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Development of the CFD code through the Mathematica® program to simulate an adsorption column.

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En lo tocante a la ciencia, la autoridad de un militar no es superior al humilde razonamiento de una sola persona.

Galileo Galilei

En primer lugar, agradezco a Dios por acompañarme en este camino y hacer posible la finalización de este grado.

A mis padres, a mi tío, a mis hermanas y a mi hermano por apoyarme, animarme y creer que siempre podría. A mis compañeras/os por su ayuda y alegría. También a todos los profesores que he tenido a lo largo de mis estudios por enseñarme, tenerme paciencia y por dejarme ver que estudiar no es algo aburrido o pesado, sino una manera de conocer, crecer, sorprenderte e impulsarte a soñar.

Finamente, nombrar a dos profesores, Josep Maria Lliteras quien me aconsejo y animo a seguir este grado y al Dr. Joan Llorens Llacuna quien me mostro que a partir de un programa se puede simular la realidad y con su ayuda ha sido posible realizar este trabajo de fin de grado.

Muchas gracias.

CONTENTS

SUMMARY

The simulation programs allow to describe real systems. One of the most important fields is computational fluid dynamics (CFD) that it studies the behaviour of fluids at rest or in motion.

In this work, it is developed of the CFD code through the Mathematica® program to simulate a fixed bed adsorption column.

The mathematical model that is used was described by Chatzopoulos and Varma. This model contains two adsorbate mass balances, one for the liquid phase and the other for the solid phase. Each balance contains two contour conditions. The concentration in each phase is related to the equilibrium equation, in this case, the Langmuir isotherm is used.

The model describes the variation of solute concentration in the column and inside the particle as a function of position and time.

The numerical results obtained through simulation were very similar to the experimental results, with a maximum error < 4%. With this check, concentration profiles were simulated in the column and in the particle.

Keywords: Adsorption, Langmuir isotherm, mathematical model, simulation, computational fluid dynamics (CFD).

RESUMEM

Los programas de simulación permiten describir sistemas reales. Uno de los campos más importantes es la dinámica de fluidos computacional (CFD) que estudia el comportamiento de los fluidos en reposo o en movimiento.

En este trabajo, se desarrolla el código CFD a través del programa Mathematica® para simular una columna de adsorción de lecho fijo.

El modelo matemático que se utiliza fue descrito por Chatzopoulos y Varma. Este modelo contiene dos balances de material de adsorbato, uno para la fase líquida y el otro para la fase sólida. Cada balance contiene dos condiciones de contorno. La concentración en cada fase se relaciona a través de la ecuación de equilibrio, en este caso, se utiliza la isoterma de Langmuir. El modelo describe la variación de concentración de soluto en la columna y dentro de la partícula en función de la posición y el tiempo.

Los resultados numéricos obtenidos a través de la simulación fueron muy parecidos a los resultados experimentales, con un error máximo < 4%. Con esta verificación, se simularon perfiles de concentración en la columna y en la partícula.

Palabras clave: Adsorción, Isoterma de Langmuir, modelo matemático, simulación, dinámica de fluidos computacional (CFD).

1. INTRODUCTION

The adsorption is a surface phenomenon, the molecules or atoms from another phase are attached to surface of the adsorbent. These molecules or atoms are called adsorbates. Depending on the type of the bond between the adsorbent and the adsorbate, adsorption may be physical or chemical.

The physical adsorption o physisorption is based in a van der Waals interaction between the adsorbent and the adsorbate. In this process there is not exchange of electrons, but there are intermolecular attractions where the energy is favourable. The characteristics are:

- The van der Waals forces are relatively weak. The adsorption enthalpy values are comparable with the condensation enthalpy values.
- The adsorbate retains its identity, since the enthalpy change is small. In other words, insufficient to lead to bond breaking.
- The process is reversible.

The chemical adsorption o chemisorption involves an exchange of electrons between adsorbates and adsorbent surface, in that way the molecules or atoms stick to the surface by forming a strong chemical bond (generally covalent bond).

- The bond is consequently much stronger, it has a small distance and it is more stable at high temperatures than the physical adsorption.
- The enthalpy values are high on the region of 200 kJ/mol.
- The process may be irreversible.

1.1. 1^{ST} ADSORBENT

Adsorbents are solid particles which have an adsorption large surface area. Almost all adsorbents contain pores to increase this surface.

A very important property is the structure of the pore (number of pores, shape and size), since it determines the adsorption capacity and even the dynamic adsorption rate. Next, at table 1 it is shown with the classification de pores according to IUPAC.

Table 1 Classification of pores according to IUPAC.

Type	**Pore diameter d (nm)**
Macropores	$d > 50$
Mesopores	$2 \leq d \leq 50$
Micropores	$d < 2$

1.1.1. 2nd Adsorbent materials

There are a lot of adsorbent materials, but the most used in industry are: activated carbon, silica gel, and alumina. These materials provide large surface areas per unit weight. The column of adsorption that is studied has granular activated carbon (GAC) as an adsorbent.

1.1.1.1. 3rd Activated carbon

Activated carbon can be formed from the following materials: carbonaceous material, peat and wood (it is very common the coconut shell). This adsorbent has a high degree of microporosity, the pore volume ranges are between 0.7-1,8 cm^3/g and the total surface area of activated carbon per unit weight ranges are between 300 and 1500 m^2/g.

There are different types of activated carbon and they are classified based on their size, preparational methods and industrial applications.

