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Factors That Influence Stability of TiO_2 Nanocrystals Size: Taguchi Methods

O. Giuca* and I. Grozescu**

* Polytechnic University of Timisoara, Faculty of Management in Productions and Transports, 300006, 2 Victoriei Square, Timisoara Romania, oliviagiuca@yahoo.com

** National Institute of Electrochemistry and Condensed Mater Timisoara, Plautius Andronescu 1, Timisoara, Romania.

Abstract: This paper presents an experimental study on the stability checking size of titanium dioxide nanocrystals doped with Ag. Because the titanium dioxide is not toxic and can be used as photocatalysts, is used in applications requiring human contact both directly and indirectly. Obtaining method of titanium dioxide, fast hydrothermal method, is at high pressures and temperatures, and is influenced by many factors, including: particle size, concentration or pressure applied to defects in network growth environment. The methodology used to verify the size of nanomaterials offer us control over the size, structure and their properties. The experiments were performed in accordance with the method using a Taguchi L_9 experimental plan for each experimental condition was the measured five nanocrystals. The values of model adequacy indicators shows a good correlation between experimental data and those obtained based on mathematical equations of models developed.

Keywords: nanocrystals, experiments, analysis, experimental results.

1. Introduction

Because of practical applicability, nanomaterials present special properties different from macro-scale materials, but with great prospects in terms of diversification and increased technical performance.

The same time new problems have appeared theoretical and applied technology related to design their synthesis processes because each application requires a precise series of morphostructural characteristics of nanoscale materials.

Compared with other antimicrobial agents, TiO_2 attention through good stability offered, but also because it is environmentally friendly, safe, inexpensive, nontoxic, bioactive, etc. Titanium dioxide has been studied widely in recent years and improved in several ways, one of which doping with various chemicals (metal ions, metal, or other oxides) aiming at activating radiation extending to the visible spectrum, thus allowing efficient activation of the material to sunlight.

Using nanostructured materials in practice imposes some essential characteristic for efficient use.

That nanoparticles can be highly effective in practice must have a number of characteristic such as high purity and uniform chemical composition, size of nanoparticles to register in a uniform distribution is narrow and controllable, shape and morphology of nanoparticles to be identical.

In practice it is difficult to obtain nanoparticles that meet these characteristics, so the scientific world's attention is continuous directed at finding new methods of synthesis that ensures high uniformity as their property.

The current economic circumstances global market, to improve competitiveness, organizations must provide high quality products at low prices and to meet customer requirements. This purpose they must radically change their methods of design, development methods and how technology manufacturing.

One possibility to increase efficiency and competitiveness of nanomaterials, is introducing scientific design of experiments in the methods of synthesis of nanomaterials.

On one side, you can use the Response Surface Method (RSM) and on the other Taguchi robust design. An series of special physical properties of titanium dioxide make it attractive for various practical applications, and some theoretical considerations also explain the importance and necessity of scientific effort to find ways to synthesize this material by one of the most efficient and modern methods such as hydrothermal method.

2. Experimental

It is difficult to obtain a model similar to the real, so it is important to analyze a large number of influences, but by careful planning of experiments (in order to reduce them) to take account of economic and the duration of the experiment. If the most important goal of experimental research is the mathematical modeling of factors influence the action $x_1, x_2,\ldots,x_k$ the objective function studied y of the system (object, phenomenon, process), by specifying the functional dependence:

If the most important the objective of experimental research is the mathematical modeling of action to influence factors $x_1, x_2,\ldots,x_k$ the objective function studied y on system (object, phenomenon, process), by specifying the functional dependence:

$$y=f(x_1, x_2,\ldots,x_k) \qquad (1)$$

Strategy Genichi Taguchi's approach (Figure 1), is based on minimizing parasites factors (factors - noise) factors by acting on the experimental control by finding combinations of their values so that the process to meet the functional performance and also to be robust factors - noise [11].

We believe that the "performance" represents "out" a system with one or more "inputs" and when you want a performance evaluation system should be considered in turn as "desired outputs" (the ones we want to achieve) and "undesirable outputs" (the ones we want to avoid).
The first we refer to as "signals" and the other as the "noises", by analogy to with the traditional use of two terms in the expression "The Signal / Noise (S / N)" used in electronic or optoelectronic communications sector.

Unlike traditional approaches (traditional) treating these two components separately, G. Taguchi used to assess the quality of a product or process, a synthetic measure of performance with the same name (high signal / noise) that simultaneously consider both the environment and dispersion.

Standard Taguchi matrices prove large enough to satisfy most situations that interfere in the industrial practice. Taguchi matrix symbology standard is the number of experiments (number of rows of the matrix), the number of factors and interactions (number of columns of the matrix) that the number of levels.

Degree of freedom (GDL) of a factor equals the number of comparisons needed to study its effect. This, one should select the smallest matrix to provide the desired information with the goals of the experiment. Calculate the total number of degrees of freedom and choose the appropriate standard Taguchi matrix.

