FULL PAPER

Study of Silver Ions Diffusion into TiO₂NT Using Finite Elements Method

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Abstract:

The purpose of this paper is to study the diffusion of silver ions, Ag+, into TiO2 nanotubes, using Fick's second law. The mathematical simulations were carried out using the finite element method to solve this partial differential equation. A single nanotube, immersed in an aqueous solution containing Ag+ ions, composes the physical two-dimensional model. The most relevant results show that the system final concentration can be calculated in the function of solution initial concentration, of solution volume and nanotube volume. The equation obtained can be generalized to the study of diffusion for other ions in aqueous solution through nanotubular structured materials, because the equation does not take into account the diffusion coefficient of the ions. The height of nanotube is exponentially proportional to the equilibrium time, proving the relation of height with the diffusion course. On the other hand, the diameter of nanotube does not have a significant relationship with the equilibrium time. These results indicate that for ions incorporation into materials, with nanotubular structure, it should prioritize experimental conditions that favor the vertical growth of the nanotubes.

Keywords: diffusion; finite elements method; TiO₂ nanotubes

1. Introduction

The application of titanium and its alloys is extensively studied in orthopedics and orthodontics in the use as bone and dental implants [1-5]. Among the most important characteristics of biomaterials, for this application, are the biocompatibility and resistance to corrosion [6], guaranteed by the formation of a chemically inert layer of titanium dioxide on the metal surface [7]. In this context, the use of implants with nanotubular structures, such as TiO₂NT, allows the improvement of adhesion of matrix proteins, which have structures in the nanometer scale, contributing to the osseointegration process [8].

The silver decoration of biomaterials aims to reduce, eliminate or prevent bacterial colonization and infection [9]. Materials decorated and doped with silver naturally release Ag⁺, known by microbial growth inhibition [10]. Knowing the variables that influence the incorporation of ions into a nanotubular structure can bring great

advances to the area of materials surface modification. Before starting an experimental methodology, a theoretical study can bring relevant information and reduce the experimental effort.

The diffusion of metallic cations into nanotubes can be studied by computer simulation using a versatile method, such as the finite element method (FEM). This method is based on the transformation of partial differential equations (PDEs) into algebraic equations [9,10] and can be applied to stationary and transient problems, in linear or nonlinear regions for a, one, two and three-dimensional domains [11]. That way, the use of the FEM, using a software, allows correlating the concentration distributions with the desired geometry.

The diffusion simulation using the finite element method has already been used for several purposes. Rahman *et al*. [13] used the method to study the migration of chlorides into concrete, Cl⁻ ions are known by damage building structures, O'Malley *et al.* [14] studied the

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efficiency of different geometries for finite elements in the calculation of neutron diffusion and Krishnamurthy *et al.* [15] evaluated the diffusion of oxygen in cationic structures. Thus, in this work the diffusion of silver ions into nanotubular structures will be studied, utilizing Fick's second law, using the finite element method. To reduce the complexity of the problem the oxide film will consist only of a nanotube belonging to a two-dimensional model. The thickness of the oxide film, the nanotube diameter and the size of the ion supply phase will be investigated.

2. Results and Discussion

Calculation of final concentration of the system

The simulation results show the change in concentration, caused by the diffusion of Ag^+ ions from the solution bulk into the TiO_2 nanotube, is related to three parameters: solution area (equation (1)), nanotube area (equation (2)) and solution initial concentration. All the mathematical relations cited below, between these parameters and the concentration variation, are true for the conditions mentioned in section 3 (Materials and Methods).

$$A_{sol} = H_s . W_s \qquad (1)$$

where A_{sol} is the solution area, H_s is the height of solution bulk and W_s is the width of solution bulk.

$$A_n = n . H_n . W_n \qquad (2)$$

where A_n is the area of nanotube , n is the number of nanotubes, H_n is the height of a nanotube and W_n is the width of the nanotube.

