese nanoparticles. After significant exposure time they became amorphous. This phenomenon demonstrates the biological transformation of the manganese nanoparticles and may be as one of the criteria of theirs biological functionality.

Thus, the biological functionality of matters is a complex concept, which is based on their biological or physiological availability and includes properties such as permeability, solubility and biological transformation, the ability to activate physiological processes and transportation of substances.

The absence of solubility and transport processes involved in causing their accumulation and chronic toxicity. However, soluble forms with high rate of excretion and small concentrations have exceptionally transit functionality, but at higher doses, these substances can cause acute toxicity.

Metal nanoparticles, provided their gradual dissolution have a prolonged effect and can therefore be considered as an alternative to salt forms of the mineral nutrition of organisms. Therefore, the evaluation of their biological effects can be carried out only taking into account the methods of nanoparticle production, theirs morphological parameters as well as structure and phase composition.

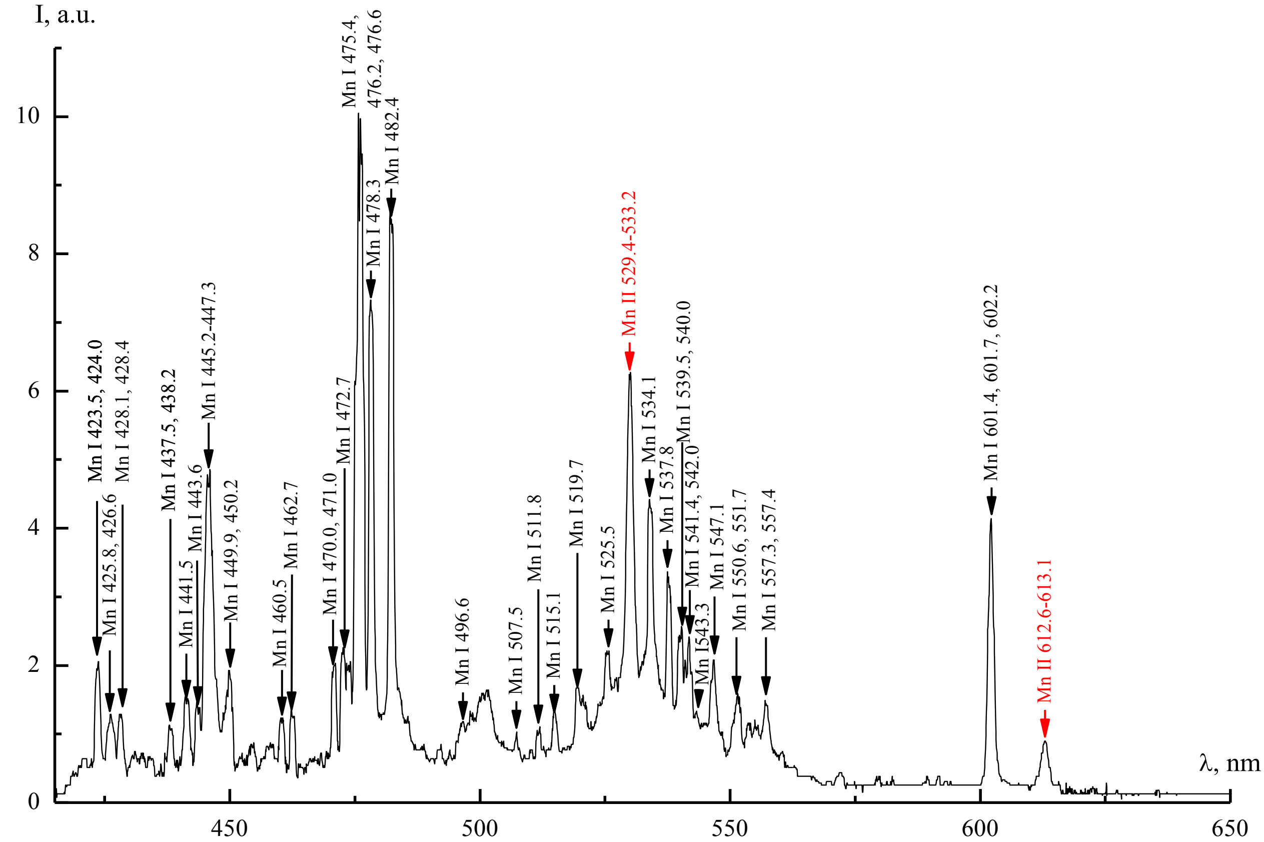


Fig. 3. Emission spectrum of microdischarge in water between manganese granules

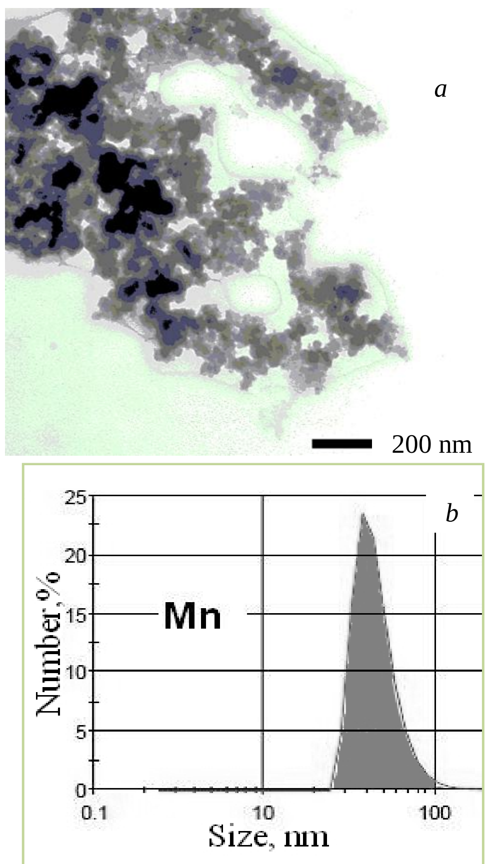
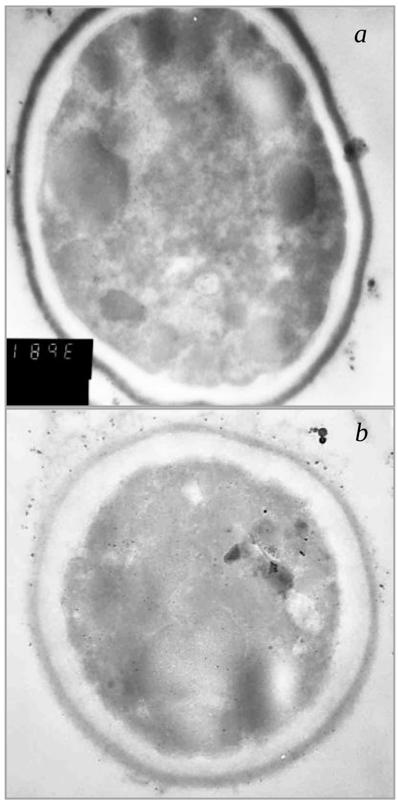


Fig. 4. TEM image of the manganese nanoparticles (a) and their size distribution (b) in a colloidal solution



TEM × 50000

Fig. 5. Transition of manganese nanoparticles through the membrane and their dissolution in the unicellular organism (Alternaria alternate): a – exposure is 1 hour; b – exposure is 19 hour

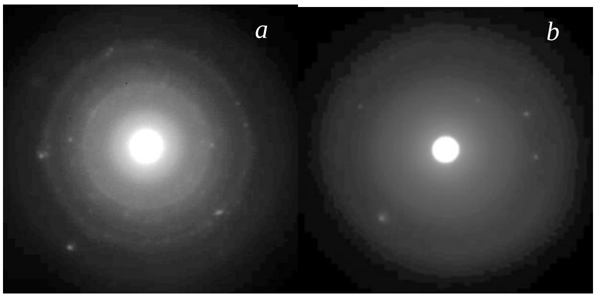


Fig. 6. Electron diffraction of primary (pilot) manganese colloidal particles (a) and particles after exposure during 19 hours (b) in solution of micromycetes culture

CONCLUSIONS

