Vol. 18, No. 2 2011

Jolanta PULIT[1*], Marcin BANACH[1] and Zygmunt KOWALSKI[1]

NANOSILVER - MAKING DIFFICULT DECISIONS

NANOSREBRO - PODEJMOWANIE TRUDNYCH DECYZJI

Abstract: Nanotechnology, a fast-growing discipline of science, is widespread in various areas of life around the world. One of the examples of nanocompounds is nanosilver, which is used in medicine, electronics, the construction industry and chemical technology as an exceptionally efficient antibacterial and antifungal agent. For centuries silver has been known for its biocidal properties, much desired when creating aseptic conditions. On the other hand, the toxic effects of nanosilver have also been observed. Silver may accumulate in the food chain, which creates the risk of a direct effect on living organisms. What is more, silver nanoparticles may cause necrosis in human tissues, and can also distort the activity of elementary components in human cells. This paper presents the benefits and risks from the use of nanosilver.

Keywords: antimicrobial activity, disinfection, nanosilver, nanotoxicology

Introduction

Nanotechnology is a dynamically growing discipline of science which has been particularly intensively researched from the beginning of the 1990s. The prefix "*nano*" originates from Greek and means "*dwarf*", which refers to the microscopic size that nanotechnology deals with. The invention of the *scanning tunnel microscope* (STM), enabling the manipulation of atomic structures, is considered an exceptionally valuable achievement contributing to the development of nanotechnology [1].

The major focus of nanotechnology is on the design, development and application of materials whose dimensions range from 1÷100 nm. With the possible manipulation of nanostructure size, particularly the reduction of the particles forming them, the designed materials can have predictable physical, chemical or biological properties. If a structure is characterised by the dimensions of 1÷100 nm, ie the dimensions relevant to single atoms (10^{-9} m) and crystals (10^{-7} m), the material can have properties which are considerably different from those typical for individual atoms or crystals [2]. In structures whose dimensions range from 1 to 100 nm, the ratio of surface area to weight, and the ratio of the total number of atoms to the surface of the structure attain sufficiently high values.

[1] Institute of Inorganic Chemistry and Technology, Cracow University of Technology, ul. Warszawska 24, 31-155 Kraków, phone +48 12 628 26 40, fax +48 12 628 20 36
[*] Corresponding author: jolantapulit@indy.chemia.pk.edu.pl

Therefore, surface properties, playing an important role, may have considerably modified chemical activity, thermal and electrical conductivity, and tensile strength. Modifications of material properties resulting from changes in the structure's size make nanomaterials very interesting from a commercial point of view. It is expected that in the future the scope of nanotechnology research will enable the development of structures demonstrating innovative properties. Today nanotechnology is a science broadly applied in various disciplines, such as biotechnology, biomedicine, molecular medicine, pharmacology, ecotoxicology, electronics and many others. Agriculture, veterinary science and the food industry also benefit from nanotechnology research to a comparable degree [3]. It has been estimated that because of its multiple applications the broadly defined nanotechnology industry will achieve a considerable profitability of ca 3 trillion USD before 2015.

Nanosilver (NAg), whose application has recently attained the profitability margin, is considered one of the most useful commercial products from the group of nanomaterials [4]. Colloidal nanosilver of a concentration of 300÷500 ppm fetches a catalogue price of ca 2000 EUR per litre, which in calculation for pure silver is ca. 60 million EUR per kilogram. However, the price for metallic silver is ca 600 EUR per kilogram.

Silver is a metal which has been used from early times, since before the Neolithic revolution. In ancient Greece, silver vessels were used for the storage of water. A pioneering method for the application of silver for medicinal purposes was described as early as in the 8^{th} century. Silver was known only in its basic form until very recently. However, with the advent of the nanotechnology era the concept of manufacturing silver on a nano-scale was born. In this way nanosilver has proven to be a fundamental nanotechnology product. Silver nanoparticles stimulate the deep interest of scientists because they offer essential advantages, such as thermal conductivity, chemical stability, and catalytic and antibacterial activity [5]. Nevertheless, there are many concerns regarding unlimited confidence in nanosilver, which are attributed to increasingly frequent reports on the toxic properties of this structure. The specific nature of a nanomolecule should be thoroughly analysed and understood in order to make the right decision about the utility of nanosilver [6]. This paper presents the benefits of the application of nanosilver in various fields of science and highlights the various risks emerging during its use.