To verify that the model adopted is appropriate to approximate the response surface, using ANOVA and regression analysis tests for absence of adequacy. Table 1 shows the analysis of variance for this regression model.

A suitable regression model to explain the variation of sample dependent. There are hypothesis tests for model parameters that help measure the effectiveness model. The test requires that the error term (it) to be independent and normally distributed with mean zero and s^2 version. The easiest way to see this is to plot the probability of normality for residual values.

TABLE 1. The analysis of variance for this regression model

Variance	Sum of squares	Degree of freedom	Average square	F_0
Regresion	SS_R	q	MS_R	
Error / residual values	SS_E	N – q - 1	MS_E	
Sum	SS_T	N - 1	MS_T	

where N is the number of observations and q is the number of independent variables.

If residual values represented graphically approaches a straight line, the idea of normality can be accepted. Given that the error term is the difference between observed values and those obtained by modelling (relation 2) where the normality assumption to assume that the values y_i are independent and normally distributed.

$$e_i = y_i - \hat{y}_i \qquad (2)$$

For the synthesis of TiO_2 nanocrystals doped with Ag by Fast hydrothermal method (FH), was applied Taguchi robust design method using an experimental plan L_9 (9 experiments), who studied the effect of four factors at three levels, variable output quality characteristic of TiO_2 nanocrystals (nano size) and the input variables are taken into account four factors: dopant concentration, duration of autoclaving, temperature autoclave and microwave power.

Hydrothermal method of crystal growth, mono or polycrystalline (the structure) and macro-, micro-or nanocrystalline (in size) is already old and venerable tradition. Many valuable methods and techniques were developed over the years for single crystal and polycrystalline growth of the various types of quartz to sapphire and ruby from protected to piezoelectric materials.

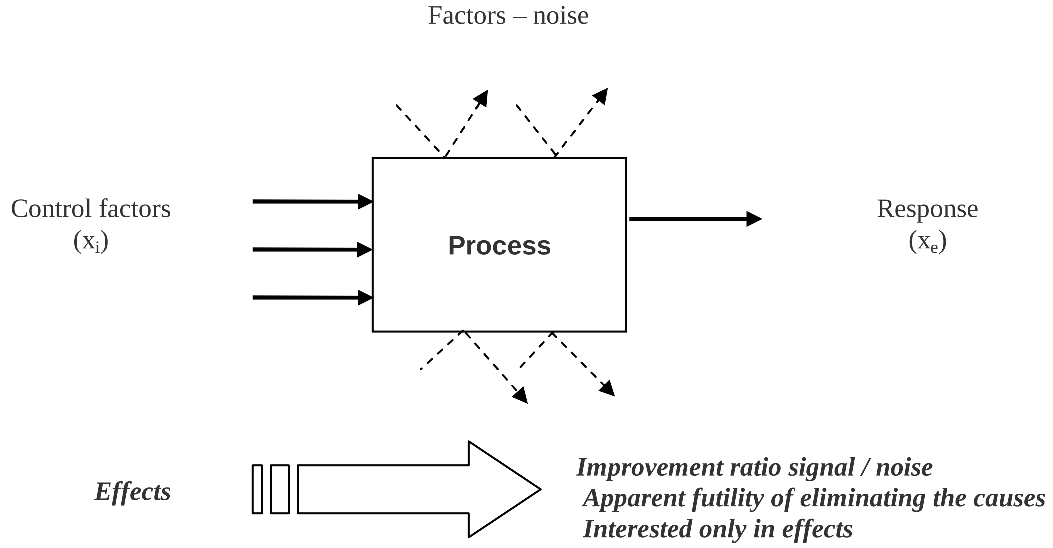

Figure 1. G. Taguchi's strategy to minimize the impact factor - noise

In recent years, a great impetus to the study takes submicron-sized crystalline materials, so-called nanocrystals (1-100) nm. Small size, adding new properties nanodimensional crystalline substance in relation to the macroscopic, are indispensable elements of these materials in physical and chemical catalysts, photovoltaic cells, fuel cells, etc.

In general, hydrothermal synthesis of nanocrystalline materials is the introduction of a closed container resistant to temperature and pressure (called an autoclave) precursors and their heating, temperature and pressure until heating leads to crystallization of substances in solution. Judicious control of temperature, pressure, process duration, the degree of filling of the autoclave, the precursor concentration, will produce nanocrystals with desired sizes and types of crystallization [1].

Obtaining the TiO_2 is usually done in small type Morey autoclaves provided with Teflon coating. Hydrothermal synthesis of TiO_2 particles is usually done at temperatures below 200^0C and pressures below 100 kbarr. These physical parameters that make using simple model autoclaves provided with a teflon coating [10].

