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SILVER NANOSTRUCTURES: CHEMICAL SYNTHESIS, CHARACTERISATION, AND APPLICATIONS

PhD THESIS – Summary

To obtain the scientific title of doctor of philosophy in
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CONTENT

EXTENDED SUMMARY OF THE DOCTORAL THESIS

Modern science has a wide development in all its fields. One of the goals of the last two decades has been to implement new solutions based on scientific research.

Nanotechnology is successful in both science and engineering, offering solutions in various fields such as medicine, catalysis, industrial activities, and agriculture.

Nanomaterials are "deliberately engineered" to guide the enhancement of their special properties, at the nanoscale.

The synthesis and processing of nanomaterials and nanostructures are essential aspects of nanotechnology. Studies on the new physical properties and their applications are possible only when the nanostructured materials have the desired size, crystal morphology, microstructure, and chemical composition. At the same time, it is very important to know and understand the properties of small particles and their potential for materials science.

With these considerations in mind, researchers have begun to address the needs of metal particle synthesis through the development of a synthetic chemistry of colloidal metals. One of the most challenging synthetic problems is the controlled generation of monodispersed nanoparticles with a size variation so small that the size selection is not required.

Recently, AgNPs have aroused special interests due to their physical and chemical properties, which are superior to those of the raw materials, due to the fact that they can be modified depending on the purpose of the final material. AgNPs have become of interest because of their applicability in a wide variety of fields, such as: antimicrobial agents; water treatment; as contrast agent for magnetic resonance imaging; for MRI imaging or in computer tomography (CT); as catalysts; as biosensors; SERS (Surface Enhanced Raman Spectroscopy) applications; for the construction of photovoltaic cells; DNA detectors; mercury, humidity, and ammonia sensors; for the manufacturing of OLED (organic light-emitting diodes) displays, etc.

The literature study referring to the identification of the current state of research in the proposed topic is presented in **PART I of the doctoral thesis.**

For decades, worldwide, nanotechnology has emerged as an extensive interdisciplinary area of research. Particular attention was paid to the design, manufacture, morphostructural characterisation, and applications of nanoparticles. This desirability is due to their unique physical and chemical properties. In general, nanoparticles are extremely small particles that range from 1-100 nm. The higher specific surface area of AgNPs is responsible for their incredible catalytic and biological/medical properties. Starting from these considerations, the objectives of this doctoral thesis are focused on the synthesis of spherical AgNPs and/or prismatic shapes by chemical methods. Thus, a studied method is the sonochemical one, starting from silver nitrate as a precursor, and a polymer, soluble starch, which is a reducing and stabilizing agent. At the same time, the photochemical synthesis method of AgNPs was studied using trisodium citrate, TSC, as a reducing agent and as a stabilising agent in the presence of UV radiation. In addition, chemical reduction was used to synthesize colloidal silver nanoprisms, where sodium borohydride, $NaBH_4$, is used as a strong reducing agent, TSC is used as a stabilising agent, and hydrogen peroxide, H_2O_2, is used as an oxidising agent. Controlling the size, shape, and structure of AgNPs is important from a technical point of view, because of the correlation between these parameters, their physico-chemical properties and implicitly their applications. To highlight these properties, i characterised the synthesised material were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), UV-vis spectroscopy, and Fourier-transform infrared spectroscopy (FT-IR).

For the theoretical evaluation of the size of spherical AgNPs, Mie theory is applied, it is a theory that describes 'elastic scattering' -without changing the wavelength- of a plane electromagnetic wave by a spherical particle. Characterised by its diameter and its complex refractive index. Mie's rigorous solution for the scattering of plane waves by homogeneous spheres has been available since 1908, but the complexity of this calculus is an impediment to its implementation. But thanks to today's computerisation and software solutions, such as MiePlot v.4.6, these rigorous calculations are achievable. Thus, MiePlot v.4.6. was used to perform the necessary calculations for the silver nanospheres synthesised by the two methods: the sonochemical method and the photochemical method.

The original contributions are presented in **PART II of the doctoral thesis**.

The general objective of the PhD thesis is to synthesise AgNPs by chemical methods. The aim of the synthesis is to obtain AgNPs of different shapes and sizes with different applications.

In general, the synthesis of AgNPs is carried out using three different approaches, namely: physical methods, chemical methods, and biological methods. Each method has its advantages and disadvantages, the main problems being costs, particle size, and size distribution. Among the existing methods, the chemical method is the most widely used because it provides an easier way to synthesise AgNPs in solution. Chemical methods use water or organic solvents to prepare AgNPs. This process typically uses three main components, such as (1) metal precursors, (2) reducing agents, and (3) stabilising agents.

The specific objectives of the thesis are: (i) the synthesis of AgNPs using the sonochemical, photochemical, and chemical reduction methods; (ii) structural and morphological characterisation of the synthesized AgNPs; (iii) theoretical evaluation of the spherical AgNPs size using Mie theory; (iv) establishing the antimicrobial activity of AgNPs for heterotrophic bacteria, but also specific cultures such as: *Staphylococcus aureus; Escherichia coli; Pseudomonas aeruginosa; Shigella flexneri; Candida albicans*; (v) comparative study regarding the antimicrobial response for different types of synthesised AgNPs, performing diffusometric studies and determinations of the minimum inhibitory concentration/ minimum fungicidal concentration; (vi) obtaining a new material with catalytic properties, by functionalising alumina with AgNPs, by impregnation, in order to photochemically degrade the Congo Red dye, present in aqueous solutions.

The activities undertaken to achieve the objectives of this doctoral thesis were the following.