For different values of solution initial concentration, the ratio $\Delta c/c$ is constant:

$$\Delta c \propto c \qquad (3)$$

where Δc is the concentration variation of the system and c is the initial concentration of the solution.

In terms of diffusion, an increase in the initial concentration of the system raises the gradient intensity existent between the solution concentration in the bulk and the solution inside the nanotube, which has zero concentration. In this way, the silver ions will diffuse more strongly

and in more quantity to the nanotube, leading to a greater concentration variation.

The concentration change, *Δc,* is inversely proportional to the solution area, A_{sol}:

$$\Delta c \propto \frac{1}{A_{sol}} \qquad (4)$$

This correlation reflects that for large values of solution area, the concentration variation is smaller. This finding can be explained in terms of ratio R defined in equation (5). In a larger solution area, a smaller amount of diffused ions is required for the nanotube, about to total amount, so that the concentration of the system is homogeneous. That is, for smaller values of R and, consequently, higher A_{sol} the concentration variation becomes larger.

$$R = \frac{q_{dif}}{q_{tot}} \qquad (5)$$

where R is the ratio between diffused and total ions, q_{dif} is the amount of diffused ions into the nanotube and q_{tot} is the amount of total ions presents in system.

To determine the proportionality between the nanotube area and the concentration variation, it is necessary to change both the diameter and height of the nanotube and the number of nanotubes. In addition, it is pertinent to evaluate if the parameters mentioned above do not affect this relation. For this, thirteen sets of simulations are performed, described in Table 1. The results are expressed in the form of straight equations obtained by linear regression.

Each set represent ten simulations performed according to the parameters above and varying the size quoted. Therefore, the proportionality between the nanotube area (A_n) and the concentration change (Δc) is:

$$\Delta c \propto A_n \qquad (6)$$

Observing the set of similar simulations, which were performed for one and two nanotubes, it is possible to conclude that it is the area of nanotube that influences the variation of the concentration of the system, regardless of the amount of nanotubes.

An increase in the nanotube area causes an increase in the ratio R, that is, more ions are diffused into the interior of the nanotube in relation to the total amount of ions. In this way, there is an increase in the concentration variation.

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Table 1. Detail of the simulation sets.

N°	Amount of nanotubes	c (mol.L^{-1})	Variable dimension	A$_{sol}$ (µm²)	Equation of the line
1	1	0.250	H$_n$	4000	$\Delta c = 0.062 \times 10^{-3} A_n$
2	1	0.250	W$_n$	4000	$\Delta c = 0.063 \times 10^{-3} A_n + 0.001 \times 10^{-3}$
3	1	0.500	H$_n$	4000	$\Delta c = 0.125 \times 10^{-3} A_n + 0.001 \times 10^{-3}$
4	1	0.500	W$_n$	4000	$\Delta c = 0.126 \times 10^{-3} A_n - 0.001 \times 10^{-3}$
5	2	0.500	H$_n$	4000	$\Delta c = 0.062 \times 10^{-3} A_n$
6	2	0.250	W$_n$	4000	$\Delta c = 0.062 \times 10^{-3} A_n$
7	2	0.500	H$_n$	4000	$\Delta c = 0.125 \times 10^{-3} A_n - 0.001 \times 10^{-3}$
8	2	0.500	W$_n$	4000	$\Delta c = 0.125 \times 10^{-3} A_n - 0.001 \times 10^{-3}$
9	1	0.250	H$_n$	1000	$\Delta c = 0.248 \times 10^{-3} A_n + 0.003 \times 10^{-3}$
10	1	0.250	H$_n$	3000	$\Delta c = 0.083 \times 10^{-3} A_n + 0.004 \times 10^{-3}$
11	1	0.250	H$_n$	5000	$\Delta c = 0.050 \times 10^{-3} A_n$
12	1	0.250	H$_n$	10000	$\Delta c = 0.025 \times 10^{-3} A_n$
13	1	0.250	H$_n$	20000	$\Delta c = 0.012 \times 10^{-3} A_n$

Considering all the proportionalities identified, it can be write the following mathematical relation:

$$\Delta c = a \frac{A_n c}{A_{sol}} \qquad (7)$$

Where the concentration variation is defined according to equation (8):

$$\Delta c = c - c_f \qquad (8)$$

where Δc is the change in concentration, c is the initial concentration of the solution and c_f is the final concentration of the system.