Hydrothermal synthesis of TiO_2 nanocristalitelor generally starts from amorphous gels in the presence of pure distilled water or various mineralized as hydroxides, chlorides and fluorides of alkali metals at different pH values.[8] As precursors to titanium alkoxide can be used both compounds [9] and non alkoxide [12] in hydrothermal synthesis of TiO_2 in acidic or alkaline depending on the desired morphostructural characteristics [6]. Hydrothermal method was used to obtain TiO_2 layers deposited on different surfaces of Ti and its alloys [5, 11, 17].

Into a beaker were added titanium izopropoxid double distilled water and stirring continuously. Silver nitrate was added as a doping solution, the pH adjustment will be done with nitric acid solution Heat treatment was performed in thermostatic bath filled with silicone oil. Be noted that before the introduction of the oil bath thermostatted autoclave, it was previously heated to processing temperature.

Preliminary experiments were performed, samples synthesized Ag doped TiO_2 and control factors are presented in Table 2.

TABLE 2. Parameters of synthesis of Ag-doped TiO_2 samples, synthesized by fast hydrothermal method

Sample	Ag concentration [%]	Time autoclaving [min.]	Autoclaving temperature [^{0}C]
$P1_{FH}$ (15-150)	2	15	150
$P2_{FH}$ (30-150)	2	30	
$P3_{FH}$ (15-200)	2	15	200
$P4_{FH}$ (30-200)	2	30	
$P5_{FH}$ (15-150)	3	15	150
$P6_{FH}$ (30-150)	3	30	
$P7_{FH}$ (15-200)	3	15	200
$P8_{FH}$ (30-200)	3	30	

After autoclaving, the obtained material was filtered and washed with distilled water in order to remove secondary reaction compounds. Verification of Ag ions presence into washing solution has been done by using calcium chloride. It has not been observed any AgCl precipitate, meaning that all Ag quantity has been consumed in reaction. The conclusion drawn from these results is that structure and crystalline form of Ag doped TiO_2 nanoparticles sytnhesized through MF are, in first instance, influenced by dopant quantity and thermal treatment.

In table 3 are presented the average dimensions of nanoparticles, calculated with Scherrer equation (relation 3).

$$D = \frac{K \bullet \lambda}{\beta \bullet \cos\theta} \qquad (3)$$

where:

λ – wave length of X radiation (λ = 0.15406 nm), K – Scherrer constant (K = 0.89), θ – diffraction angle, β – width at half height for different peaks from diffractogram.

TABLE 3. Average dimensions of Ag doped TiO2 nanoparticles synthesized through MF

Material type	Nanoparticles dimension (nm)
$P1_{FH}$ (15-150)	4,85
$P5_{FH}$ (15-200)	5,03

The results obtained allowed to conclude that the structure and crystalline forms of TiO_2 nanocrystals synthesized by hydrothermal method are influenced by the amount of fast dopant, and heat treatment.

3. Results and Discussion

Performance of the experiments to check the size stability of Ag-doped TiO_2 nanocrystals in the fast hydrothermal synthesis, to apply Taguchi method, the objective being to determine the optimal combination of factors in order to achieve a target of 5 nm with a tolerance of ± 0 , 2 nm size nanocrystals

We chose a standard Taguchi L_9 matrix (4 factors at 3 levels each). Table 4 presents levels of factors and measurement results for the 9 experiments. Note that for each experimental condition were measured every 5 nanocrystals.

The theory analyzes the main effects of factors on the size of nanoparticles. Table 5 shows the estimated main effects of factors, each standard deviation which measures the effect of sampling error. Standard deviation is based on a total error of 4 degrees of freedom, for a perfectly orthogonal plan, all individual values of the factors (V.I.F.) is to 1, and Figure 2 shows the effects in descending order, the vertical line determines which effects are significant in terms statistically (Standardized Pareto Diagram for factor effect).

TABLE 4. Factor levels and experimental results under standard Taguchi L_9 matrix

Exp.	Concentation dopant	Time autoclaving	Autoclaving temperature	Microwave oven power	Dimension
	%	min.	°C	W	nm
1	2	15	150	800	4.82
2	2	30	200	1000	4.9
3	2	45	250	1200	5.13
4	3	15	200	1200	5.01
5	3	30	250	800	4.88
6	3	45	150	1000	4.81
7	4	15	250	1000	5.02
8	4	30	150	1200	5.04
9	4	45	200	800	5.04

TABLE 5. Estimated effects of nanoparticle size

Effect	Estimate	Standard deviation	V.I.F.
Media	4.96111	0.0301795	
A: Concentration dopant	0.0833333	0.0739244	1.0
B: Time autoclaving	0.0433333	0.0739244	1.0
C: Autoclaving temperature	0.12	0.0739244	1.0
D: Microwave power	0.146667	0.0739244	1.0