Obtaining nanomaterials

Work to develop manufacturing methods and identify nanostructures formed by noble metals has been carried out in many laboratories from the very beginning of the nanotechnology era. Cubes, prisms, discs, plates, triangles, rods and nanotubes are the major shapes of noble metals analysed on the nanoscale and being the focus of attention of scientists, who continue to search for more innovative areas of science where these forms can be applied. However, they have already found very many applications in photography, catalysis, biological marking, optoelectronics, sensors, antibacterial products and others. The reaction method is one of parameters affecting the quality of obtained nanomolecules (eg reduction can be a chemical, photochemical or electrochemical process). The quantitative and qualitative composition of used reagents, the presence of stabilizers, pH value, temperature, order of mixing components, the use of electrophilic or nucleophilic compounds, as well as the proportion of the used reducer also have considerable influence.

These parameters are crucial for the size, morphology, shape, stability and colour, as well as physical, chemical and magnetic properties of obtained nanocompounds [7, 8].

Obtaining nanosilver

To expand and improve knowledge of the methods for nanosilver synthesis, scientists usually refer to nanotechnology, a discipline of modern chemical synthesis. Each of the methods for the manufacture of nanosilver has its particular advantages, but also its limitations. Parameters which largely depend on the chosen reaction method concern molecule shape, its stability and the presence of agents protecting its core, as well as yield and impurities in the final product. Although the literature describes a broad range of superb and innovative methods for obtaining nanosilver, only a few of them are concerned with the mainstream production. The most popular and best known method to obtain nanosilver is the reduction of silver nitrate with a reducing agent (eg sodium borohydride). Photoreduction with UV light is also one of the leading methods. In addition, regardless of the vast number of publications on "green" technologies with which to obtain nanosilver, research into developing a fully environmentally-friendly production method for NAg is still in progress [9, 10]. The characteristics of the most popular methods for obtaining nanosilver are presented below.

Chemical reduction is the most common of all methods to obtain silver nanoparticles. The most important advantages it offers include high yield of non-aggregated nanoparticles, low price and ease of performance. This method is based on the reduction of silver nitrate ($AgNO_3$) with a reducing agent in the presence of a suitable amount of stabilizer, which controls the growth of silver nanoparticles undisturbed by aggregation. Example reducing agents include sodium borohydride ($NaBH_4$) and hydrazine (N_2H_4). Panigrahi et al used glucose, a weak reducing agent, but the obtained product was not uniform [11]. Polyoxyethylene sorbitan monolaurate, a stabilizer commercially known as TWEEN 20, was used by Nia in research to obtain colloidal silver [12]. The most important parameters of this method are: starting concentration of $AgNO_3$, ratio of molal concentrations of reducing agent to silver nitrate, and the concentration of the stabilizer [13, 14].

Another method of obtaining nanosilver is based on photochemical reduction. This method is valuable as it allows the blending of all the reacting substrates before the reaction is initiated. The core of the method is the fast reduction of silver cations, and small-size nanoparticles are seized by kinetic methods [3]. Kempa and collaborators developed a photoreduction method [15] in which they used *N*-methylnifedipine as a reducing agent. For that purpose, the mixture of silver chlorate(VII) ($AgClO_4$) and *N*-methylnifedipine was irradiated with a UV lamp, and silver nanoparticles of 1÷7 nm diameter were obtained [15].

Laser ablation, a new method to obtain nanosilver which has been frequently analysed in the last decade, involves the superficial reaction between liquid and a solid body suspended in it [16]. In this process a pulsating laser beam directed at the surface of a solid body causes a "discharge" of material from the surface of the solid body, which then migrates to the surrounding liquid (reducing liquid medium) in a bubble form. Ethylene or diethylene glycol are used as the liquid medium. The quality and appearance of molecules depend on the laser parameters and the concentration of the liquid medium. The advantage offered by this method is the ability of the migration of a considerable amount of material from the solid body to the liquid. Moreover, nanomolecules obtained using this method are characterised by high purity, stability, spherical shape and resistance to aggregation [3, 17].

Vacuum ion sputtering is another method used to synthesize nanosilver. For that purpose, a 30 $\mu A/cm^{-2}$ current is directed at a target located at a 10 cm distance under variable energy levels. A beam diameter of approx. 50 mm is one of the key parameters. Nanosilver particles are formed on a silica gel matrix after irradiation with ions. A positive aspect of this method is the high purity of the obtained nanoparticles [3].

Reetz and Helbig were the first to develop, in 1994, an innovative method for obtaining nanoparticles by an electrochemical method [18]. In principle, this method is based on the dissolution of metal on an anode, and then the reduction of the obtained transitional metal salt on the cathode, which leads to the formation of metal particles stabilized with tetraalkyl ammonium salts. In a similar procedure nanosilver was obtained through the potentiostatic or galvanostatic polarization of silver in an ethanol solution. The major advantage of the above method is the high purity of particles and the control of their size through the compensation of the current density, with no need to add surface active agents. In addition, it does not require expensive equipment and instrumentation [18].