Substituting equation (8) into equation (7), and isolating c_f, the following mathematical function is obtained:

$$c_f = - a \frac{A_n c}{A_{sol}} + c \qquad (9)$$

Performing linear regression again, but now using equation (9), where $x = A_n.c/A_{sol}$ and $y = c_f$, the following results are obtained (Table 2):

Table 2. Equations parameters obtained through equation (9).

N°	c (mol.L^{-1})	A$_{sol}$ (µm²)	Equation
1	0.250	4000	$c_f = - 0.997 A_n c/A_{sol} + 0.250$
2	0.250	4000	$c_f = - 1.010 A_n c/A_{sol} + 0.250$
3	0.500	4000	$c_f = - 0.998 A_n c/A_{sol} + 0.500$
4	0.500	4000	$c_f = - 1.009 A_n c/A_{sol} + 0.500$
5	0.250	4000	$c_f = - 0.998. A_n c/A_{sol} + 0.250$
6	0.250	4000	$c_f = - 1.000. A_n c/A_{sol} + 0.250$
7	0.500	4000	$c_f = - 1.001. A_n c/A_{sol} + 0.500$
8	0.500	4000	$c_f = - 1.003. A_n c/A_{sol} + 0.500$
9	0.250	1000	$c_f = - 0.992. A_n c/A_{sol} + 0.250$
10	0.250	3000	$c_f = - 0.997. A_n c/A_{sol} + 0.250$
11	0.250	5000	$c_f = - 0.999. A_n c/A_{sol} + 0.250$
12	0.250	10000	$c_f = - 0.999. A_n c/A_{sol} + 0.250$
13	0.250	20000	$c_f = - 1.000. A_n c/A_{sol} + 0.250$

The value of the constant a is 1,000, obtained through the average of the angular coefficients of the equations of Table 2. Applying this value in equation (9) and showing the initial concentration, the following equation is obtained:

$$c_f = c (1 - \frac{A_n}{A_{sol}}) \qquad (10)$$

Considering a tridimensional model, where all TiO$_2$ nanotubes have the same dimensions, the equation (10) can be generalized to a more realistic model, this way:

$$c_f = c(1 - \frac{V_n}{V_{sol}}) \qquad (11)$$

where c_f is the final concentration of the system, c is the initial concentration of the solution, V_n is the nanotube volume, considering a cylindrical geometry (equation (12)), and V_{sol} is the solution volume.

$$V_n = \frac{1}{4} \pi . n . H_n . W_n^2 \qquad (12)$$

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where n is the number of nanotubes (equation (13)), H_n is the height of a nanotube and W_n is the diameter of a nanotube.

$$n = \mu.A \qquad (13)$$

where μ is the amount of nanotube per area of TiO_2, given in m^{-2}, and A is the surface area of the oxide, given in m^2.

The dilution equation

The simulation of the diffusion phenomenon of Ag^+ cations gives concentration data as a function of time, which allows to relate how the solution area, the initial solution concentration and the nanotube area affect the final concentration of the system. However, this correlation can be analyzed through the dilution phenomenon, and its respective equation (equation (14)). In terms of the dilution, the solution containing Ag^+ in the bulk is diluted by the solution with zero concentration inside the nanotube.

$$c_i.V_i = c_f.V_f \qquad (14)$$

where c_i is the initial concentration of solution, V_i is the initial volume of the solution, c_f is the final concentration and V_f is the final volume.