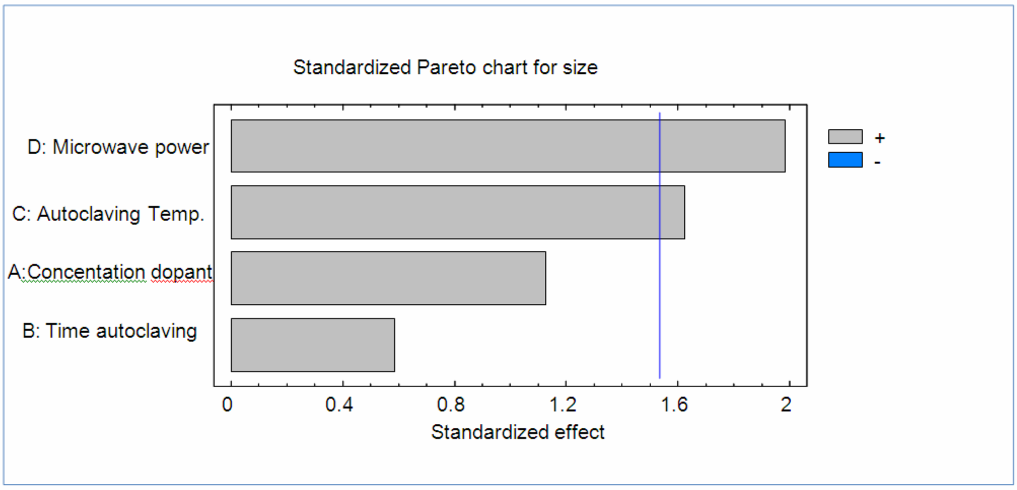

Figure 2. Chart Pareto of standardized effect size factors

TABLE 6. Table ANOVA (plan experiences L_9)

Source	Sum of squares	Gdl	Average square	Report F	Values p
A: Concentration dopant	0.0104167	1	0.0104167	1.27	0.3227
B: Time autoclaving	0.00281667	1	0.00281667	0.34	0.5892
C: Autoclaving temperature	0.0216	1	0.0216	2.64	0.1799
D: Microwave power	0.0322667	1	0.0322667	3.94	0.1183
Total error	0.0327889	4	0.00819722		
Total (correction)	0.0998889	8			

In Table 6 presents the ANOVA table that contains the values "p" can be used to test the statistical significance of each effect. ANOVA table partitions the variability in size of nanoparticles in separate components for each effect. Be tested statistical significance of each effect by comparing the mean square error of approximation of experimental. In this case two effects have values of "p" less than 0.2 indicating that they are significantly different from zero; have 80% significance level, with the possibility of correlations at a significance level of 20%. Results indicate that the factor model explains 67.1746% of the variability associated with size. The standard error of the estimate shows that the standard deviation of residuals is 0.0905385.

In relation (4) is presented regression equation, in the order I model associated to experiences plan L_9, and the values of variables are specified in the original units.

$$Size_{nanoparticles}[nm] = 4.18611 + 0.41667 \cdot Concentration_{dopant}[\%] + 0.00144444 \cdot Time_{autoclaving}[\min] + 0.0012 \cdot Temperature_{autoclaving}[^{\circ}C] + 0.000366667 \cdot Power_{oven}[W] \quad (4)$$

Table 7 presents informations on the size of nanoparticles generated on the order I model associated to experiences plan L_9, measured values, their predicted values based on the model predicted values for average and their limits with a probability of 95% (signification of 5%).

For maintenance of response (nanoparticle size) to 5 nm, table 8 presents the optimized combination of factors levels. The calculated values presented in the table are those for optimal condition. It can be observed that the levels of factors at optimum condition are consistent with ones presented in average effects and interactions of factors previously presented.

Figures 3 to 14 are estimated response surfaces, contours of estimated response surface size nanocrystals, depending on factors. Note that the surface height is the forecast for the size of nanoparticles on a space determined by two factors, the remaining two factors are maintained at their average values.

TABLE 7. The size of nanoparticles generated on the order I model associated to experiences plan L_9

No.	Values measured	Values predicted	Lower limits environments predicted P=95%	Upper limit environments predicted P=95%
1	4.82	4.76444	4.54275	4.98614
2	4.9	4.91944	4.78696	5.05193
3	5.13	5.07444	4.85275	5.29614
4	5.01	5.01278	4.84519	5.18036
5	4.88	4.94778	4.78019	5.11536
6	4.81	4.92278	4.75519	5.09036
7	5.02	5.04111	4.8446	5.23762
8	5.04	5.01611	4.8196	5.21262
9	5.04	4.95111	4.7546	5.14762

TABLE 8. Optimized combination of factors levels plan L_9

Factors	Min	Max	Optimum	Optimal value
Concentration dopant	2.0	4.0	2.96591	5
Time autoclaving	15.0	45.0	30.0915	
Auticlaving temperature	150.0	250.0	212.838	
Microwave power	800.0	1200.0	1067.56	