Microwave irradiation is another method used to synthesize nanoparticles, and it was successfully used to obtain nanosilver and nanogold. When a microwave beam goes through the dielectric coating of the material, radiation energy transforms into thermal energy and the material's temperature increases [19].

Green synthesis is an interesting method used to obtain nanosilver and is based on the synthesis of silver nanoparticles using *Bacillus subtilis* bacteria. The enzymatic reaction is enabled by the mediation of nitrate reductase in the bacterial culture. The reaction mechanism involves the reduction of metal ions stimulated by bacteria. However, this process has not been researched in detail. It is likely that the reduction of Ag^+ ions and further growth of silver nanoparticles are stimulated by both reductase and electrons originating from the compound, as well as peptides or proteins [20]. Enzyme synthesis of nanosilver offers a great number of advantages for large-scale production, and the process is also uncomplicated to perform [21].

Properties of nanosilver

Silver, together with gold and other rare and precious metals, has been used by people for thousands of years. It has found various applications in medicine, dentistry, the jewellery industry, photography, the production of explosives and others. Vessels coated with silver were used in ancient times for the storage of water and wine, and Hippocrates, the "father of medicine", wrote that silver had beneficial healing and anti-disease properties [22]. Silver compounds were used as the main cure for infections during World War I, until the advent of antibiotics. In 1884 C.S.F. Crede, a German obstetrician, administered silver nitrate solution to treat *Gonococcal Ophthalmia*, and this was probably the first scientifically documented use of silver. Later on, silver sulfadiazine cream was used for the antibacterial treatment of burns. With the advent of the antibiotic age, the popularity of silver as an antibacterial agent gradually decreased. However, in later periods advances in modern science strengthened the role of silver as a highly important material in many areas [23].

Despite the very popular positive perception of the attractive properties of nanosilver, the toxicology and health hazards resulting from the use of silver nanoparticles should also be understood and emphasized. The toxicity of silver has been known for centuries [24]. Scientists have claimed that the use of nanosilver may cause side effects, and the evaluation of silver's toxicity requires a profound knowledge of its metabolism and decomposition in living organisms [6]. Unfortunately, toxicology aspects are frequently overlooked or ignored [25]. Recent *in vivo* and *in vitro* studies demonstrated that nanosilver absorbed via the skin or inhaled may cause negative health effects, and the use of medicinal products containing silver nanoparticles may increase the risk of chronic diseases [26, 27]. For that reason world supervisory authorities and scientific public information centres began to focus their attention on the potential harmful effects of nanocompounds. The *US Environmental Protection Agency* (USEPA) has taken action in order to explain the reasons for adding nanosilver to various consumer products available in supermarkets. Concerns regarding the uncontrolled effects of nanotechnology have lead to the establishment of environmental and political organizations whose operation is focused on reducing the use of silver nanoparticles, the introduction of stricter regulations and, in extreme cases, a total ban on the use of nanosilver [6]. A more detailed understanding of the nature of the emerging hazards caused by nanotechnology will enable everybody concerned to make reasonable decisions concerning the use of nanosilver and other nanomaterials.

Benefits of nanosilver applications

The human body is frequently exposed to microorganisms such as bacteria, fungi, yeast and viruses. A considerable number of materials containing organic and nonorganic substances with potential antibacterial properties have been analysed. Silver nanoparticles, characterised by specific surface and a large proportion of superficial atoms, have been thoroughly investigated owing to their unique physical and chemical properties. Research has demonstrated that silver ions have a remarkably strong bacteriostatic effect. The results of recent studies demonstrated that metal binds with microbial proteins in the reaction with a thiol group (-SH), which leads to protein inactivation. This process is considered the most important among all others resulting in protein inactivation.

In their paper Cho et al presented [28] the effect of nanosilver against *Staphylococus aureus* and *Escherichia coli*. In an experiment they used two solutions of colloidal 10 nm nanosilver stabilised with *poly-(N-vinyl-2-pyrrolidone)* (PVP) and *sodium dodecyl sulphate* (SDS). *S. aureus* and *E. coli* were used as Gram-positive and Gram-negative bacteria, respectively. It was found that PVP-stabilised nanosilver demonstrates especially strong antibacterial activity against both bacteria. Moreover, the nanosilver solution considerably inhibited the growth of both *S. aureus* and *E. coli*. The study demonstrated the lowest effective concentration of nanosilver solution to be 50 ppm for *Staphylococus aureus* and 100 ppm for *Escherichia coli.*

Yan et al have developed a method for the production of nanosilver-coated granules to be used as an antibacterial and antifungal agent. The product inactivates a broad spectrum of bacteria, including *Staphylococus aureus*, *Chlamydia trachomatis*, *Providencia stuarti*, *Vibrio vulnificus*, *Bacillus subtitilis*, and *Streptococus paratyphi* [29].