- Establishing optimal conditions for the synthesis of spherical AgNPs via the sonochemical method, namely: precursor:reducing agent: stabilising agent ratio, pH, ultrasonication time, ultrasonication bath temperature, AgNPs stability;
- Establishing the optimal conditions for the synthesis of spherical AgNPs via the photochemical method, namely: precursor:reducing agent:stabilising agent ratio, pH, UV irradiation time, influence of the distance between the synthesised material and the UV irradiation source, AgNPs stability;
- Establishing the optimal conditions for the synthesis of colloidal AgNPs nanoprisms by chemical reduction, namely: precursor:reducing agent:stabilising agent: oxidizing agent, AgNPs stability;
- Structural and morphological characterisation of the synthesized AgNPs via chemical methods (sonochemical, photochemical, and chemical reduction);
- Theoretical evaluation of the size of the spherical AgNPs using Mie theory;
- Establishing the optimal conditions for the textile material made of cotton, gauze, to load it with AgNPs, conditions such as: solid: liquid ratio (S:L), pH, contact time, initial concentration of AgNPs;

- Establishing the adsorption mechanism of AgNPs onto the textile material made of cotton, gauze;
- Studies onto the antimicrobial activity of the textile material made of cotton, gauze, loaded with AgNPs, by using cultures of heterotrophic bacteria, but also specific cultures, as: *Staphylococcus aureus*; *Escherichia coli*; *Pseudomonas aeruginosa*; *Shigella flexneri*; *Candida albicans*;
- Comparative antimicrobial activity study for the different types of AgNPs synthesised by different chemical methods (sonochemical, photochemical, and chemical reduction), by conducting diffusometric and minimum inhibitory concentration studies;
- Obtaining a new material with photocatalytic properties, we functionalised alumina with AgNPs for the photochemical degradation of Congo Red dye.

Multiple AgNPs synthesis methods aim to use organic molecules because, following the interaction with the silver particles, they offer stability against oxidation and agglomeration, or they can even act only as a matrix. In this regard, polymer molecules have been widely used because their long chain provides many binding sites where nanoparticles can be stabilised.

One of the original contributions, presented in **Chapter 4**, is in the **use of soluble starch as a reducing and stabilising agent for the synthesis of AgNPs through the sonochemical method.** Soluble starch is also known for an environmentally friendly and relatively inexpensive reducing agent.

The optimal synthesis conditions were established, namely: precursor:reducing-stabilising agent ratio, pH of the reaction mass, ultrasonication time, ultrasonication bath temperature, and the stability of the synthesized AgNPs. At the same time, it was established that the size and shape of the synthesised AgNPs depend very much on the stage of the nuclei formation and their growth stage.

It is important that the oxidation process of the carbonyl groups (specific to starch) occurs at a higher rate, to cover the need for electrons to reduce the silver ions. Therefore, the increase in pH leads to an increase in the solubility of starch, by 'breaking' the granules, followed by the degradation of macromolecules to obtain smaller fragments, thus increasing its solubility and the reduction capacity necessary to obtain AgNPs.

In order to highlight the presence of AgNPs and also to establish the optimal synthesis conditions, UV-vis spectra were recorded in the 300-700 nm range. As a function of pH, the zeta potential of the colloidal particles was also determined.

The importance of the amount of soluble starch in the AgNPs synthesis process by the sonochemical method was highlighted by recording UV-vis spectra at different $AgNO_3$:soluble starch massic ratios.

According to surface plasmon resonance (SPR), existing at the wavelength of $\lambda \sim 420$ nm, the predominant presence of spherical AgNPs is confirmed, a fact also supported by the brown colour, which is specific to the excitation of the surface plasmon resonance of spherical AgNPs, which intensifies with increasing starch concentration, indicating to us that there is a correlation between starch concentration of starch, and the concentration of spherical AgNPs present in the solution. At the same time, we can state that with the increase in the $AgNO_3$:soluble starch ratio, respectively increasing the quantity of soluble starch, the concentration of AgNPs increases. This conclusion is supported by the fact that the absorbance increases, which is directly proportional to the concentration of AgNPs present in the solution.

Furthermore, the value of full width at half maxima (FWHM), obtained using Gaussian-type fits, indicates that the material synthesised using a ratio of $AgNO_3$:soluble starch, 1:4, presents the highest monodispersity (FWHM – 134 nm), while in the case of the matherial synthesized in AgNO3: soluble starch, 1:5 ratio, which has a higher FWHM (FWHM – 178 nm), part of the starch remains unreacted after the synthesis is completed, thus being in excess.

In order to establish the optimal ultrasonication bath temperature for the synthesis of AgNPs, UV-vis spectra were recorder at different temperatures. It was observed that as the temperature of the ultrasonic bath increased, the specific absorbance of AgNPs increased. We can also state that, with increasing absorbance, the concentration of AgNPs also increases. At the same time, the FWHM decreases with increasing temperature, finding that for the material obtained at $80^\circ C$, the FWHM is 133, with an R^2 of 0.99751, which confirms an increase in monodispersity. This desideratum is due both to the fact that a higher temperature facilitates the hydrolysis of starch and to the fact that the ultrasonication process itself facilitates the hydrolysis of starch and intensifies its depolymerisation. Therefore, the optimal temperature in the ultrasonication bath is $80^\circ C$.

From the UV-vis spectra recorded at different ultrasonication times, it was concluded that the optimal ultrasonication time is 60 minutes, in order to obtain a low FWHM (133 nm) and a high absorbance, which corresponds to a higher concentration of AgNPs present in the solution, compared to 30 or 90 minutes of ultrasonication.

pH plays an important role during the synthesis of AgNPs. Depending on the pH, AgNPs have different sizes. To study the influence of pH on AgNPs synthesis, UV-Vis spectra at different pH values were recorded. The absorption band in the visible range $350 – 550$ nm is specific to AgNPs, and the surface plasmon resonance, SPR, being at different wavelengths, depending on the pH value, this indicates the formation of AgNPs. It can be observed that with an increase in pH (increasing the amount of NaOH present), the absorbance increases, which indicates an increase in AgNPs concentration. Since absorbance peaks starting with pH>10 have a specific Gaussian curve shape, it can be stated that the particle sizes are uniformly distributed.

FWHM is also observed to decrease with an increase in the amount of NaOH, implicitly an increase in pH, having 92 nm (after a Gaussian fit) with an $R^2 = 0,98358$ for pH=8, and 63 nm (after a Gaussian fit) with an $R^2 = 0,9964$ for pH=13. This highlights that as the pH increases, the monodispersity of the nanoparticles also increases.