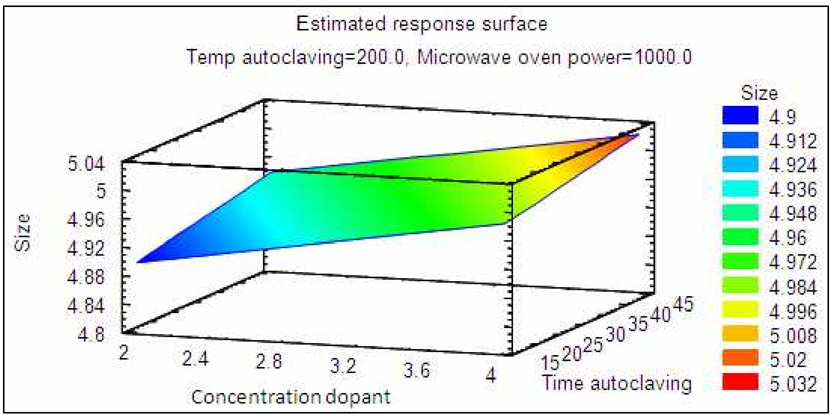

Figure 3. Estimated response surface (concentration dopant – time autoclaving)

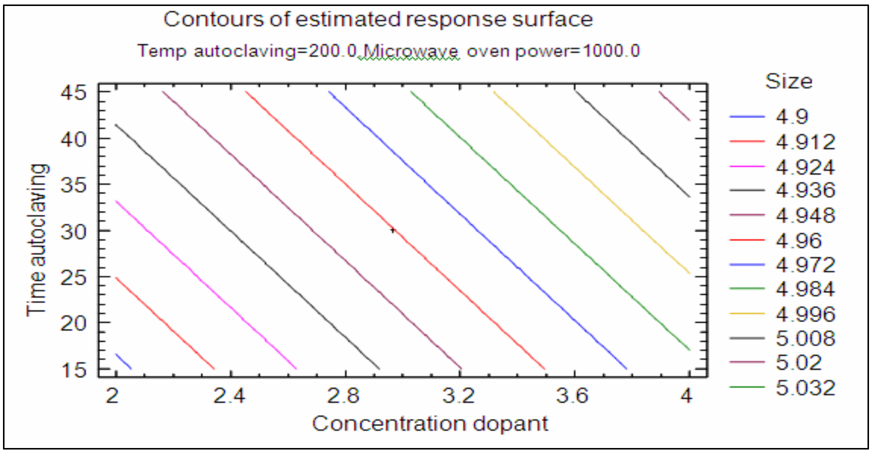

Figure 4. Contours of estimated response surface (concentration dopant – time autoclaving)

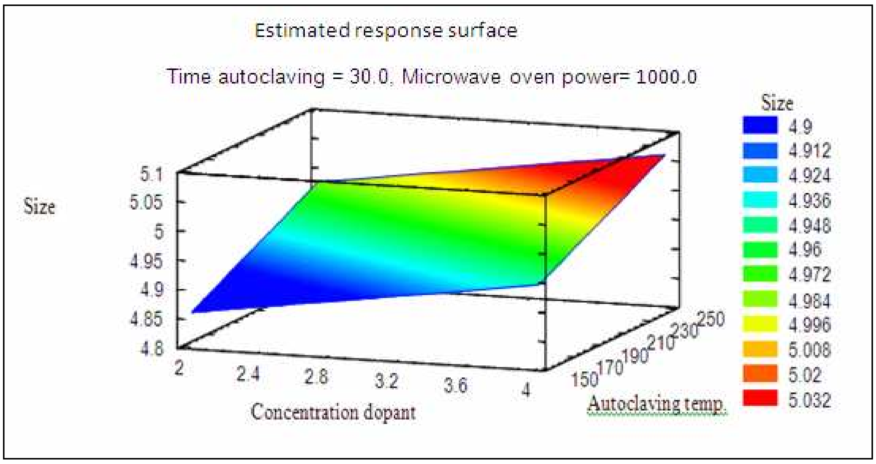

Figure 5. Estimated response surface (concentration dopant – autoclaving temperature)

