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Silver Nanoprismas Production Optimization by Using Fatorial Design

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Abstract: The science and technology in nanoscale have attracted considerable attention in the last years; the expected impact of thenanostructured materials can improve the quality of life. The nanoparticles are thermodynamically unstable and have a natural tendency to aggregate and growth. Therefore, the great current challenge consists precisely in the preparation of stable and monodisperse nanomaterials, with regard to both size and the form of particles, which can be manipulated, scattered, deposited upon substrates without losing their characteristics. So they can be efficiently used in technology and biomedical applications, the nanostructured materials with the Silver nanoparticles (AgNp's), should be able to remain stable for long periods, without loss of its properties, or structural modifications. This way, the search for new synthesis methods or functionalization focused on increasing the chemistry stability of nanoparticles it has become an important subject of research and study. The lack of planning it is often the cause of failure of an investigation; however, rare are the researchers who apply the statistic before making their experiments. This requires a set of observations and planning of experiments it is therefore, essential to indicate the design in which the verified hypothesis. The hypotheses are verified with the use of statistical analysis methods that depend on the manner in which the observations were obtained. Therefore, design factorial and analysis of results are linked closely and should be used in sequence in the scientific research of different areas of knowledge. Before that, the objective of this work is to perform the AgNp's synthesis applying factorial design to set a trend and control of wavelength.

Keywords: Factorial design, silver nanoprismas, Nanotechnology.

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1. Introduction

The science and technology at the nanoscale have attracted considerable attention in the last years, the expected impact of the nanostructured materials can have on improving the quality of life. The research and development in nanotechnology aimed the manipulation of structures in nanoscale, and integrate then so to form larger systems. Thus, it is expected that the advance of nanoscience stimulate exploration of new phenomena [1]. Starting from the coming inheritance of nanotechnology, the nanoparticles are defined as small object that behaves with a whole unit in terms of its transport and properties. It is classified according with the size, may or may not display related assets related to it.

Mainly, anisotropic nanoparticles of noble metals (gold and silver) are receiving a lot of attention due to new scientific applications and technologies exploring its optic properties [2]. Generally, these applications are based on three fundamental characteristics of the optical response onmetallic nanoparticles: the high sensibility to changes in the chemical local vicinage, the location of the magnetic fields of the incident radiation below the diffraction limit and the subsequent generation of nearby courses of fields of high intensity. The high sensibility to changes in chemical vicinage has been used to develop gas sensors [3] or molecules in high-performance solution, with very slow detection limits. Besides that, the coverage the particles by molecular receptors has allowed the fabrication of specific sensors for different molecules (protein and DNA) or even bacteria and viruses with superior performance of traditional detection methods (fastest speed and smaller of sample required. The localization effects have been explored, for example, to develop waveguides [4] and others optic dispositive in manometry scale [5]. The light manipulation below the diffraction limit by metallic nanostructures has been consolidated with a new area called plasmonic. One of the perspective majors of plasmonic is the interaction of manometry photonic components with the conventional macroscopic radiation sources and as the performance with interface between photonic dispositive and electronics [6]. Finally, high intensities of the nearby courses generate little intense signals with the Raman Effect, molecular fluorescence, the second harmonic generation and magnetic-optical of Kerr effect. The high intensification recently allowed the obtaining Raman Specters and fluorescence individual molecules deposited on the nanoparticles surface [7].

On the other hand, the optic properties of metallic nanoparticles has recently been explored as tool to control size and shape of particles produced by the colloid synthesis. The use of photochemical methods has allowed the production of triangular silver nanoprismas in large amounts and with controlled size by the wavelength of the incident radiation [8]. It is known the optical nanometais comportment strongly depends on the size and shape of the nanoparticles. This means that nanoparticles of the same metal may present various optic properties and lend themselves to various applications since they have different shapes and sizes. Although described in literature,the processes for obtaining of colloid metallic nanoparticles of different shapes, such as cubes, cylinders and discs, the mechanisms involved in formation and growth of these morphologies are not yet known [9].

The synthesis of noble metals attracts increasing interest due to its new and different characteristics compared to the macroscopic phase. While the size effects were intensively studied in the last decades, the dependence with the form has been farmed only recently, due to the intrinsic difficulty of producing nanostructures with well-defined forms and in large quantities. Thus, the big challenge currently consist exactly in preparing stables nanomaterials (in other words, remaining in this size range without undergoing decomposition and without aggregation and growth) and monodisperses, both with respect to size and shape of its particles, which can be handled, dispersed, deposited on substrates without losing its characteristics. So they can be efficiently utilized in technology and biomedical applications, the nanostructured materials, with the silver nanoparticles should be able to remain stable for long periods, without losing its properties, or structural modifications [10]. Thus, the search for new synthesis and functionalization methods aimed to increase the chemical stability of nanoparticles and has become an important subject of research and study on the changes in material properties become highly dependent on their size and it is the basis in which science on the nanoscale (nanoscience) is based [11].

