MATHEMATICAL MODELING AND SIMULATION OF COPPER DIOXIDE NANOPARTITCLES MORPHOLOGY

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Abstract. A drawback in the synthesis of copper dioxide nanoparticles is that because it operates at a control nanoscale morphology and size is difficult to handle, as for example a small increase or decrease in temperature or concentration; It generates big changes. Therefore, a mathematical model from the reaction kinetics taking place in the synthesis is proposed. This mathematical model is from type reaction-diffusion. The control parameters give an idea of model parameters to be varied to obtain a morphology and specific particle size. These control parameters are given by the pH and the initial concentration of the reactants employed in the synthesis copper dioxide nanoparticles. The analysis of linear stability of reaction-diffusion model is realized and fullfil the diffusion-driven instability.

Keywords: Mathematical model, Turing instability, nonlinear chemical, copper nanoparticles.

Introduction.

Metal nanoparticles are of great interest because they have optical, electronic, catalytic, magnetic or antimicrobial properties that differ significantly from the properties of metals on a larger scale [1]. Nanomaterials can be obtained with different particle size and morphology (spheres, tubes, wires, etc.), which is unknown as it relates to chemical synthesis parameters. Among the metals most used for synthesis of metallic nanoparticles are Gold, Silver and Copper, the latter being the least explored in this area, but with characteristics and properties even superior to the metals already mentioned; Such as its electrical conductivity, low price, stability at high frequencies and mainly that Mexico is the 4th place in the world to obtain this metal [2].

Advances in recent decades in nonlinear science, which has recently emerged as a metacensity that ranges from physics to mathematics; Through biology, chemistry, and an extensive field etc., have revealed that most obey the same laws [3].

Thus, deterministic systems have become a potentially useful tool for the study of space-time structures, which are generally focused from a mathematical point by non-linear equations in partial derivatives, such as the Navier-Stokes equations for fluid or diffusion-reaction systems to describe a large number of both chemical and biological systems [4].

For this reason, the aim of this work is to obtain the size and morphology of nanoparticles of copper oxide by means of computer simulation, in order to obtain the main parameters that must be varied to define specific sizes and morphologies. Later they will be compared with those obtained experimentally in other works; Proposing with this a simple and quick way of synthesizing them, which will save time, money and effort.

Mathematical Model.

Out-of-equilibrium systems are described in a mathematical way by non-linear differential equations, which gives us the space-time evolution of the dynamic variables. For most of the studied chemical systems it is assumed that the only spatial coupling is due to linear diffusion, so that it is governed by reaction-diffusion equations [5]. Therefore, the following reaction mechanism is proposed, which is obtained from the synthesis of copper nanoparticles [6]:

$$Cu(CH3COO)_2 \rightarrow Cu^{+2} + 2CH_3COO^{-1}$$
$$NaOH \rightarrow Na^{+1} + OH^{-1}$$
$$Cu^{+2} + 2OH^{-1} \rightarrow Cu(OH)2$$
$$Cu(OH)2 + C_6H_8O_6 \rightarrow Cu^{+2} + 2H_2O + C_6H6O_6^{-2}$$
$$2Cu^{+2} + C_6H_6O_6^{-2} + H_2O \rightarrow Cu_2O + C_6H_6O_6 + 2H^{+1.}$$

From this mechanism, the following variables and constants belonging to the synthesis are proposed:

$x= Cu^{+2}$ $y= C_6H_6O_6^{-2}$

$a=Cu(CH_3COO)2$ $b=NaOH$ $c=C_6H_8O_6$

By replacing these variables and constants in the proposed reaction mechanism, we obtain that:

$$a \rightarrow x + 2CH_3COO^{-1}$$
$$b \rightarrow Na^{+1} + OH^{-1}$$
$$x + 2OH^{-1} \rightarrow Cu(OH)2$$
$$Cu(OH)2 + c \rightarrow x + 2H_2O + y$$
$$2x+y+H_2O \rightarrow Cu_2O+C_6H_6O_6 +2H^{+1}$$

And of this reduced reaction mechanism, it is easy to obtain the reaction rates as:

$V_1 = k_1 [a]$
$V_2 = k_2 [b]$
$V_3 = k_3 [x][OH^{-1}]^2$
$V_4=k_4c[Cu(OH)_2] = k_4k_3xc[OH^{-1}]^2$
$V_5 = k_5 [x]^2 [y][H_2O]$

And by applying to the reduced reaction mechanism the mass action law and substituting the reaction rates obtained above, the following diffusion reaction system is obtained:

$$\frac{d[x]}{dt} = k_1[a] - k_3[x][OH^{-1}]^2 + k_3k_4[x][OH^{-1}]^2 - k_5[x]^2[y][H_2O],$$