Building materials are a characteristic application of nanosilver as a biocidal agent. In their patent Horner et al reported that silver nanoparticles used as a component of building materials for roofing, insulation, cladding, wall lining, etc. considerably contributed to the inactivation of bacteria, fungi and harmful algae in comparison with silver-free materials

[30]. Kwon et al developed a paint formula containing 30 ppm silver nanoparticles, which is used for coating cast surfaces [31].

The application of nanosilver in medicine is a particularly important area. Roe et al reported the development of nanosilver-coated polymers which are used for plastic catheters. A coating of silver nanoparticles has an antibacterial and disinfecting effect. The *in vitro* tests confirmed growth inhibition in the bacterial layer which was sustained for 72 hours [32]. It is expected that after relevant studies on humans this method of using nanosilver will be introduced on a broad scale [9].

Nanosilver is also applied as an antibacterial additive for *poly*(*methyl methacrylate*) (PMMA), used in bone implants [33]. This concerns, for example, prosthetics of the knee or hip joint. Scientists have suggested that the use of elements made of nanosilver and PMMA will considerably reduce bacterial resistance to antibiotics administered during treatment [9].

Studies have also been conducted to explain the anti-inflammatory mechanisms of action for nanosilver. Anti-inflammatory properties of silver nanoparticles were evaluated in dermal contact in pigs. The study demonstrated that nanosilver significantly reduced inflammatory states, which was reflected in reduced levels of neutrophil infiltration found during biopsy [34].

There is also a dressing with nanosilver used on wounds and scalds. The hydrophilic coating formed by nanocomposite fibre with nanosilver incorporated in its structure comes into a direct contact with a wound or skin surface and its major purpose is disinfection and blood absorption [35]. Pictorial applications of nanosilver and silver nitrate in medicine are presented in Figure 1.

Another interesting application of silver nanoparticles is in the treatment of air from air-conditioning systems in meat processing plants. One of the problems faced by the meat industry is the contamination of products with microorganisms which migrate during slaughter, cold room storage or during meat processing. Microbial growth creates high risk and the air becomes a significant source of contamination, because proliferating microorganisms, mostly pathogenic, migrate mainly into the ambient air. There are various sources of contamination: natural, eg water, soil, putrefying vegetable or animal parts, and anthropogenic sources, eg storage of municipal waste and wastewater treatment. Air is the natural living environment for microorganisms, but because of various chemical and physical factors and the deposition of nutrients it becomes nothing more than the medium for the migration of microbes, not an ecological niche. Therefore, the air supplied to production halls, as one of the microbial risk factors, must be filtered, which also involves another risk of contamination, because filters operating under conditions favourable to microorganisms (moisture and high temperature) may be a site for their growth. This results in low quality air and unpleasant odours, leading to the proliferation of bacteria, fungi and mould on meat products. To counteract this problem a system was designed for the coating of filters with chemical substances characterised by a strong antibacterial activity. Nanosilver was used for this purpose, and studies demonstrated that filters with incorporated silver nanoparticles allow for the almost complete elimination of microorganisms from the air [36]. Also in this case, the antimicrobial efficiency of nanosilver was confirmed, and an additional advantage was the use of nanosilver in low concentrations, ie expressed in ppm, which results from its very large specific surface and high biological activity [36].