At the same time, the recorded spectra show that the sample synthesised at pH=12.5 has a surface plasmon resonance, SPR, at the wavelength of $\lambda=412$ nm, while the sample synthesized at pH 13, has an SPR at $\lambda=401$ nm, indicating that the sample synthesized at pH=13 presents AgNPs of smaller sizes. Therefore, a higher concentration of NaOH and a higher pH facilitates a faster and complete reduction of silver ions, thus obtaining a higher concentration of AgNPs with a higher monodispersity, and also obtaining smaller AgNPs. In conclusion, the **optimal pH for AgNPs synthesis is pH=13.**

The electrokinetic evaluation (Zeta potential) of AgNPs was performed depending on the pH value, respectively, the amount of NaOH and its effect. From the obtained results, it concludes that, with the increase of NaOH, respectively a pH increase, the Zeta potential increases in absolute value and at the same time the electrical charge of the nanoparticles. Materials that are synthesised at pH between 12-13 have a zeta potential <-30 mV, indicating that their stability is very good, so they have a much lower risk of agglomeration. This increase in stability with increasing pH may be due to the fact that a basic solution facilitates starch hydrolysis, leading to the appearence of C=O and –COOH groups that are fixed on the surface of AgNPs, giving them a strong negative charge, thus achieving thus the electrostatic repulsion between the nanoparticles, keeping them in dispersion. At a high pH, the formation of AgOH and Ag_2O takes place, and they are reduced more easily, at a higher speed, which causes an increase in the concentratino of AgNPs and the formation of small particles.

Thus, the optimal synthesis conditions are as follows: AgNO3: starch massic ratio of 1:4; pH=13, ultrasonication bath time 60 minutes and ultrasonication bath temperature, 80ºC.

From the SEM micrographies it was observed that the AgNPs are spherical monodisperse or polydisperse, their sizes ranging between 20-40 nm.

In the EDX spectrum, the specific silver peak was highlighted, which is specific to the presence of AgNPs. The pressure of C and O can be attributed to the carbonyl, C=O, and carboxil, -COOH groups existing in the reaction mass.

In order to specifically/profoundly characterise the morphology of the synthesized material under optimal conditions, transmission electron microscopy (TEM),TEM, as well as high-resolution transmission electron microscopy (HRTEM), and selected area diffraction (SAED) for the crystallographic analysis of AgNPs were used.

From the TEM micrographs it was observed that the geometric shape of the nanoparticles is quasi-spherical. From the SAED analysis, it was observed that the most intense diffraction spots correspond to the (111) and (200) crystallographic planes, which are specific to the centered cubic crystal structure of silver.

From the results obtained, it could be observed that the predominant AgNPs are the 33 nm sized particles, but also the fact that, in addition to these, there are also coarser particles with the size of 43 nm, as well as finer particles, of 23 nm.

From the FT-IR spectrum it was observed that vibrations of the carboxyl, -COOH, and carbonyl C=O groups are found. These vibrations are due to the presence of these groups on the AgNPs surface.

Following the UV-Vis spectra obtained after 3 days, 7 days, 30 days and 250 days, it was observed that although there are changes in the surface plasmon resonance (SPR) of the material, which indicates a change in the morphology of the material, these changes are not significant, in the material synthesized under optimal conditions ($AgNO_3$:starch ratio of 1:4, pH=13, ultrasonication time of 60 minutes, ultrasonication bath temperature of 80ºC, being stable even after 250 days.

The use of photochemical processes for the synthesis of AgNPs allowed for an easy, fast, and efficient production of silver nanoparticles with controlled properties without the use of toxic chemical reagents or sophisticated equipment. **Chapter 5** presents the effect of the variation of experimental parameters, parameters such as: pH of the reaction mass, the UV irradiation time, the distance from the irradiation source, the influence of the nature and concentration of reducers on the synthesis of AgNPs, as well as on the particle size, shape, and colloidal stability.

The photochemical process begins with the reduction of the silver precursor from its +1 valence (Ag^+) to its zero valence state (Ag^0) by the photocatalytic action of the reducing agent, TSC. Ag^0 forms nucleation centres or nuclei which subsequently grow and aggregate to give rise to AgNPs. Thus, UV radiation was used as an "activator" for TSC.

This "activation" was achieved through the delivery of 'packets of energy' in the form of photons; the mechanism of this synthesis can be expressed by the following reactions: the first process is the decomposition of TSC under the influence of UV radiation, resulting in acetone-1,3-dicarboxylate, followed by the reduction of silver to metallic silver, and the second process is a complexation process.

In order to highlight the presence of AgNPs and also to establish the optimal synthesis conditions, the influence of some parameters that influence the synthesis of AgNPs are studied, namely: AgNO3: TSC ratio, UV irradiation time, the distance from the UV irradiation source, pH of the reaction mass, and stability of the synthesized AgNPs.

To establish the optimal $AgNO_3$:TSC ratio, the amount of TSC was varied while keeping constant the amount of $AgNO_3$, the UV irradiation time, 60 minutes, pH = 8, and the distance between the irradiation source and the sample, 3.5 cm, and UV-Vis spectra were registered in the range of 300-700 nm.

From the recorded UV-vis spectra and from the full width at half maxima (FWHM) values, obtained using a Gaussian type fit, it can be concluded that the **optimal ratio AgNO₃:TSC is 1:7**, because it indicated that this material is the most monodisperse, as well as the fact that the AgNPs present in this solution have the smallest size.