In a two-dimensional system, c_i is the concentration of solution (c), V_i can be replaced by the area of solution (A_{sol}), c_f is the final concentration of the system (c_f) and V_f is the sum of the solution area (A_{sol}) with the area of solution inside the nanotube (A_n). Substituting these variables into (equation (14)) and isolating c_f, the following equation is obtained:

$$c_f = c\left(\frac{A_{sol}}{A_{sol}+A_n}\right) \qquad (15)$$

Comparing the final concentration, c_{f1}, calculated by obtained equation (equation (10)) and the final concentration, c_{f2}, calculated by dilution equation (equation (15)), it is observed that the difference between the concentration calculated with the two equations is low. The results are represented in Table 3 for different values of nanotube area, and in Table 4 of different values of solution area.

Table 3. Comparison between the final concentrations calculated from the equation obtained and to the dilution equation for different values of A_n.

A_n (μm^2)	A_{sol} (μm^2)	c_{f1} (mol.L^{-1})	c_{f2} (mol.L^{-1})	difference
0.7	4000	249.9563x10^{-3}	249.9563x10^{-3}	0.0
1.4	4000	249.9125x10^{-3}	249.9125x10^{-3}	0.0
2.1	4000	249.8688x10^{-3}	249.8688x10^{-3}	0.0
2.8	4000	249.8250x10^{-3}	249.8251x10^{-3}	1x10^{-07}
3.5	4000	249.7813x10^{-3}	249.7814x10^{-3}	1x10^{-07}
4.2	4000	249.7375x10^{-3}	249.7378x10^{-3}	3x10^{-07}
4.9	4000	249.6938x10^{-3}	249.6941x10^{-3}	3x10^{-07}
5.6	4000	249.6500x10^{-3}	249.6505x10^{-3}	5x10^{-07}
6.3	4000	249.6063x10^{-3}	249.6069x10^{-3}	6x10^{-07}
7.0	4000	249.5625x10^{-3}	249.5633x10^{-3}	8x10^{-04}

Table 4. Comparison between the final concentrations calculated from the equation obtained and to the dilution equation for different values of A_n.

A_n (μm^2)	A_{sol} (μm^2)	c_{f1} (mol.L^{-1})	c_{f2} (mol.L^{-1})	difference
3.5	1000	249.1250x10^{-3}	249.1280x10^{-3}	3x10^{-06}
3.5	3000	249.7083x10^{-3}	249.7086x10^{-3}	3x10^{-07}
3.5	5000	249.8250x10^{-3}	249.8251x10^{-3}	2x10^{-07}
3.5	10000	249.9125x10^{-3}	249.9125x10^{-3}	0.0
3.5	20000	249.9563x10^{-3}	249.9563x10^{-3}	0.0

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The increase in the nanotube area, as well as, decrease in the solution area, leads to an increase in the difference between the final concentrations calculated with each equation. That is, the higher the A_n/A_{sol} ratio, the greater the difference of calculated values. This confirmation is in agreement with the observed experimentally, considering that the volume of solution is always higher, in order of magnitude, to the volume of nanotubes.