The underwater spark discharge between manganese granules was studied. The emission spectrum of this discharge consists of the Mn I and some Mn II spectral lines with upper electron levels up to 12 eV.

Investigations by JEOL JEM-2100F microscope and Malvern Zetasizer Nano showed that average size distribution of manganese particles is in the range from 30 to 50 nm.

TEM images of micromycetes cuts showed incorporation of metal nanoparticles into the membrane. The dissolution of the manganese nanoparticles, entered into the cell, was also observed. Electron diffraction showed that interaction with micromycetes leads to the destruction of polycrystalline structure of the manganese nanoparticles. After significant exposure time they became amorphous.

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ОБОГАЩЕНИЕ КОЛЛОИДНЫХ РАСТВОРОВ НАНОЧАСТИЦАМИ В ПОДВОДНОМ ИСКРОВОМ РАЗРЯДЕ

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Исследовали подводный искровой разряд между гранулами марганца. Для диагностики такой разрядной плазмы использовали методы оптической эмиссионной спектроскопии. Этот разряд использовался для приготовления коллоидного раствора с наночастицами марганца. Проанализированы биологические применения такого коллоида. Механизм воздействия наночастиц металла и их трансформация при взаимодействии с биологическими объектами изучались на культуре Alternaria alternata.

ЗБАГАЧЕННЯ КОЛОЇДНИХ РОЗЧИНІВ НАНОЧАСТИНКАМИ В ПІДВОДНОМУ ІСКРОВОМУ РОЗРЯДІ

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Досліджували підводний іскровий розряд між гранулами марганцю. Для діагностики такої розрядної плазми використовували методи оптичної емісійної спектроскопії. Цей розряд використовували для приготування колоїдного розчину з наночастинками марганцю. Проаналізовані біологічні застосування цього колоїду. Механізм дії наночастинок металу та їх трансформація при взаємодії з біологічними об'єктами вивчалися на культурі Alternaria alternata.