(1)

$$\frac{d[y]}{dt} = k_3k_4[c][x][OH^{-1}]^2 - k_5[x]^2[y][H_2O].$$

In order to standardize variables, the following changes of variables are proposed:

$$X = \propto[x] \quad ; \quad Y = \beta[y] \quad ; \quad T = \tau t \quad ; \quad A = \delta[a] \quad ; \quad B = \epsilon[b] \quad ; \quad C = \sigma[c].$$

Using these variables are replaced in the respective nonlinear ordinary differential equations, by convenience dividing the equations between [OH^{-1}] and realizing an algebraic procedure in the new equations we can clear the adimencional variables in terms of the constants of speed of which they are It follows that:

$k_1 = \delta$; $\sigma = \frac{k_3k_4}{\sqrt[3]{k_5}}$; $\beta = \sqrt[3]{k_5} = \alpha$; $\tau = [OH^{-1}] \propto$, $[OH^{-1}] = \frac{f}{h}$donde 10^{-14} =f y [H^{+1}]= h.

Finally, substituting these definitions into equations (1) and imposing the continuity equation on these resulting kinetic equations, we obtain that:

$$\frac{\partial X}{\partial T} = \frac{h}{f}A - \frac{f}{h}(1 - C)X - hX^2Y + D_X\nabla^2X,$$

(2)

$$\frac{\partial Y}{\partial T} = \frac{f}{h}CX - hX^2Y + D_Y\nabla^2Y.$$

Results.

To obtain the computational simulation, we obtain the global reaction mechanism and the rate constants of the synthesis of copper oxide nanoparticles. Subsequently, variables were assigned to the chemical species, which are indispensable for the formation of nanostructures. The next step is to analyze the space-time evolution of the mathematical model, which will be solved in three dimensions by means of computational software, thus obtaining the type of instability of our systems; Which is directly related to the formation of the morphology of nanoparticles.

A) Lineal stability analysis: To obtain these results, we follow the analysis method proposed in the references [7-9]:

1 Obtaining fixed points: By definition of equilibrium points or fixed points(A_0, C_0) [7], the which fullfil, the following conditions of the equations (2): $\nabla^2X = 0, \nabla^2Y = 0, \frac{\partial X}{\partial T} = 0$and $\frac{\partial Y}{\partial T} = 0$ Substituting the last equations in (2), we get:

$$R(X_0, Y_0) = \frac{h}{f}A - \frac{f}{h}(1 - C)X_0 - hX_0^2Y_0 = 0, \tag{3}$$

$$M(X_0, y_0) = \frac{f}{h}CX_0 - hX_0^2Y_0 = 0,$$

which can be solved to obtain: $X_0 = \frac{h^2}{f^2}A, Y_0 = \frac{f^3C}{h^4A}$.The graphs of this fixed point shows a subcritical bifurcation, takes A as the variable in the first equation and C in the second equation.

2. Obtaining the Jacobian: Following with the linear stabillity analysis, is proposed a solution in form of a small disturbance arround fixed points (A_0, C_0) such that: $\Phi = A_0 + \Phi_0 exp(\Lambda t - i\vec{k}\cdot\vec{r}), \Psi = C_0 + \Psi_0 exp(\Lambda t - i\vec{k}\cdot\vec{r})$. Substituting this solution in the equations (2), disregarding terms of order greater than the quadratic and after of simplifying algebraic terms, is obtained that:

$$\begin{pmatrix}\Lambda & 0\\ 0 & \Lambda\end{pmatrix}\begin{pmatrix}\Phi\\ \Psi\end{pmatrix} = J(X_0, Y_0)\begin{pmatrix}\Phi\\ \Psi\end{pmatrix} - k^2\begin{pmatrix}D_X & 0\\ 0 & D_Y\end{pmatrix}\begin{pmatrix}\Phi\\ \Psi\end{pmatrix} \tag{4}$$

where $J(X_0, Y_0) = \begin{pmatrix}R_x & R_y\\ M_x & M_y\end{pmatrix} = \begin{pmatrix}\frac{f}{h}(C-1) - 2hX_0Y_0 & -hX_0^2\\ \frac{f}{h}C - 2hX_0Y_0 & -hX_0^2\end{pmatrix}\begin{pmatrix}\Phi\\ \Psi\end{pmatrix}$ where *R*, *M* fulfill the equation (3) and $R_x, M_y$are their partial derivatives, respectively.

3. Obtaining the trace and the determinant of the Jacobian: Tr$[J(X_0, Y_0)]$, $\| J(X_0, Y_0) \|$ are the trace and the deterinant of jacobian$J(X_0, Y_0)$respectively, which are obtained substituting the fixed points, the approximation $\frac{f}{h} \approx 1$ and the method for foundk^2which has been follow this procedure described in [10]. And hence here:

$$\text{Tr}[J(A, C)] = \frac{\sigma - 1}{2}\left(hA^2 - \frac{1+C}{\sigma}\right), \tag{5}$$

$$\| J(A, C) \| = \left(fA^2 - \frac{(1 + C + \sigma hA^2)^2}{4\sigma}\right)$$

where $\sigma = D_X/D_Y$.