To establish the optimal UV irradiation time on AgNPs synthesis, the massic ratio AgNO₃:TSC=1:7, pH=8 and the distance between the UV irradiation source and the sample, 3.5 cm, were kept constant, varying only the irradiation time with UV. From the obtained UV-vis spectra, it results that the representative spectrum of the sample that was irradiated with UV for 90 minutes has the SPR at λ=405 nm, which indicates the presence of coarse AgNPs that could form aggregates. The UV-vis spectrum of the sample irradiated with UV for 30 minutes shows a relatively low absorbance, which indicates a rather low concentration of AgNPs compared to the sample that was irradiated with UV for 60 minutes. Although the FWHM is lower for the sample irradiated for 90 minutes, indicating good monodispersity, the presence of SPR at λ=405 nm doesn't justify the use of 90 minutes of UV irradiation. **Thus, the optimal irradiation time is 60 minutes, and the subsequent studies will be carried out using an irradiation time of 60 minutes.**

To establish the effect of the distance from the UV irradiation source on the AgNPs synthesis, the AgNO₃:TSC ratio, the pH of the reaction mass and the UV irradiation time were kept constant, varying only the distance of the sample from the irradiation source. From the obtained spectra it can be observed that, in the case of using the smallest distance possible between the UV irradiation source and the sample, 3.5 cm, it presents the highest absorbance, which implicitly indicates the highest concentration of AgNPs.

Thus, in conclusion, the distance between the UV irradiation source and the sample of 3.5 cm is considered to be optimal.

The equation used to determine the measured irradiance and power output of the fluorescent lamp was established by Keitz. Keitz's equation is the basis of a proposed study to quantify the total flux of an ultraviolet lamp, thus his equation is:

$$P = \frac{I2\pi DL}{2\alpha + \sin 2\alpha} \quad \text{from where the irradiance 'I' can be determined:}$$

$$I = \frac{P\,(2\alpha + \sin 2\alpha)}{2\pi DL}$$

Where:

P - power of UV lamp [W]

I – radiation intensity [W/m^2]

L – tube length [m]

D – distance [m]

$$\alpha = \text{ArcTan}\left[\frac{L}{2D}\right] \text{ rad}; \quad \sin\alpha = \frac{L}{\sqrt{4D^2 + L^2}} \;;\; \cos\alpha = \frac{2D}{\sqrt{4D^2 + L^2}} \;;\; \sin 2\alpha = 2\sin\alpha \cdot \cos\alpha.$$

Thus, this equation was used to determine the radiation intensity required for an optimal synthesis. For the calculation, the following were considered: the length of the tube (L) used is 40 cm; the distance travelled by the radiation (D) is 3.5; 7 and, respectively, 10 cm to the irradiated sample (I); the power of the UV tube is given by the manufacturer, and is 6 W. From the obtained results, it can be seen that there is a correlation between the UV-Vis spectra and the irradiance obtained using the calculus, namely the differences between the sample located at 7 cm and the one at 10 cm are very small, compared to the rather large difference between

the sample located at 3.5 cm and the one at 7 cm, a fact which also emerged from the UV-Vis spectra.

To establish the effect of pH on the reaction mass, the mass ratio of $AgNO_3$:TSC, the UV irradiation time and the distance between the UV irradiation source and the sample were kept constant, varying only the pH of the reaction mass between 8-11.

Although the sample with pH = 8 does not have the lowest FWHM value, it has the highest absorbance, which is implicitly directly proportional to the concentration of AgNPs present in the solution. Therefore, the **optimal pH specific to this synthesis is considered pH=8.**

After establishing the optimal synthesis parameters and knowing the required irradiance for an optimal synthesis, the necessary dosage of UV radiation was determined to achieve an optimal synthesis, resulting in a dosage of 770 kJ/m^2.

Thus, the optimal synthesis conditions are as follows: $AgNO_3$:TSC ratio of 1:7; pH=8; the UV irradiation time of 60 minutes, and the distance between the UV irradiation source and the sample of 3.5 cm.

To characterise the morphology of the synthesized AgNPs under optimal conditions, scanning electron microscopy, SEM, was used, through which it was observed that the AgNPs are spherical and polydisperse, with particle sizes of 24-55 nm.

The EDX spectrum confirms their presence. C, O, and Na are elements specific to trisodium citrate. The high carbon concentration is also due to the sample preparation method (dropwise deposition of the AgNPs solution on the carbon strip).

In order to characterise more profoundly the morphology of AgNPs, transmission electron microscopy, TEM, high resolution transmission electron microscopy, HRTEM, and selected area electron diffraction, SAED (crystallographic analysis of the silver nanoparticles), were employed. The TEM micrographs show that the colloidal silver particles have a spherical/quasi-spherical shape. The SAED analysis shows that the most intense diffraction points corespond to the (111), (200) and (220) crystallographic planes, which are specific to the centered cubic crystal structure of silver. Also from the AgNPs size distribution, it can be seen that the average diameter of the nanospheres is 15 nm.

From the FT-IR spectrum obtained for the optimal synthesised AgNPs sample, it can be observed that in the range of the wavenumber 3000-3500 cm^{-1} a vibration specific to the O-H bond appears, and at the wavenumber of ~1633 cm^{-1} a specific C=O vibration bond appears.

After determining the optimal synthesis conditions, the study on the stability of AgNPs was carried out, which shows that the nanoparticles are stable after 610 days.

In **Chapter 6**, an original approach was presented regarding the synthesis of silver nanoprisms, by chemical reduction, using $NaBH_4$ as a reducing agent, and trisodium citrate, TSC, as a complexing/stabilising agent.

To synthesize the silver nanoprisms by chemical reduction, the following reagents were used: (i) precursor:silver nitrate, $AgNO_3$; (ii) reducing agent:sodium borohydride, $NaBH_4$; (iii) stabilising agent:trisodium citrate, TSC, ($Na_3C_6H_5O_7$), and (iv) oxidising agent: hydrogen peroxide, H_2O_2.

The *optimal conditions* for the synthesis of nanoprismatic AgNPs colloidal particle by the chemical reduction method were established, namely: precursor:reducing agent:stabilising agent:oxidizing agent ratios, and the stability of AgNPs.