Influence of nanotube's height and diameter on diffusion

To discuss the influence of both the diameter and the height of the nanotube on the diffusion of silver cations, it is necessary to define a time parameter. The equilibrium time, t_{eq}, is defined as the time required for the net velocity to be zero, according to the derivative of the graphs *c versus t* plotted during the simulations (Figure 1).
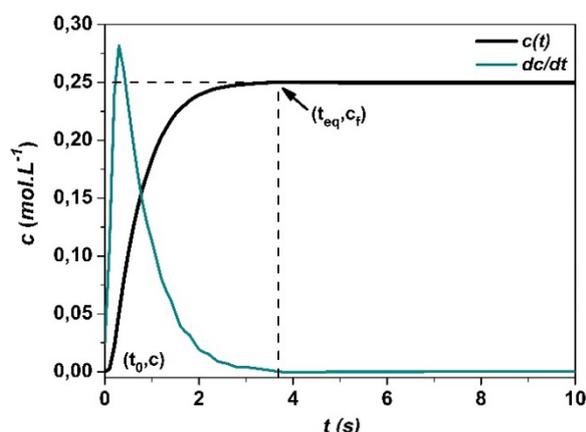
Figure 1. Graph of the concentration as a function of time on the bottom of the nanotube, indicating the points (t_{eq}, c_f) e (t_0, c), where t_{eq} is the defined time parameter, c_f is the final concentration of the system, t_0 is the initial time and c is the initial concentration ate the bottom of the nanotube.

The higher the nanotube, the longer the time required for the concentration of the system to be constant, and consequently the longer the time t_{eq}. This is because the distance to the base of the nanotube becomes bigger, increasing the time required for the Ag⁺ to diffuse into the less concentrated region. Figure 2 shows the time t_{eq} for different heights of nanotube.

The figure above shows that the equilibrium time is exponentially proportional to the height of

the nanotube, indicating that the time for diffusion to occur completely is gradually larger for large values of height. This same relation is evidenced in the curves of the concentration at the bottom of the nanotube as a function of time for different height values also show the influence of height in the diffusion (Figure 3).

Differently from what is observed for different heights of nanotube, an increase in the diameter does not entail a significant change in the curve *c versus t*, that is, the value of the diameter does not interfere in the diffusion of silver ions into the interior of the nanotube. This can be seen in the graph of Figure 4.
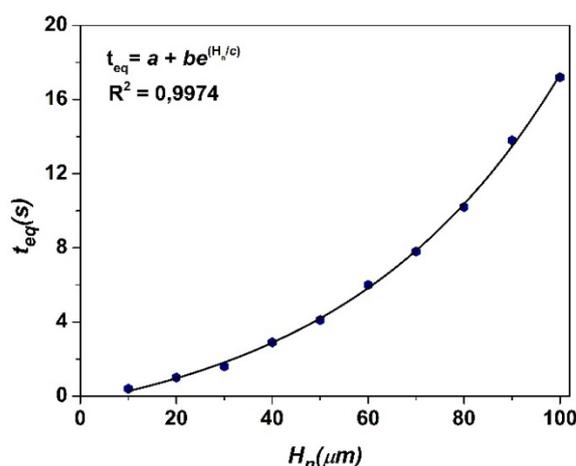
Figure 2. Graph of the time t_{eq} as a function of height of nanotube, where *a*, *b* and *c* are constants.
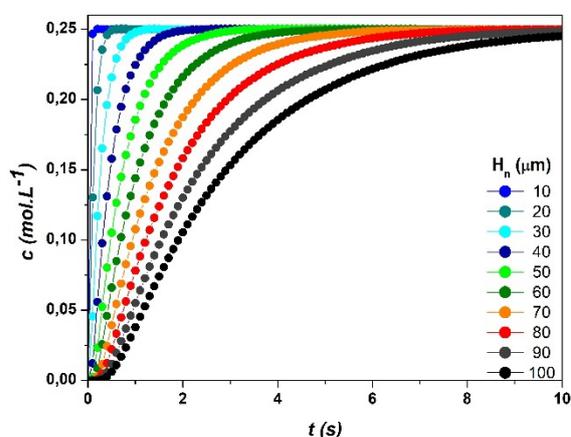
Figure 3. Graph of Ag⁺ concentration at the bottom of the nanotube as a function of time for different heights of nanotube.