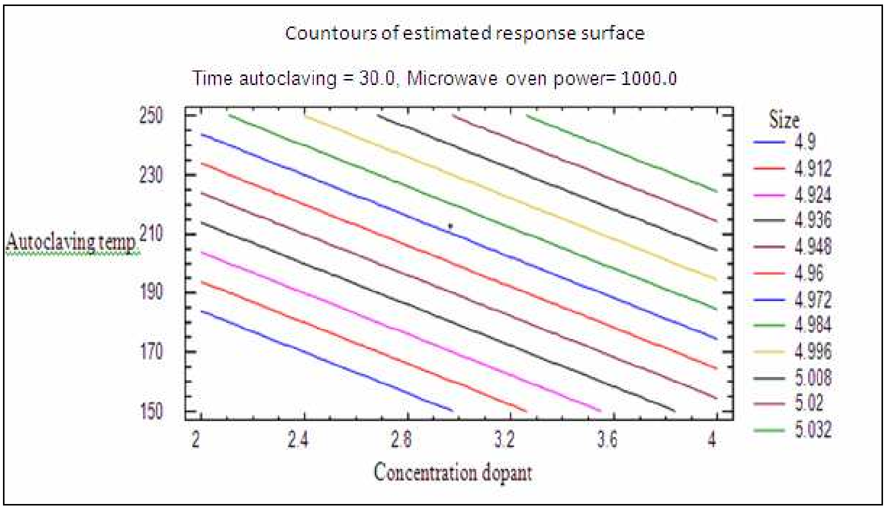

Figure 6. Contours of estimated response surface (concentration dopant – autoclaving temperature)

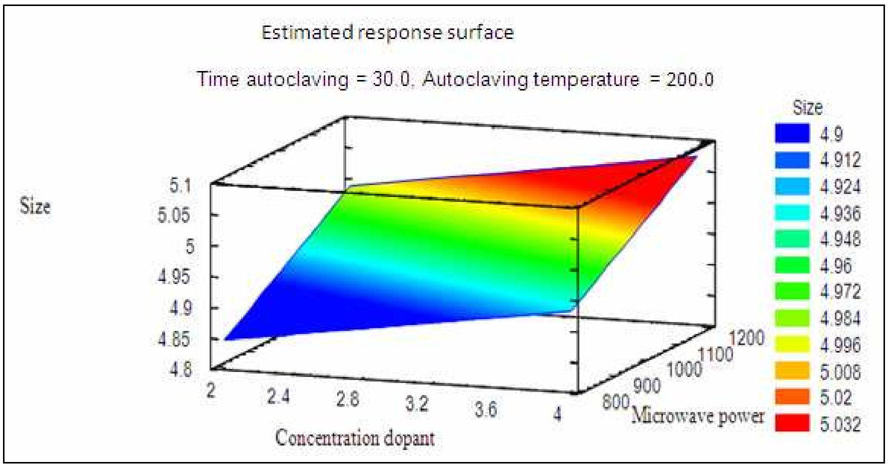

Figure 7. Estimated response surface (concentration dopant – microwave oven power)

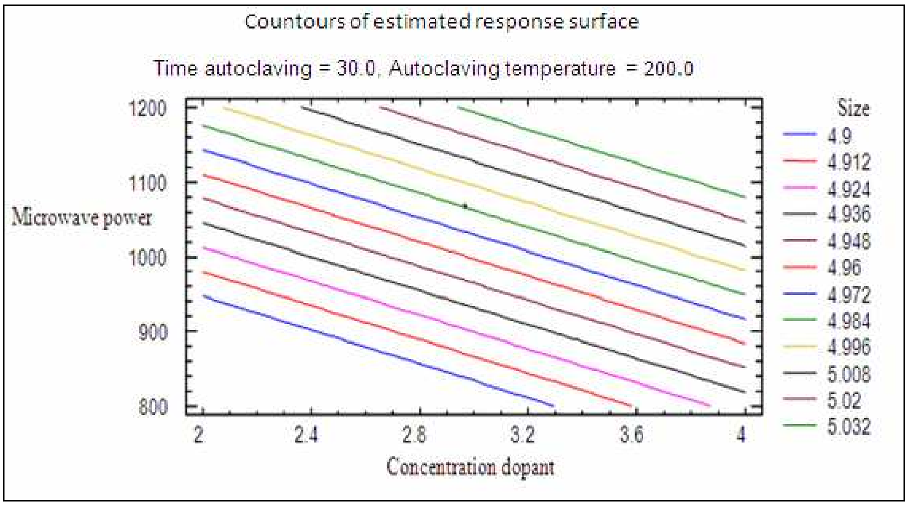

Figure 8. Contours of estimated response surface (concentration dopant – microwave oven power)