The synthesis of colloidal silver nanospheres involves the reduction of $AgNO_3$ in the presence of $NaBH_4$. As the silver ions are reduced, the silver atoms begin to form aggregates, thus resulting in the first AgNPs in the presence of the stabilising agent, TSC. Trisodium citrate acts as a pH buffer, maintaining a neutral or slightly alkaline pH (pH 7-8), reacting with the resulting nitric acid. First of all, TSC complexes silver, associating with silver ions present on

the surface of a nanoparticle, giving the surface of the nanoparticle a negative electrical charge, thus realising electrostatic repulsion between the nanoparticles, which implicitly leads to their stabilisation. H_2O_2 acts as an oxidising agent, used to facilitate the formation of silver nanoprisms, being, in fact the main reagent involved in changing the geometry of colloidal nanospheres into colloidal nanoprisms.

In order to highlight the presence of prismatic colloidal nanoparticles, but also to establish the optimal synthesis conditions, the influence of the parameters involved in AgNPs synthesis is studied, namely: the amount of reducing agent, the amount of stabilising agent, the amount of oxidising agent, in order to establish the optimal $AgNO_3$:$NaBH_4$:TSC:H_2O_2 mass ratios. At the same time, the stability of AgNPs is studied.

The influence of the **amount of NaBH₄** on the synthesis of colloidal silver nanoprisms and the evolution of the morphology was followed by plotting the UV-vis spectra in different ratios $AgNO_3$:**$NaBH_4$**:TSC:H_2O_2 establishing the fact that the specific spectrum of the ratio $AgNO_3$:**$NaBH_4$**:TSC:H_2O_2=1:**0,92**:2,4:16,3 has an SPR at λ=435 nm, which is characteristic of silver nanospheres. The sample synthesised at the ratio of AgNO3:**$NaBH_4$**:TSC:H2O2=1:**1,00**:2,4:16,3 has an SPR at λ=480 nm, indicating a change in the morphology of the material. After completion of the synthesis, a ratio of AgNO3:**$NaBH_4$**:TSC:H2O2=1:**1,02**:2,4:16,3 the colour of the solution is red and it shows an SPR at λ=514, which also indicates a change in morphology. The absorbance increased as well, indicating an increase in AgNPs concentration. The sample synthesised at the ratio of AgNO3:**$NaBH_4$**:TSC:H2O2=1:**1,04**:2,4:16,3 shows lower absorbance compared to the previous ratio, indicating that the concentration of AgNPs present in the solution decreased. Furthermore, the change in surface plasmon responance, at λ=558 nm proves that there has been another change in the AgNPs morphology, a change that can also be seen in the color variation from reddish/pink to indigo blue. The last sample obtained at the ratio of AgNO3:**$NaBH_4$**:TSC:H2O2=1:**1,10**:2,4:16,3, presents an SPR at λ=665 nm, SPR which indicates the presence of colloidal silver nanoprisms.

The ratio in which the optimal amount of NaBH₄ is used is AgNO₃:NaBH₄:TSC:H₂O₂ = 1:1,10:2,4:16,3.

The influence of the amount of TSC onto the synthesis of colloidal silver nanoprisms was determined using the same amount of $AgNO_3$, $NaBH_4$ and H_2O_2, varying only the amount of TSC, and recording UV-vis spectra.

From the resulting spectra we can see that the material synthesised at the ratio of $AgNO_3$:$NaBH_4$:**TSC**:H_2O_2=1:1,10:**1,6**:16,3 has a lower absorbance than the others, indicating the presence of a lower concentration of AgNPs. The spectrum recorded for the sample synthesised at the ratio of $AgNO_3$:$NaBH_4$:**TSC**:H_2O_2=1:1,10:**2,4**:16,3 shows a higher absorbance, indicating that there is a higher concentration of AgNPs, while the specific spectrum of the synthesized material at a ratio of $AgNO_3$:$NaBH_4$:**TSC**:H_2O_2=1:1,0:**3,2**:16,3 has a lower absorbance. This can be attributed to the fact that a higher concentration of the stabiliser, TSC does not allow an efficient reaction speed in order to have an optimal synthesis of colloidal silver nanoprisms, which also leads to the appearance of larger sized nanoparticles.

The ratio in which the optimal amount of NaBH₄ is used for the synthesis is AgNO₃:NaBH₄:TSC:H₂O₂ = 1:1,10:2,4:16,3.

After obtaining the optimal quantity of the reducing agent, $NaBH_4$ and the optimal quantity of the stabilising agent, TSC, it was sought to optimise the synthesis by studying the effect of H_2O_2 on the morphological evolution of AgNPS, through UV-vis spectra.

According to the results, it can be observed that the material synthesised material at the ratio of $AgNO_3$:$NaBH_4$:TSC:**H_2O_2**=1:1,10:2,4:**8,5** presents an SPR at λ=408 nm, indicating the predominant presence of spherical AgNPs, indicating that there was no change in AgNPs morphology, signaling that a larger amount of H_2O_2 is required. The representative spectrum

of the material synthesised material at AgNO$_3$:NaBH$_4$:TSC:**H$_2$O$_2$** = 1:1,10:2,4:**14,5** ratio presents an SPR at λ=552 nm, demonstrating that a morphological change occurred, a change that resulted in a color change from golden yellow to red, and the fact that the absorbance decreased proves that there was a decrease in AgNPs concentration. The specific spectrum of the synthesised material at the ratio of AgNO$_3$:NaBH$_4$:TSC:**H$_2$O$_2$** = 1:1,10:2,4:**15,5** has an SPR at λ=620 nm and also shows a colour change to indigo blue, indicating the presence of silver nanoprisms in the solution. In the case of AgNO$_3$:NaBH$_4$:TSC:**H$_2$O$_2$** = 1:1,10:2,4:**16,3**, a transition was observed to azure blue from golden yellow, a transition which indicates the predominant presence of colloidal silver nanoprisms, having an SPR at λ=665 nm. Regarding the material synthesised at a ratio of AgNO$_3$:NaBH$_4$:TSC:**H$_2$O$_2$** = 1:1,10:2,4:**17,0** a return to the reddish colour was observed, the spectrum having SPR at λ=533 nm, indicating that a larger amount of H$_2$O$_2$ does not favour the synthesis of silver nanoprisms, so **the following studies were carried out using the ratio of AgNO$_3$:NaBH$_4$:TSC:H$_2$O$_2$ = 1:1,10:2,4:16,3.**