Using experimental designs based on statistical principles the researchers can extract from system under study as much useful information, making a minimum number of experiments. For this, there are various techniques available to scientists and engineers to improve or optimize systems, processes and products. These techniques are powerful tools with which several specific objectives can be achieved.

The factorial design is an analytical strategic useful and its main application lies in screening of the most relevant variables of a particular analytical system [12]. After this screening process of the most significant variables are performed experiments that allow refinement and a better knowledge of the system under study [13]. In this context, higher education and postgraduate data analysis precisely through experimentation is an essential procedure for the understanding of chemometric tools and especially those aimed to optimization. In order to improve the synthesis of silver nanoparticles to study efficient and economically, the combined effect of several factors on a variable answer of interest, can be applied a factorial design determines which factors have significant effects on the response and, also, how the effect of a factor varies with the levels of other factors. It also allows establishing and qualifying the correlations between the different factors. Given the above, it turns out that without the use of factorial design of experiments, important interactions between factors cannot be detected and maximum optimization of the system may take more time to be achieved [14].

As proved tool factorial design has been the Response Surface Methodology (RSM) that analyzes the effects and interactions though empirical models from the modeling and analysis of problems in which variable response of interest is influenced by several independent variables or factors and whose objective is to optimize the response variable.Thus, the study aims to obtain AgNp's stable in the range of 900nm from the application of factorial design.

2. Materials and Methods

Nowadays, there are several methods to synthetize the nanoparticles in liquid phase. Though each method has specific characteristics, the colloidal synthesis, generally, is based in four components: medium, precursor, reducing agent and stabilizer. The medium is the liquid phase in which the chemical reaction will occur. The precursor is the chemical compound that will provide the material to form the particles. In the case, of metal nanoparticles, generally, uses a salt of a metal salt. In this case, the use of a reducing agent to reduce the ion transforming the metal class is required. The stabilizer also known as a binder is a molecule that covers the surface of the nanoparticles, keeping them spaced apart from each other and dispersed in the middle [15].

Initially, it is done a fixation of the independent variables from 4 reagents that will be used, as can be seen on Table 1:

Table 1 – Factors and levels used in factorial design. A = $AgNO_3$ ($mmol.L^{-1}$), B = SCT (mL), C = H_2O_2 (μL), D = $NaBH_4$ ($mmol.L^{-1}$)

Factors	Lower Level (-)	Central Point (0)	High Level (+)
A	20	25	30
B	1,0	1,25	1,50
C	50	55	60
D	60	75	90

Then, it is made the fatorial design 2^{4-1} making use of STATISTIC program. From the factorial design is made the synthesis of silver nanoprismas, according to the following levels interactions (Table 2):

Table 2- Factorial Design 2^{4-1}

Reagents/experiments	$AgNO_3$ (μL)	$Na_3C_6H_5O_7$ (mL)	H_2O_2 (μL)	$NaBH_4$ ($mmol.L^{-1}$)
1.	-	0	0	-
2.	-	0	0	+
3.	+	0	0	-
4.	+	0	0	+
5.	0	-	-	0
6.	0	+	-	0

7.	0	-	+	0
8.	0	+	+	0
9.	0	0	0	0
10.	0	0	-	+
11.	0	0	-	+
12.	0	0	+	-
13.	0	0	+	+
14.	-	-	0	0
15.	+	-	0	0
16.	-	+	0	0
17.	+	+	0	0
18.	0	0	0	0
19.	0	-	0	-
20.	0	-	0	+
21.	0	+	0	-
22.	0	+	0	+
23.	-	0	-	0
24.	+	0	-	0
25.	0	0	+	0
26.	+	0	+	0
27.	0	0	0	0

For the synthesis of AgNp's initially place it in a beaker containing 30mL distilled water leaving the same under stirring. Then add, respectively, the amounts of reactants set by factorial design shown in Table 2. In the last step of synthesis, at the time of addition of $NaBH_4$, the rotation speed of the magnetic stirrer is increased, so that, it may have to obtain the AgNp's stable and the desired morphology as set out in the literature. Which typically, a rapid reduction, with a strong reducing agent, under vigorous stirring leads to a homogeneous nucleation and, therefore, the production of nanoparticles with a relatively narrow size distribution [15]. The analysis of the samples are performed in a spectrophotometer. Initially, the sample passes blank, and after laying the analysis of interest solution programming the instrument to cover a band ranging from 300nm to 1100nm.

3. Results and Discussion

The graphic obtained by the specter of Uv – Vis in relationship with AgNp's is characterized by the presence of three absorption peeks. Which are given at different wavelengths, connected to a result of quantum confinement of such particles and are related to surface Plasmon resonance changes –the frequency at which conduction electrons oscillate in response to the alternating electric field of the incident electromagnetic radiation. This phenomenon, called surface Plasmon band, occurs when the driver's dimensions are reduced, and small nanoparticles of metals with free electrons in the conduction band such as Pt, Ag and Au, for example, suffer resonance effects between the conductors electrons and electromagnetic radiation incident [16].