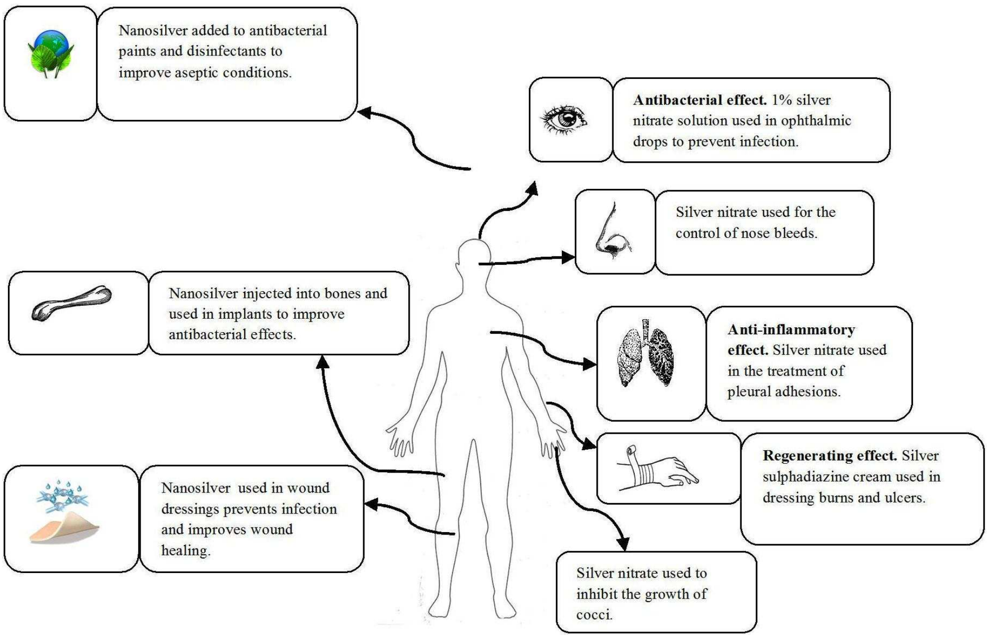

Fig. 1. Applications of nanosilver and silver nitrate in medicine [9]

Another current problem is the optimisation of conditions under which farm animals are kept. More specifically this concerns gas emissions, particularly those generating odours, like ammonia. Gas emission sources include animal faeces and fodder, as well as process equipment. Unpleasant gases released from the ground remain in the air and in the vicinity of farms, which is problematic for the environment and for local inhabitants. This problem has lead to the development of a preparation containing nanosilver as the major component to eliminate both the ammonia emission and microbial growth [37].

For a long time nanosilver has been used in animal breeding as a component of disinfecting agents for transport chambers or facilities for keeping animals. Owing to the lack of information concerning the direct effect of nanosilver on animals, a laboratory study was performed to evaluate the level of ammonia emissions from ovine faeces after the use of a preparation comprising silver nanoparticles and a mineral sorbent. The study demonstrated that the use of the preparation reduced ammonia emissions from the ground. In addition, the study revealed that increasing the preparation dose did not increase its effectivity, which indicates the pointlessness of using higher doses. It is believed that the manufacture of preparations containing nanosilver and environmentally-friendly natural sorbent offers a promising perspective for counteracting ammonia emissions from animal faeces. In this case the biocidal properties of nanomolecular silver are an additional advantage, as they also prevent ammonia formation in the process of bacterial synthesis [37].

Nanosilver is used in agriculture to a wide extent because of its specific properties. Nia described a number of studies monitoring the reaction of plants after contact with colloidal nanosilver obtained by chemical reduction [38]. The study concerned testing a broad range of plant products, eg citrus and other fruits, cereals and olive trees. The experiment demonstrated that in all cases spraying nanosilver on plants resulted in their faster growth and the formation of longer roots. In addition, the size of leaves increased and they regenerated.

Progress in the germination of wheat grains after treatment with silver nanoparticles was the subject of a detailed study. For that purpose nanosilver solutions of 0, 20, 40, 60 and 80 ppm concentrations were used. After one week wheat grains grew by 70, 78, 90, 96 and 90% respectively. The study demonstrated that nanosilver significantly accelerates the germination of wheat grain. Similar experiments were also carried out on rape, cotton and maize grains, and the results were comparable. Another study investigated the reaction of olive trees after the immersion of juvenile plants in nanosilver solution and planting in a glasshouse. The study demonstrated that the use of nanomolecular silver solution reduced the incidence of root diseases. Nia also reported that strawberry plants sprayed with nanosilver solution were resistant to diseases and their fruits and leaves were larger [38].

These examples demonstrate that the use of a colloidal nanosilver solution may considerably improve the growth and health of various plants.

Hazards associated with the use of nanosilver

Potential toxicity is the major feature of nanosilver raising concerns. Four aspects should be considered when analysing the emerging risk: hazard identification, toxicity assessment levels, exposure assessment levels, and hazard characteristics. Additional external factors may influence the toxicity of nanosilver, such as size, particle shape or deviations in the intensity of its biological activity [6].

The migration of nanostructures into the natural environment is one of the currently encountered problems. Depending on the type, nanoparticles may be absorbed by air, water or soil [39]. In each of these media, silver particles may remain for a long time without significant activity, or they can be absorbed by living organisms. In other words silver nanoparticles may create an ecotoxic hazard due to biodegradation, or as a compound accumulated in living organisms in the food chain [40]. The US Environmental Protection Agency reported that nanosilver migrates to the trophic chain from body care products containing silver nanoparticles, such as sunbathing creams, which easily migrate to water bodies; in this process nanosilver may be absorbed by living organisms [41].