4. Obtaining eigenvalues: substituing $J(X_0, Y_0)$ in the equation (4) and solving, the determinant and its eigenvlues $\Lambda(\varphi_0, \psi_0, k^2)$ are obtained, which take the form:

$$\Lambda(X_0, Y_0, k^2) = Tr(X_0, Y_0, k^2) \pm \sqrt{[Tr(X_0, Y_0, k^2)]^2 - \| J(X_0, Y_0, k^2) \|}, \quad (6)$$

where $\mathrm{Tr}[J(X_0, Y_0, k^2)] = \mathrm{Tr}[J(X_0, Y_0)] - (D_X + D_Y)k^2$, $\| J(X_0, Y_0, k^2) \| = \| J(X_0, Y_0) \| + (M_Y D_X + R_X D_Y)k^2 + D_X D_Y k^4$, with $\mathrm{Tr}[J(X_0, Y_0)]$ and $\| J(X_0, Y_0) \|$ fulfill the quations (5), when the fixed points are replaced with the approximation $\frac{f}{h} \approx 1$and later of found k^2in terms of the constants *A*, *C*. The results of eigenvalues evaluation given for the equation (6) are showed in the Fig. 1 a).

B) Numerical Solution: In this section with the aim of consider the spatial behavior in the nonlinear partial differential equations, is need to solve the equations (2) numerically. This system of equations are solved using the discretization of the laplacian method, which has been follow this procedure for the temporal integration described in [10].

A seed cube of 128 side nodes is taken as the initial condition, when $A = 0.00023, C = 0.00072, pH = 9, \sigma = 0.01$ at room temperature becomes a sphere, which is in agreement with Yakui et al. [6], where it is observed that from a cubic morphology, it is nucleating until obtaining a completely spherical morphology, as can be seen In Fig. 1 (b). These control parameters are obtained from the experimental values of the chemical synthesis of copper nanoparticles [6].

Therefore, maintaining a constant pH, it is necessary that the model reproduces at least three types of morphologies: cubes, pseudocubes and spheres. The transitions between these morphologies are determined by diffusion, since if the diffusion is minimal $\sigma < 0.01$, then depending on the shape of the seed, this will influence the morphology at the moment of the nucleation mechanism. In this state the dynamics behave as diffusion-driven or Turing-type instability [11].

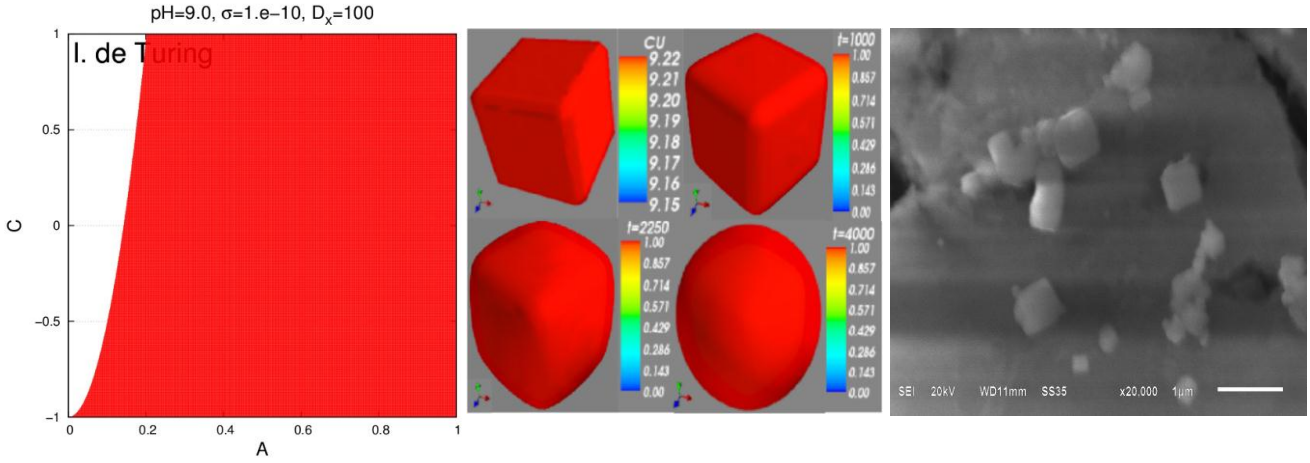

Figure 1 – Left imagen: phase space of Turing, central imagen: spatio-temporal evolution of equations (4), and right imagen: SEM of synthesis chemical of cupper nanoparticles of 50 mn of large approximately

Conclusion.

We find that indeed our proposed mathematical model reproduces the morphologies obtained in an experimental way by simulating computational simulation. The morphology depends on the shape of the seed (initial conditions) that serves to initiate the nucleation process, whereas the growth is given by the kinetics of the reaction, as well as the diffusion process. This has profound implications for generating nanostructured materials, which can be used as bactericides.

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