The AgNp's formation was observe by spectral analysis using Uv-Vis spectroscopy method. Analysis by infrared spectroscopy observe the spectrum generated the data show in Figures 1, 2 and 3.

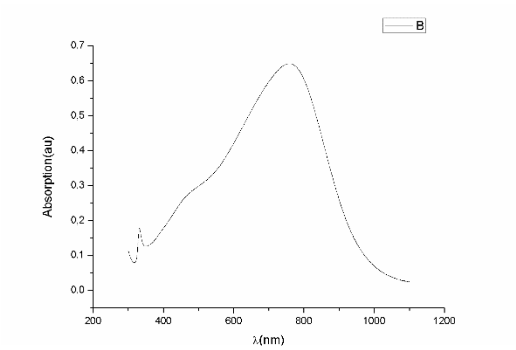

Figura 1. Uv-Vis spectra of the AgNp's

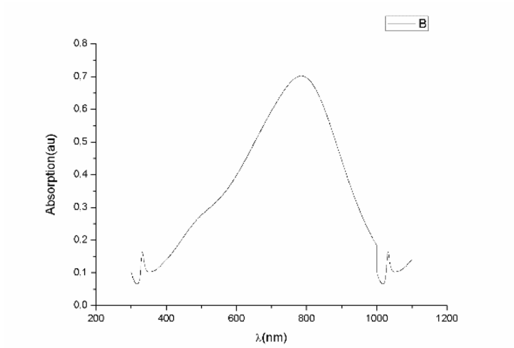

Figura 2. Uv-Vis spectra of the AgNp's

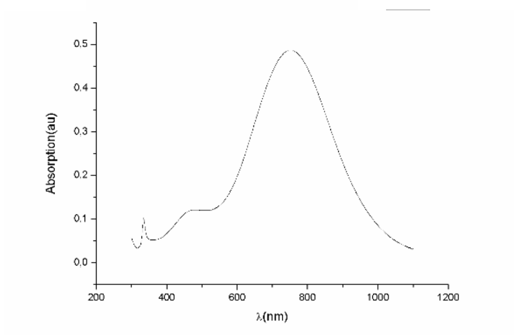

Figura 3. Uv-Vis spectra of the AgNp's

With the interaction between factors, which can be seen in Figures 1, 2 and 3, which received respectively 788.3 nm, 763.7 nm, 757.3 nm can determine the growing trend from the method response surface (SRM).

The response surface methodology is a statistical technique used for modeling and analyze problems in which the dependent variable influenced by several factors, whose objective is to optimize this response 17. The response surface techniques are very useful mathematical tools when it has interest in optimizing a process where you have the influence of various factors on a response variable, ie, response surface models it might be explored to determine great conditions to work or sensitivity of the response variable to change the levels of the factors of interest (Figure 4).

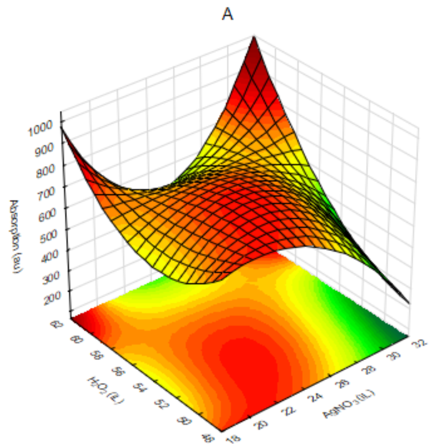

Figura 4. Superfície de resposta. software STATISTICA

The SRM confirms the results observed by examining the wavelength increase due to variation in factors A and C.

The results obtained where analyzed and evaluated their maximum wavelength band formed in relation to other results published in the literature, as with the work of SILVA J.N., which deals with AgNp's synthesis using factorial design in which there was variation oxidizing and reducing agent, keeping fixed the stabilizing agent to ensure the stabilization of the particles formed. Then it was observed the formation of AgNp's at a maximum wavelength of 579.5 nm, which did not correspond to the result estimated from the factorial design but showed that the formation of AgNp's can also be achieved by the variation of H_2O_2 and $AgNO_3$.

4. Conclusion

From the results obtained it was noticed a growing trend in the wavelength of AgNp's in 900nm objectified initially, however, the result was different than expected determined from the determination and concentrations $Na_3C_6H_5O_7$ and $NaBH_4$, reduced volume of $AgNO_3$ and increasing the volume of H_2O_2, an increase in the higher wavelength band to 900nm. With the growing trend of certain wavelength by SMR, the breaking of volume variation of $AgNO_3$ and H_2O_2 allows the application of a new experimental design and improved results.

Acknowledgments

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