Blaster and collaborators carried out an analysis and its results contributed to the assessment of the effects of nanosilver released from plastic materials on the ecosystem of the Rhine river [43]. The scientists demonstrated that silver nanoparticles were absorbed by sludge and wastewater, bringing a future risk of spreading on farming lands, which can consequently lead to bioaccumulation and toxicology hazard [1, 42]. Bilberg and collaborators studied the effects of nanosilver on respiration levels in Eurasian perch [43]. Fish gills are in direct contact with the ambient water, making them potentially exposed and vulnerable to suspended silver nanoparticles. Scientists investigated the effect of silver nanoparticles on oxygen consumption. Perch were exposed to concentrations of 63, 129 and 300 μg/l nanosilver, plus controls for comparison, which were fish not exposed to nanosilver. Oxygen consumption was measured by automated intermittent closed respirometry. Final findings demonstrated that exposure to nanosilver results in impairment of tolerance to hypoxia (oxygen shortage) [43]. *In vitro* studies demonstrated that silver nanoparticles also cause other toxic damage to cells originating from various living organisms (Table 1).

Table 1

Toxic effects of nanosilver on mammalian cells [4]

NAg size [nm]	Type of mammalian cells	Dose	Exposure time [h]	Observations
15	mouse spermatogonial stem cells	5÷10 µg/cm^3	24	reduced mitochondrial function, increased leakage of LDH (*lactic dehydrogenase* [44])
15	rat neuroendocrine cells	50 µg/cm^3	24	reduced mitochondrial function and dopamine level
7-20	human skin neoplastic cells	6.25÷50 µg/cm^3	24	reduced cellular function, oxidative stress, DNA fragmentation
100	human mesenchymal stem cells	2.5÷5 µg/cm^3	24	reduced chemotaxis of cells
5-10	human liver cells	0.5÷10 µg/cm^3	28	oxidative stress
25	human full thickness abdominal skin	0.46÷2.32 ng/cm^2	24	NAg particles are able to migrate via damaged skin to inside the cells
18	hamster liver cells	11 µg/cm^3	2.9	apoptosis

The negative effects of nanosilver on human health are a crucial problem. The use of nanosilver in body care products and fabrics essentially increases the exposure of human skin to it [4]. Kulthong et al demonstrated in their study on artificial human skin that silver may be transferred from deodorants to human sweat. The dynamics of nanosilver release are determined by its concentration in a product, product structure, pH value and sweat formulation [45]. Paddle-Ledinek et al investigated the interaction of keratinocytes with a wound dressing containing nanosilver. Study results demonstrated that the wound dressing containing silver nanoparticles had the strongest cytotoxic effect. In addition, Lam and collaborators reported that dressings containing nanocrystalline silver are cytotoxic to keratinocytes and fibroblasts and should not be used for local skin treatment. Moreover, it was found that fibroblasts are more sensitive to nanosilver than keratinocytes [4]. Arora et al concluded that silver nanoparticles caused cell necrosis and oxidative stress in human neoplastic cells. In another study the same team of scientists found that nanosilver migrated to cells and caused damage to DNA and apoptosis in liver cells [46]. Studies identified the liver and lungs to be the major organs prone to the effects of silver nanoparticles. Hussain et al, in their studies on rat liver cells, demonstrated that nanosilver caused considerable deterioration in cell structure [47]. The results exhibited, eg reduced mitochondrial membrane potential. These findings provide convincing evidence that nanosilver cytotoxicity potentially contributes to the development of oxidative stress in liver cells. A study was carried out using a non-cytotoxic dose of nanosilver <0.5 µg/cm^3. Results demonstrated that even this concentration caused the expression of genes responsible for the apoptosis of human liver cells. Therefore it can be concluded that nanosilver is a harmful substance even if the exposure dose is not cytotoxic [4].

Experiments investigating the effect of inhaled nanomaterials demonstrated that lungs are an easy target for nanosilver, which may additionally migrate via the nasal pathway to the brain. However, there is a limited amount of evidence concerning toxic effects on lung cells [48].

Nanosilver may also have a negative effect on the human reproductive system. This is possible due to the use of various commercially available products, such as intimate body care preparations. Braydich-Stolle et al demonstrated that nanosilver has a toxic effect on germinal stem line cells, causing reduced mitochondrial function and permeability of the cellular membrane [4].

The advantages of nanosilver used in building materials [30] were analysed from the different angle of negative effects of silver nanoparticles in the construction industry. In their study Kaegi et al evaluated the levels of released metallic silver nanoparticles from paints coating the facade of a building which was specially designed for the experimental purpose [49]. The facade was exposed to natural weather conditions for one year. The core of the experiment was to measure the amount of nanosilver contained in run-off water surrounding the building after rainfall. A strong leaching of silver nanoparticles was observed at the initial stage of the experiment. The maximum measured concentration of nanosilver was 145 $\mu g/dm^3$. It was found that after 12 months approx. 30% of nanosilver particles size <15 nm had migrated into the environment from the coating.