According to the SEM results, it can be seen that the shape of the silver nanoparticles from the initial material (with the colour of light yellow), with a ratio of AgNO$_3$:NaBH$_4$:TSC:H$_2$O$_2$=1:1,10:2,4:8,5, is spherical, fact which is also supported by the UV-vis spectrum, having an SPR at λ=408 nm. The following three materials synthesised at the ratios:

AgNO$_3$:NaBH$_4$:TSC:H$_2$O$_2$=1:1,00:2,4:16,3;
AgNO$_3$:NaBH$_4$:TSC:H$_2$O$_2$=1:1,02:2,4:16,3 and
AgNO$_3$:NaBH$_4$:TSC:H$_2$O$_2$=1:1,04:2,4:16,3 represent intermediate phases, in which silver nanospheres, nanowires and colloidal silver nanoprisms are present, and in the material synthesised at the ratio of AgNO$_3$:NaBH$_4$:TSC:H$_2$O$_2$ = 1:1,10:2,4:16,3, ratio in which it was observed that the predominant morphology of the nanoparticles is prismatic, fact which also is proven by the UV-Vis spectrum (having an SPR at λ= 665 nm).

From the EDX spectrum, C and O peaks can be observed, which are specific to TSC. The presence of Na is due to the presence of sodium borohydride (NaBH$_4$) and trisodium citrate (Na$_3$C$_6$H$_5$O$_7$), while a presence of the specific Ag peak is associated with the presence of colloidal silver nanoprisms.

From the size distribution of colloidal silver nanoprisms, it can be seen that the average particle size is 57 nm.

The FT-IR spectrum highlights the specific groups of the stabiliser agent used, TSC, namely: C=O, -COOH groups, groups that attach to the surface of the colloidal silver nanoprisms, thus achieving electrostatic repulsion, giving them colloidal stability.

To study the stability over time of the synthesised material at the optimal conditions (ratio of AgNO$_3$:NaBH$_4$:TSC:H$_2$O$_2$=1:1,10:2,4:16,3; pH=7-8) UV-Vis spectra were obtained at various time intervals (3,7, 30 and 100 days).

The results obtained show that the colloidal silver nanoprisms are stable for 100 days. They did not undergo major changes in terms of FWHM and absorbance during their monitoring.

In **Chapter 7** of the doctoral thesis, it was desired to theoretically estimate the diameter of the spherical AgNPs obtained by the sonochemical and photochemical methods, using Mie's theory.

Ideally, all nanoparticles should have the same diameter (monodisperse), but this is not possible. The monodispersity of the colloidal system varies depending on the reducing agent used and specific synthesis parameters. To obtain accurate results, the following steps are necessary: (i) rapid reduction of AgNO$_3$ which leads to a solution with a higher monodispersity, (ii) ultracentrifugation or nanofiltration, in order to remove the coarse colloids from the resulting solution.

In order to theoretically estimate the diameter of the spherical AgNPs obtained after the synthesis, by the sonochemical method, the sample with optimal synthesis parameters was used: AgNO$_3$:starch = 1:4 ratio, pH = 13, ultrasonication time of 60 minutes, and ultrasonic bath temperature of 80°C. The selected theoretical diameters are in the range of 30-36 cm.

In the case of spherical AgNPs obtained by the **photochemical method** under optimal synthesis conditions, which are: AgNO$_3$:TSC=1:7 ratio; pH=8; the UV irradiation time of 60 minutes and the distance between the UV irradiation source and the sample of 3.5 cm. The theoretical selected diameters were in the range of 40-46 nm.

Following the calculations made, using the MiePlot software, the following conclusions emerge.

- In the case of spherical AgNPs obtained following the sonochemical, and photochemical synthesis methods, the absorbance is directly proportional to the concentration of spherical AgNPs present in the solution, which in turn decreases with the increase of the AgNPs diameter;
- There is a close correlation between the morphology of spherical AgNPs and the wavelength of the SPR;
- From the spectra obtained of the spherical AgNPs synthesized through the sonochemical method, the SPR of the synthesized material is at λ = 401 nm, wich an absorbance of 0.61; the spectrum obtained based on the theoretical calculations that is the closes to the experimental spectrum is that of the AgNPs with a specific diameter of 34 nm (33±3 nm), having an SPR at λ=397 nm with an absorbance of 0.60. The results are also proven by the TEM micrographs.
- From the spectra obtained of the spherical AgNPs synthesized by the photochemical method, it emerges that the SPR of the synthesized material is at λ = 404 nm, having an absorbance of 0.66; the theoretical spectrum obtained, which is similar to the experimental one, is specific to spherical AgNPs of 44 nm (44±3 nm), having an SPR at λ=404,5 nm with an absorbance of 0.67.

The physical, chemical and mechanical properties of AgNPs are well known, which is why they are known to be used in applications such as electronics, electrotehnics, biotechnology and bioenergy, the textile industry, medicine, pharmacy, optics, and environmental protection.

In **Chapter 8**, the emphasis was placed on two of the most important applications of AgNPs, namely medical and industrial applications.

Multifunctional applications of AgNPs have been presented; for example, as antibacterial, antifungal, antiviral, anti-inflammatory, antiangiogenic, or anti-cancer agents and the mechanism of anticancer activity of AgNPs. In the textile industry, cotton is considered a traditional material, with a multitude of applications, being soft and with high adsorbent properties. In the medical field, textiles are used, such as surgical gowns, dapes, surgical masks, gauze, bandages, etc. which are most exposed to bacteria and viruses, if the protective layer is not resistant to microorganisms, it may pose a risk to the health of the user. On a daily basis, microorganisms can easily multiply under optimal conditions of humidity and temperature. Therefore, to reduce bacterial populations, in the biomedical field and to minimize infections with pathogens, the use of an antimicrobial textile material is of particular concern.