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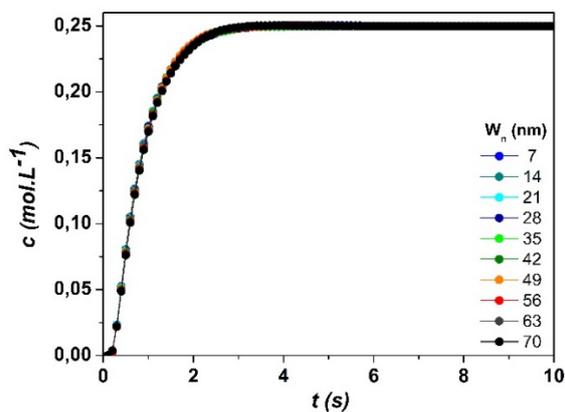
Figure 4. Graph of Ag+ concentration at the bottom of the nanotube as a function of time for different diameters of nanotube.

3. Material and Methods

A nanotube, the TiO₂ layer and the aqueous solution containing Ag+ ions represent the two-dimensional domain (Figure 5). Nanotubes are formed during the anodization process, by the evolution of metastable pores into TiO₂ oxide. The formation of nanotubes occurs by the attack of fluoride ions on the oxide barrier layer [16]. The barrier layer is formed by the anodization process and because it is compact [16], it does not interfere in the diffusion process of the ions that will be considered in this work. For the incorporation of silver ions, it is considered that a nanotubular film, after the anodizing process, is submerged in a solution containing a known concentration of silver ions. In this work, the ionic solution will be called bulk. For the purpose of implementing the physical model, a two-dimensional model was considered where the height and width of the solution are given by H_s and W_s, respectively, and the height and diameter of nanotube are represented, respectively, by H_n and W_n.

The commercial software *Comsol Multiphysics*® was used to perform the simulations using the finite element method, as well as for the construction of the two-dimensional model. The mesh is made up of finite triangular elements, and is refined in the region where the nanotube is located (Figure 6), because in this region there is an accelerated change of concentration [17].

For calculation purposes, the interior of the nanotube has zero concentration and the bulk

solution concentration may assume any constant value other than zero. In addition, all boundaries presented, except at the top of the nanotube, do not allow flow of matter.
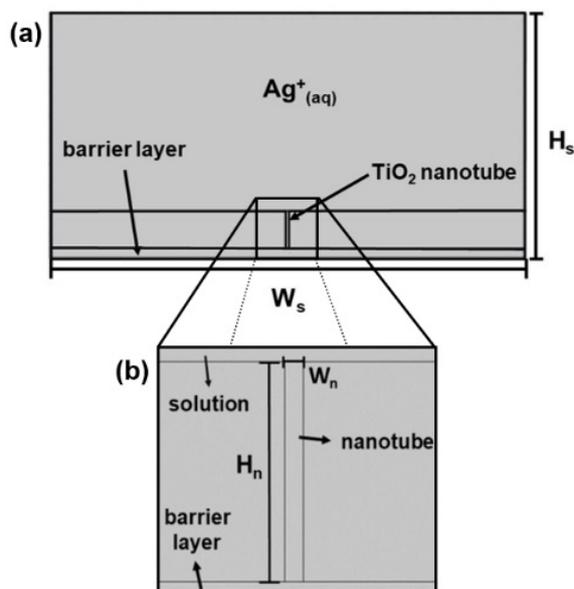
Figure 5. 2D model representing the solution of Ag+, a TiO₂ nanotube and the TiO₂ barrier film, where (a) represents the entire domain, and (b) is an enlargement of the region where the nanotube is located.
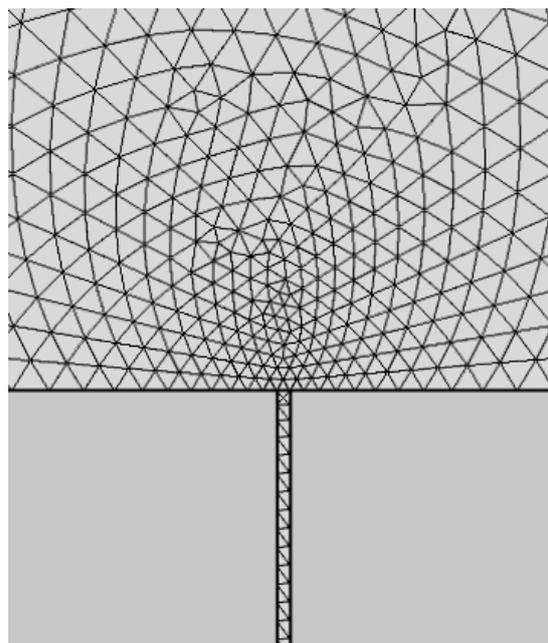
Figure 6. Finite element mesh plotted on the geometric model.