Conclusions

The properties of nanosilver are very important in industry, medicine and other disciplines where biocidal activity plays a significant role. Unfortunately, studies demonstrated that nanosilver also creates a hazard to human health. In addition, silver nanoparticles also create a toxicology hazard to the natural environment and living organisms.

The objective assessment of silver's benefits and potential hazards resulting from its use can certainly help in making reasonable choices and key decisions in various areas of nanotechnology. This should lead to the full exploitation of the bacteriocidal and fungicidal properties of silver in concentrations which are non-toxic to humans and animals.

Acknowledgements

The scientific work is financed in the years 2010-2013 as research project 4111/B/H03/2010/39.

References

[1] Bystrzewska-Piotrowska G., Golimowski J. and Urban P.L.: Waste Manage., 2009, **29**, 2587-2595.
[2] Kelsall R.W., Hamley I.W. and Geoghegan M.: Nanotechnologie. Wyd. Nauk. PWN, Warszawa 2009.
[3] Kowalska-Góralska M., Zygadlik K., Dobrzański Z., Patkowska-Sokoła B. and Kowalski Z.: Przem. Chem., 2010, **89**, 460-433.
[4] Ahamed M., AlSalhi M.S. and Siddiqui M.K.J.: Clin. Chim. Acta, 2010, **411**, 1841-1848.
[5] Vaidyanathan R., Kalishwaralal K., Gopalram S. and Gurunathan E.: Biotechnol. Adv., 2009, **27**, 924-937.
[6] Linkov I., Satterstorm F.K. and Corey L.M.: Nanomed. - Nanotechnol., 2008, **4**, 167-171.
[7] Khan Z., Al-Thabaiti S.A., Obaid A.Y. and Al-Youbi A.O.: Colloid Surface B, 2011, **18**, 513-517.
[8] Uzio D.: Saudi Aramco, R&DC, Process & Catalysis, Dhahran 31311.
[9] Chaloupka K., Malam Y. and Seifalian A. M.: Trends Biotechnol., 2010, **28**, 580-588.
[10] Courrol L.C., Rodrigues de Oliveira Silva F. and Gomes L.: Colloid Surface, 2007, **305**, 54-57.
[11] Panigrahi S., Kundu S., Ghosh S.K., Nath S. and Pal T.: J. Nanopart. Res., 2004, **6**, 411-414.
[12] Nia J.R., inventor; 2009 Jan 15, Preparation of colloidal nanosilver. U.S. patent 2009/0013825 A1.
[13] Song K.C., Lee S.M., Park T.S. and Lee B.S.: Korean J. Chem. Eng., 2009, **26**, 153-155.
[14] Chieh L. and Chou K.S.: J. Chin. Inst. Chem. Eng., 2008, **39**, 673-678.