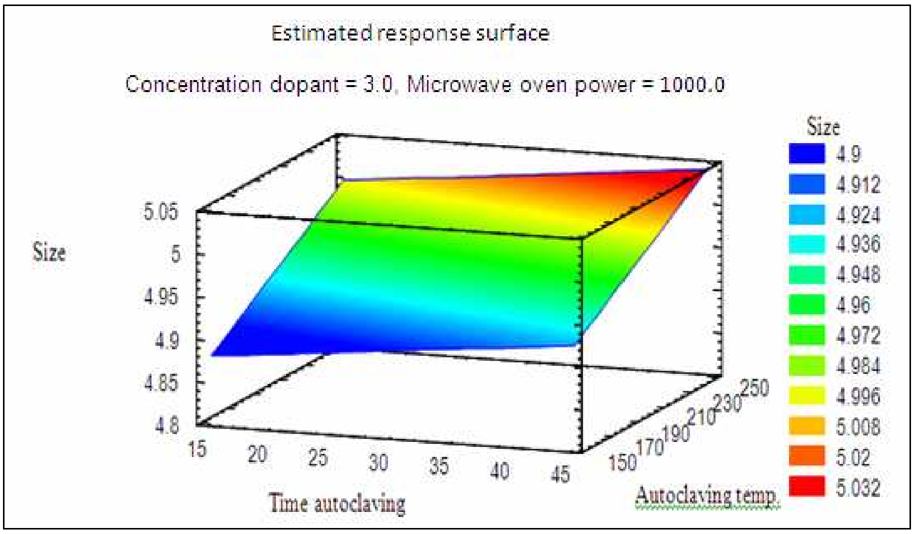

Figure 9. Estimated response surface (time autoclaving –autoclaving temperature)

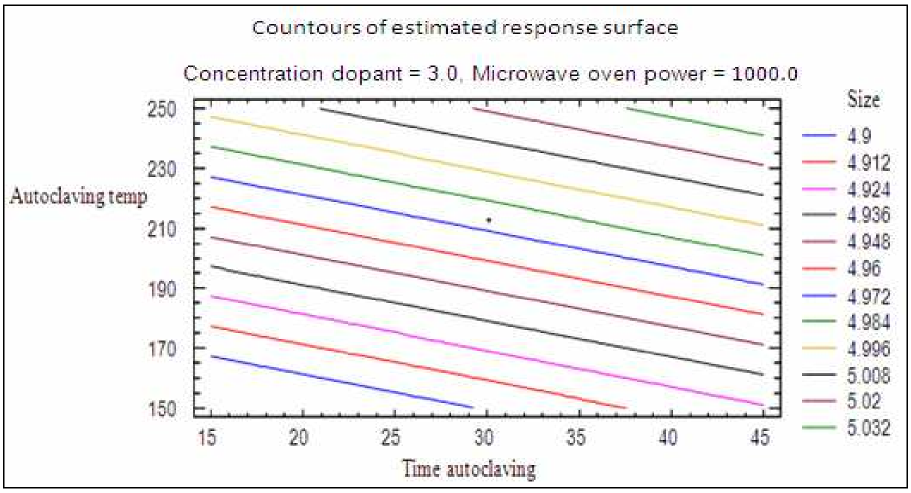

Figure 10. Contours of estimated response surface (time autoclaving – autoclaving temperature)

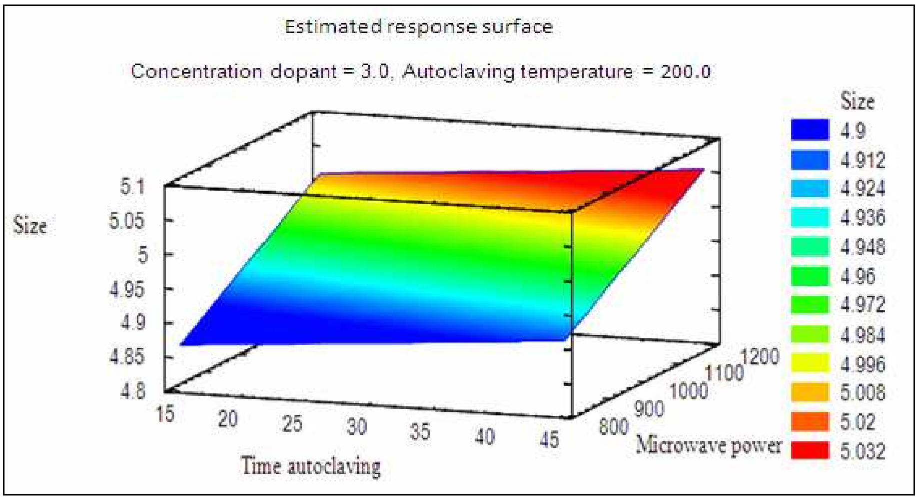

Figure 11. Estimated response surface (time autoclaving – microwave oven power)

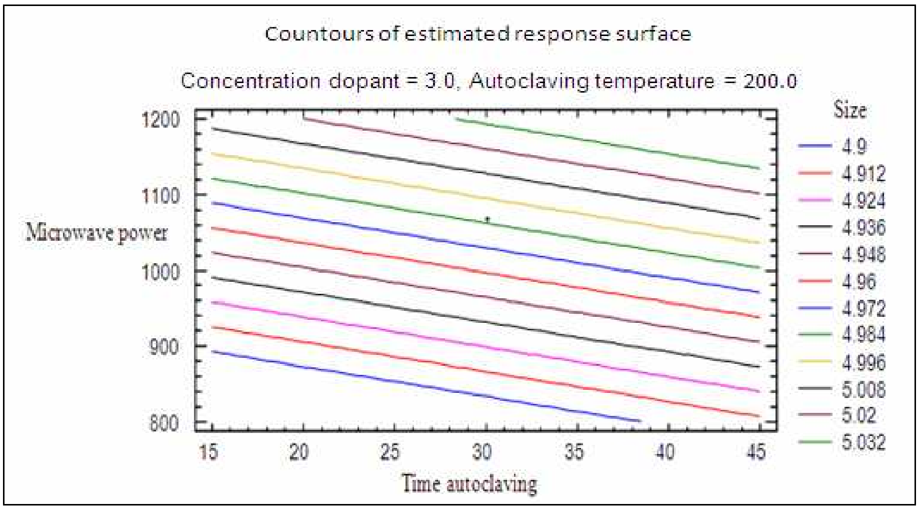

Figure 12. Contours of estimated response surface (time autoclaving – microwave oven power)