For the construction of the mathematical model of diffusion, the Einstein relation (equation

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(16)) was used to determine the diffusion coefficient of Ag$^+$ ions in aqueous solution. This constant is a necessary parameter for the Fick's second law (equation (17)).

$$D = \frac{uRT}{zF} \qquad (16)$$

where D is the diffusion coefficient, u is the ionic mobility, R is the gas constant, T is the temperature, z is the ion charge and F is the Faraday constant.

$$\frac{\partial c}{\partial t} = \nabla \cdot (D\nabla c) \qquad (17)$$

The concentration at any point in the domain is calculated by this partial differential equation using the finite element method. The simulations were carried out using the parameters, constants and variables, described in Table 5.

Table 5. Description of the parameters used during the simulations.

Name (symbol)	Classification	Minimum value; interval; maximum value [unit]
Height of solution bulk (H_s)	Variable	10; 10; 100 e 100; 50; 600 [µm]
Height of nanotube (H_n)	Variable	10; 10; 150 [µm]
Diffusion coefficient of Ag$^+_{(aq)}$ (D)	Constant	1.603×10^{-9} [m^2/s]
Initial concentration of solution (c)	Variable	0.05; 0.05; 0.50 [mol.L^{-1}]
Diameter of nanotube (W_n)	Variable	0.07; 0.07; 0.7 [µm]
Width of solution bulk (W_s)	Variable	50; 50; 150 [µm]
Temperature (T)	Constant	298.15 [K]
Simulation time (t)	Constant	20 [s]

In order to obtain the proportional mathematics presented in section 2 (Results and Discussion), the simulations are performed with all fixed parameters, except one, in which one is interested. This procedure was repeated for all the variable parameters mentioned in the Table 5 above.

4. Conclusions

Using a simple two-dimensional model, it was possible to determine which variables are directly involved in the change of the Ag$^+$ concentration. The concentration change is caused by the diffusion of these ions from the bulk into the nanotube. The connection of the studies carried out leads to a mathematical relationship that calculates the final concentration as a function of the initial solution concentration, the solution volume, and the nanotube volume.

The analysis of the problem through two distinct phenomena, diffusion and dilution, shows that the mathematical data are close. This is evidenced when comparing the results calculated by the mathematical equation obtained and the dilution equation. The difference of the calculated final concentration between the two equations is minimal for A_n/A_{sol} ratios, that is, for large values of solution area and small values of nanotube area. This result shows that the spatial domain of the simulation performed should be carefully delimited to minimize such errors.

The mathematical relationship found may apply to real situations when extrapolated to three dimensions. The generality can also be covered for the study of diffusion of other ions in any material with nanotubular structure, because, the equation does not take into account the diffusion coefficient of the material.

The height of the nanotube, unlike the diameter, is directly related to the time required for the concentration of the system to be constant, t_c, that is, the complete diffusion of the ions into the nanotube is slower for larger heights. This result shows that for the incorporation of chemical species into materials with nanotubular structure, the experimental conditions that favor the vertical growth of the nanotubes must be considered.

It is important to emphasize that this study considers only the concentration change caused by diffusion. The adsorption phenomenon of the silver ions in the nanotubular material was not considered, new studies must be carried out to implement this phenomenon.

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