[15] Kempa T., Farrer R.A., Giersig M. and Fourkas J.T.: Plasmonics, 2006, **1**, 45-51.
[16] Liu Q.X., Wang C.X. and Yang G.W.: Eur. Phys. J., 2004, **41**, 479-483.
[17] Pearce S.R.J., Henley S.J., Claeyssens F., May P.W., Hallam K.R., Smith J.A., Rosser K.N.: Diam. Relat. Mater., 2004, **13**, 661-665.
[18] Khaydarov R.A., Khaydarov R.R., Gapurova O., Estrin Y. and Scheper T.: J. Nanopart. Res., 2009, **11**, 1193-1200.
[19] Jiang H., Moon K., Zhang Z., Pothukuchi S. and Wong C.P.: J. Nanopart. Res., 2006, **8**, 117-124.
[20] Saifuddin N., Wong C.W. and Nur Yasumira A.A.: E-J. Chem., 2009, **6**, 61-70.
[21] Ingle A., Rai M., Gade A. and Bawaskar M.: J. Nanopart. Res., 2009, **11**, 2079-2085.
[22] Murr L.E.: Mater. Charact., 2009, **60**, 261-270.
[23] Chen X. and Schluesener H.J.: Toxicol. Lett., 2008, **176**, 1-12.
[24] Silver S.: *Bacterial silver resistance: molecular biology and uses and misuses of silver compounds*. FEMS Microbiol. Rev., 2003, **27**, 341-353.
[25] Kagan V.E., Bayir H. and Shvedova A.A.: Nanomedicine, 2005, **1**, 313-316.
[26] Seaton A. and Donaldson K.: Lancet, 2005, **365**, 923-924.
[27] Shvedova A.A., Kisin E.R., Mercer R., Murray A.R., Johnson V.J. and Potapovich A.I.: Amer. J. Physiol. Lung Cell., 2005, **289**, 698-708.
[28] Cho K., Park J., Osaka T. and Park S.: Electrochim. Acta, 2005, **51**, 956-960.
[29] Yan J. and Cheng J., inventors; 2002 Apr 30, Nanosilver - containing antibacterial and antifungal granules and methods for preparing and using the same. U.S. patent 6379712 B1.
[30] Horner C.J., Kumar A. and Nieradka K.R., inventors; 2006 Dec 7, Nanosilver as a biocie in building materials. U.S. patent 2006/0272542 A1.
[31] Kwon H., Yun H., Kim I. and Go S., inventors; 2005 Dec 29, Antibacterial paint containing nano silver particles and coating method Rusing the same. U.S. patent 2005/0287112 A1.
[32] Roe D., Karandikar B., Bonn-Savage N., Gibbins B. and Roullet J.B.: J. Antimicrob. Chemoth., 2008, **61**, 869-876.
[33] Alt V., Bechert, T., Steinrucke P., Wagener M., Seidel P., Dingeldein E., Domann E. and Schnettler R.: Biomaterials, 2004, **25**, 4383-4391.
[34] Nadworny P.L., Wang J., Tredget E.E. and Burrell R.E.: Nanomedicine, 2008, 4, 242-251.
[35] Ma R. and Yu Y., inventors; 2007 Dec 20, Nano-silver wound dressing. U.S. patent 2007/0293799 A1.
[36] Kowalski Z., Makara A., Banach M. and Kowalski M.: Przem. Chem., 2010, **89**, 434-437.
[37] Schiffman S.S.: J. Anim. Sci., 1998, **76**, 1343-1355.
[38] Nia J.R., inventor; 2009 Mar 19, Nanosilver for preservation and treatment of dieseases in agriculture field. U.S. patent 2009/0075818 A1.
[39] Nowack B. and Bucheli T.D.: Environ. Pollut., 2007, **150**, 5-22.
[40] SCENIHR. 2006. The appropriateness of existing methodologies to assess the potentat risks associated with engineered and adventitious products of nanotechnologies. Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR), European Commission.
[41] EPA. 2007. Nanotechnology White Paper. US Environmental Protection Agency Report EPA 100/ B-07/001, Washington.
[42] Blaster S.A., Scheringer M., MacLeod M. and Hungerbuhler K.: Sci. Total Environ., 2008, **390**, 396-409.
[43] Bilberg K., Malte H., Wang T. and Baatrup E.: Aquat. Toxicol., 2010, **96**, 159-165.
[44] Marchat L., Loiseau P.M. and Petek F.: Parasitol. Res., 1996, **82**, 672-680.
[45] Kulthong K., Srisung S., Boonpavanitchakul K. Kangwansupamonkon W. and Maniratanachote R.: Part. Fibre Toxicol., doi:10.1186/1743-8977-7-8.
[46] Arora S., Jain J., Rajwade J.M. and Paknikar K.M.: Toxicol. Lett., 2008, **179**, 93-100.
[47] Hussain S.M., Hess K.L., Gearhart J.M., Geiss K.T. and Schlager J.J.: Toxicol. in Vitro, 2005, **19**, 975-983.
[48] Soto K., Garza K.M. and Murr L.E.: Acta Biomater., 2007, **3**, 351-358.
[49] Kaegi R., Sinnet B., Zuleeg S., Hagendorfer H., Mueller E., Vonbank R., Boller M. and Burkhardt M.: Environ. Pollut., 2010, **158**, 2900-2905.

NANOSREBRO - PODEJMOWANIE TRUDNYCH DECYZJI

Instytut Chemii i Technologii Nieorganicznej, Wydział Inżynierii i Technologii Chemicznej
Politechnika Krakowska

Abstrakt: Nanotechnologia jako szybko rozwijający się obszar nauki jest rozpowszechniona w różnych dziedzinach życia na całym świecie. Jednym z przykładów nanosubstancji jest nanosrebro, które wykorzystuje się w medycynie, elektronice, budownictwie, technologii chemicznej oraz jako wyjątkowo skuteczny środek przeciwbakteryjny i antygrzybiczy. Od wieków znane są jego właściwości biobójcze, które są bardzo pożądane przy tworzeniu warunków aseptycznych. Jednak zaobserwowano wręcz toksyczne w skutkach działanie nanosrebra. Może ono kumulować się w łańcuchu pokarmowym, co stwarza ryzyko bezpośredniego oddziaływania na organizmy żywe. Co więcej, nanosrebro może spowodować obumieranie tkanki ludzkiej, a także zaburzyć działanie elementarnych składników komórek człowieka. Poniższe opracowanie ma na celu przedstawienie korzyści i szkód płynących ze stosowania nanosrebra.

Słowa kluczowe: nanosrebro, dezynfekcja, aktywność antymikrobiologiczna, nanotoksykologia