In the industrial field, starting from the idea that, in general, to obtain the best microstructure and properties, a material must be carefully prepared from the synthesis stagestage, and taking into account that there are problems in reproducing their special properties and in their use by routine in practical applications, we studied to obtain a material with directed properties starting from hydrated alumina and AgNPs. This material

has significant catalytic properties, highlighted by the photocatalytic degradation of Congo red dye, RC.

In order to determine the most effective material in terms of antimicrobial capacity, a comparative study was carried out using the three syntheses of AgNPs presented in previous chapters. The materials studied are those obtained under optimal established conditions, namely: (i) **sonochemical method**: $AgNO_3$:starch ratio of 1:4; pH=13, ultrasonication time 60 minutes, and the temperature of the ultrasonication bath of 80ºC; (ii) **photochemical method**: $AgNO_3$:TSC ratio of 1:7; pH=8; UV irradiation time of 60 minutes, and the distance between the UV irradiation source and the sample of 3.5 cm; (iii) **chemical reduction**: $AgNO_3$;$NaBH_4$:TSC:H_2O_2 = 1:1,10:2,4:16,3; pH=7-8.

Diffusimetric studies were carried out, using the CLSI 2020 methodology, as well as studies to determine the minimum inhibitory concentration (MIC) and minimum fungicidal concetration (MFC). Five microorganisms belonging to reference cultures (ATCC, Microbiologics, France) were used to test their sensitivity under the action of the synthesised material.

According to the results obtained, it can be stated that AgNPs synthesised by the sonochemical method present a much more pronounced inhibition zones compared to the particles synthesized by the other two methods.

This can be attributed to the fact that the mass ratio precursor:stabilizer used in the case of AgNPs synthesis via the sonochemical method ($AgNO_3$:starch ratio = 1:4) is much higher compared to the other two synthesis methods (photochemical and respectively chemical reduction), and due to the fact that the sonochemical method presents the higher monodispersity, thus the predominantly AgNPs size is 33 nm, fact which implicitly leads to obtain a much higher amount/concentration of AgNPs. At the same time, the sonochemical method ensures a better dispersion of the reactants in the system.

This fact allows for diffusion in the culture medium of a higher concentration of AgNPs.

However, since the synthesised material by the sonochemical method presented a larger inhibition zone, it was observed that, in the case of the photochemically synthesized material the minimum inhibitory concentration is much lower. This may be due to the fact that the photochemically synthesised material also contains much smaller particles (15 nm) in addition to the coarse one, comparted to the material synthesized by the sonochemical method (33 nm) which is monodisperse, a fact that allows AgNPs to easily penetrate the microbial membrane, thus giving it a much more effective antimicrobial capacity.

The material synthesised by chemical reduction (silver nanoprisms) does not show a very good antimicrobial activity, which is mainly due to the size of the particles (55 nm).

Following these conclusions, the following tests were performed with the material synthesised by the sonochemical method under optimal conditions, namely: $AgNO_3$:starch = 1:4 ratio; pH = 13; ultrasonication time of 60 minutes, and the temperature of the ultrasonication bath of 80ºC. To highlight the antibacterial properties of the synthesised AgNPs, under optimal conditions, the AgNPs solution was deposited (by adsorption) on the surface of some pieces of textile material, cotton, gauze (TB).

For this, specific parameters for the adsorption process were established, namely: adsorbent:absorbent ratio, contact time, temperature and initial concentration of colloidal silver, and their influence onto the adsorption capacity of the gauze. So:
- With an increase in the S:L ratio, the efficiency of the adsorption process increases, but above the ratio of S:L = 0,3g:25mL, the efficiency remains constant, around 70%. Further studies were carried out with 30 pieces of TB, the equivalent of 0,3 g of TB, a larger amount being useless;

- With an increase in contact time and temperature, the adsorption capacity of TB also increases. After 4 h, the adsorption capacity of TB remains approximately constant, 2 mg AgNPs/g TB. The temperature influences the adsorption process, but not significantly, so it is not necessary to work at temperatures higher than 298 K. Therefore, it was found that the optimal contact time and temperature are 4h and 298 K;
- With an increase in the initial concentration of AgNPs, the adsorption capacity of TB increases until a given moment, when no matter what amount of AgNPs is added, the adsorption capacity remains almost constant. Therefore, it can be stated that the material reaches its **maximum adsorption capacity around the concentration of 50 mg AgNPs/L, the maximum adsorption capacity being 2,35 mg AgNPs/g TB.**
At the same time, to establish the adsorption mechanism of AgNPs on TB, kinetic, thermodynamic and equilibrium studies were carried out. Thus:
- Analysing kinetic parameters, and more precisely the values of the regression coefficient, R^2, which are very close to 1 (between 0,98 and 0,99), it can be stated that the **pseudo-second-order kinetic model describes very well the AgNP adsorption processes on TB material**. This statement is also supported by the fact that the values obtained for the calculated adsorption (q_e calc) are very close to the experimentally obtained adsorption capacity values (q_e exp).
- Based on the linearised form of the pseudo-second-order kinetic model, the activation energy associated with the AgNPs adsorption process on the TB material was calculated, which is **Ea=17,72 kJ/mol**, R^2=0,9871.
- Regardless of the value of the working temperature, the Gibbs free-energy variation has negative values. This confirms that the adsorption process is spontaneous. It is also observed that, simultaneously with an increase in the working temperature, there is a decrease in the Gibbs free energy value, which confirms that the adsorption process is *favoured by temperature*. When the slight increase in the adsorption capacity is simultaneously with the increase in temperature and with the positive values of the enthalpy, it can be stated that the *studied adsorption processes are endothermic*. The positive entropy energy (ΔS^0) suggests that the *studied adsorption process exhibits greater disorder at the liquid/solid interface*. However, the small value of the entropy variation suggests that there are no major changes in the degree of disorder at the interface level.
- Due to the fact that the value of the parameter value 1/nF (1/nF=0,29) is subunitary, it can be stated that the studied textile material has a high affinity for colloidal silver, thus obtaining convex adsorption isotherms. Taking into account the fact that the values of the heterogenity factor is $1/n_s = 0,3$, this represents a large deviation from the unitary value, which allows the statement that the **studied material has a heterogeneous surface**. It is also found that R^2 has the lowest values in the case of Freundlich isotherm, suggesting that this isotherm presents the least precision in terms of describing the studied adsorption process. It is also observed that among all the studied isotherms, the **Langmuir isotherm best describes the studied adsorption process**, since the value of the correlation coefficient R^2=0,95616 is the closest to a unitary value.
- The value of the maximum calculated adsorption capacity (qL=2,30 mg/g) is closest to the **value of the maximum adsorption capacity obtained experimentally (qm,exp=2,35 mg/g).**
- Because the mechanism of the AgNPs adsorption process on the TB material is best described by the Langmuir isotherm, it can be stated that the nanoparticles are deposited as a monolayer on the material.