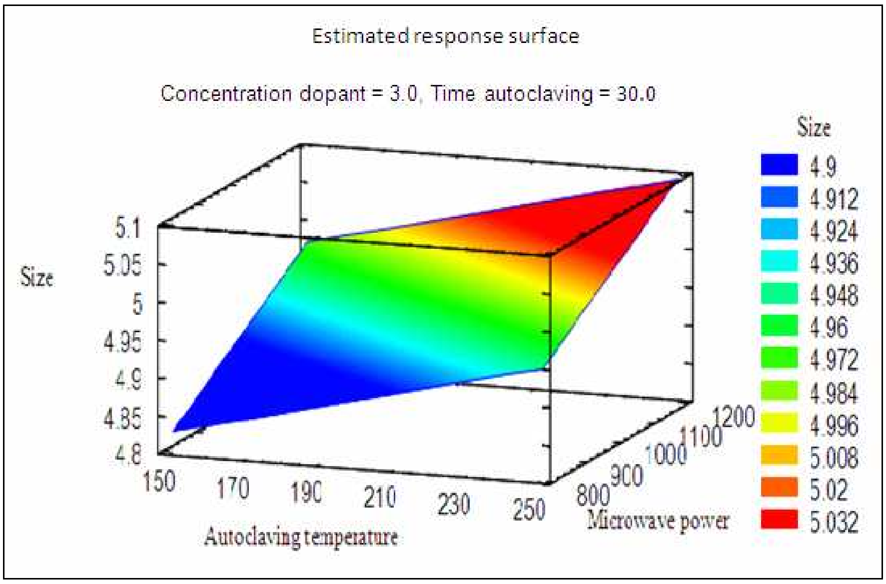

Figure 13. Estimated response surface (autoclaving temperature – microwave oven power)

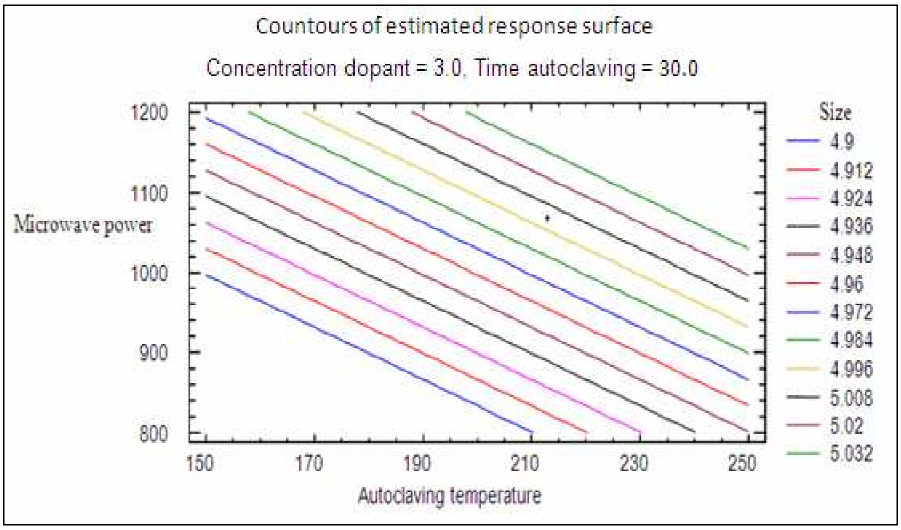

Figure 14. Contours of estimated response surface (autoclaving temperature – microwave power)

4. Conclusions

To obtain Ag doped TiO_2 nanocrystals under fast hydrothermal synthesis method was applied through the plan of experiments Taguchi L_9, obtaining a linear regression equation between the output variable (nanoparticle size) and factors, and model-order experiences associated plan 67.1746% of the variability in explaining L_9 nanoparticle size (Table 4)

If you want an accurate modelling of the system (4 factors at 3 levels) will have to take into account the interactions between factors, but if we only achieve the target value for the size of nanoparticles when first-order model can be considered satisfactory.

By programming scientific laboratory experiments, this fell substantially which resulted to a reduction of production costs and dispersion dimensional nanomaterials of desired quality, to reduce the amount of synthetic substance used and thus reduce energy consumption in line requirements and international standards of protection and natural conservation.

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