After establishing the optimal conditions for AgNPs adsorption onto the TB material, its bactericidal effect was tested for medical application.

A first step was to ***determine the minimum inhibitory concentration (MIC)*** of AgNPs on a heterotrophic inoculum, finding that the **minimum inhibitory concentration (MIC) of silver is 50 mg AgNPs/L**.

In order to highlight the effectiveness of the obtained material, in terms of its antimicrobial efficiency, in the case of its use in hospitals, microbiological studies were carried out using standardised bacterial and fungal species, as well as clinically isolated ones. To evaluate the antimicrobial efficiency of the tested material, microbiological tests were performed, by the diffusimetric method, using 5 reference strains and 5 clinically isolated microbial strains. After the specific preparation of the sample and their appropriate incubation, the inhibition diameter of the zone of inhibition was measured in mm and the results were expressed as an arithmetic mean. As a positive control, discs impregnated with antibiotics such as: Ciprofloxacin (5 µg; Oxoid), erythromycin (15 µg; Oxoid) and Caspofungin (5 µg; Oxoid) were used and as a control negative discs impregnated with 20 mL of distiller water were used. Thus:

- It can be observed that regardless of the type of microorganism tested, the inhibition diameters corresponding to the synthesised material are larger compared to those of $AgNO_3$ (precursor). It is obvious the important role in the antimicrobial efficiency of the AgNPs size, which in this case is 33 nm.
- **The material synthesised by the sonochemical method has significant biocidal properties.**
- We can see that the clinically isolated strain (*Staphylococcus aureus*) has a similar or even better bactericidal response (*Escherechia coli*) compared to the reference species. Although these clinically isolated strains normally show a better resistance to current antibiotics, it was expected to have a reduced inhibition zone if the clinically isolated bacteria were also resistant to the synthesised material.
- The clinically isolated bacterial strains used in our tests have lower resistance to the analyzed material, which is a desideratum to consider, the material having a potential use in the medical field.
- The synthesised material showed antibacterial activity in both Gram-positive and Gram-negative bacteria, even if it is slightly lower than the bactericidal activity observed for the antibiotics used as a control (considered sensitive to antibiotics). An explanation would be the interaction of AgNPs with the surface of the bacterial wall, respectively, with the enzymatic thiol groups which seem to be the first step in the degradation of bacterial cells.
- Regarding the antifungal effect of the studied material, when used in the *Candida Albicans* reference culture (ATCC 90028), the inhibition diameter of 21 mm is comparable to that presented in the CLSI 2020 specialised protocol for the antifungic Caspofungin 5 µg (22mm), falling within the range of standardised antifungic sensitivity, which proves that the synthesised material has very good antifungal properties. In the case of clinically isolated *Candida albicans*, the results are not as promising, due to the fact that the strain of this fungus shows particular resistance to the action of antifungal agents, due to its structural dimorphism, its rapid adaptation to environmental pH fluctuations, its metabolic flexibility, but also the presence of strong nutrient acquisition systems from the nutrient medium.

Knowing the catalytic properties of silver, the Al_2O_3-AgNPs material (obtained by functionalization by impregnation, by ultrasonication of Al_2O_3 with AgNPs) was used in the degradation/elimination of dyes from waste water. Congo Red was used for this study.

The AgNPs used were synthesized by the sonochemical method using the following synthesis parameters: $AgNO_3$:starch ratio of 1:4, pH=13; ultrasonication time of 60 minutes, ultrasonication bath temperature of 80°C. Aluminium hydroxide for Al_2O_3 was supplied by SC ALUM SA Tulcea (Romania), which contains >99.5% $Al(OH)_3$ and is characterised by a specific surface area of $4.6 m^2/g$ and a pycnometric density of 2.41 g/cm, and a particle size (D50) of 0.94 mm. 15 g of $Al(OH)_3$ were subjected to heat treatment at 1200°C for one hour. After one hour, the material was immersed in distilled water, with the aim of applying a thermal shock, shock which helps to obtain a better posity. Therefore, after heat treatment, it was found that the Al_2O_3 particles are more porous and smaller in size <10 μm. This fact allows us to state that Al_2O_3 has increased its specific surface, therefore implicitly its adsorption capacity. So:

- AgNPs on the Al_2O_3 surface are observed to have photocatalytic activity in the presence of light, due to the plasmonic resonance of AgNPs. Collective oscillations of the electrons, due to the surface plasmon resonance effect, from the outer band to a higher energy state result in the interaction with oxygen and the generation of free radicals. Additionally, the 'gaps' created due to electronic excitation accept an electron from the adsorbed dye and, therefore, the dye is reduced. Furthermore, the process is followed by oxidation of the dye by other free radicals generated during the oxidation process.
- The photochemical degradation process was found to proceed with good yields, demonstrating that this dye can be removed from wastewater using Al_2O_3 – AgNPs material.

Thus, AgNPs synthesis methods have developed in the past decade in accordance with the importance of the properties and applications these particles have. In addition, AgNPs based materials represent an important class of materials with applications in fields of wide interest.

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