Table 2. Types activated carbon.

	Form	Size	Surface areas	Main applications
Powdered activated carbon (PAC)	Crushed	<0.297 mm (according to the American Water Works) < 0.177 mm (according to ASTM D5158.PAC)	-	Biological treatment.
Granular activated carbon (GAC)	Granular	Mesh sizes For liquid-phase 8 x 20, 20 x 40, or 8 x 30 For vapor-phase 4 x 6, 4 x8, or 4 x 10	Ranges 0,7-1,8 cm3/g	The removal of toxic organic compounds from industrial wastewater and groundwater.
Bituminous GAC	Granular (a more fully developed pore distribution)	Mesh sizes For liquid-phase 8 x 20, 20 x 40, or 8 x 30 For vapor-phase 4 x 6, 4 x8, or 4 x 10	Approx. 900 m2/g	Water treatment. Treatment of low concentrations of low molecular weight organic compounds in water.
Lignite GAC	Granular	Mesh sizes For liquid-phase 8 x 20, 20 x 40, or 8 x 30 For vapor-phase 4 x 6, 4 x8, or 4 x 10	650 m2/g	Decolorizing.
Coconut-shell-based GACs	Granular	Mesh sizes For liquid-phase 8 x 20, 20 x 40, or 8 x 30 For vapor-phase 4 x 6, 4 x8, or 4 x 10	Over 1000 m2/g	Vapor and liquid phase applications.

Optimal working conditions using activated carbon.

- ✓ Large molecules.
- ✓ Nonpolar molecules.
- ✓ Nonsoluble or slightly soluble molecules.
- ✓ The degree of adsorption can change according to the pH and solution to be treated.
- ✓ An increase of temperature promotes an increase the rate of diffusion through the liquid but may reduce the degree of adsorption since the adsorption process is exothermic.

1.2. 1ST EQUILIBRIUM

The equilibrium between the liquid and solid phases in an adsorption system is represented through the equilibrium isotherm. This isotherm is characterized by a system and a temperature. The most important isotherm types are Langmuir isotherm, Freundlich isotherm and Dubinin-Raduskevish (DR).

1.2.1. 2nd Langmuir isotherm

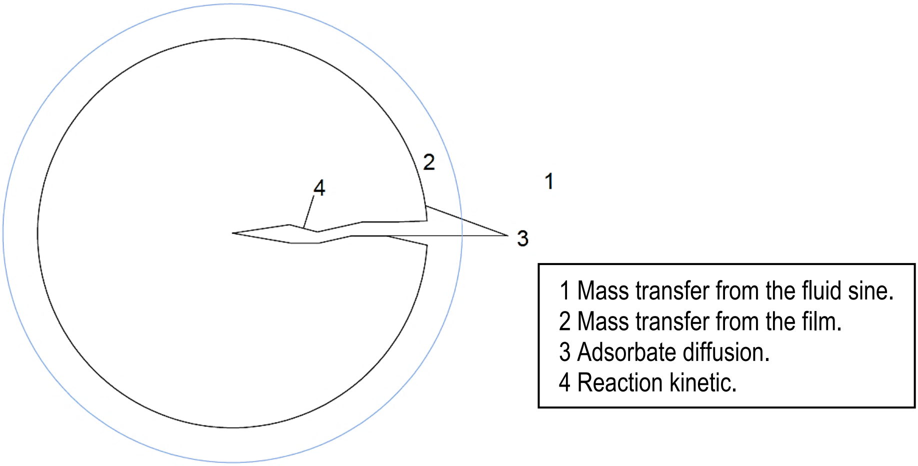
For the development of the mathematical model is used the Langmuir isotherm. The Langmuir isotherm is physically plausible and is based on three assumptions that are the following:

- The adsorption can only has a monolayer coverage.
- All sites are equivalent, individuals and the surface are uniform.
- There is not interaction between adsorbates.

1.3. 1ST MASS TRANSFER STAGES

In the adsorption process there are four mass transfer stages, as shown in Figure 1.

Figure 1. Mass transfer stages in the adsorbed particle.



For one hand, the external mass transferred to the adsorbate.

- Mass transfer from the fluid sine: Mass transfer between the surrounding fluid and fluid-film. This stage has a small resistance to mass transfer compared to the others.
- Mass transfer from the film: The film is a fluid layer surrounding the adsorbent particle and opposes a resistance to let matter passes between fluid-film and adsorption surface. The transfer is affected by the hydrodynamic conditions of the fluid.

On the other hand, the internal mass transferred to the adsorbate.

The adsorbate diffusion in an adsorbed particle includes diffusion in the pores and diffusion in external surface.

- Solid diffusion is also called microporous diffusion. This adsorption surface has pores that are so small that the adsorbate does not escape of the bond force between it and the external surface of the adsorbent particle (*Perry R.H., 1999.*).

- Pore diffusion is also called macropore diffusion. This is the diffusion of adsorbate in fluid-filled pores. The adsorbate escapes from force field of the adsorbent surface due that the pores are big enough (*Perry R.H., 1999.*).

Finally, the kinetic reaction.

- The kinetic reaction is not usually a determinant stage of the process and occurs between adsorbent and adsorbate. Adsorption occurs through the exchange of electrons or intermolecular attractions.

2. OBJECTIVES

The main objective of this work is to build a computer program using Mathematica® program to simulate an adsorption column and see what happens inside the column and the adsorbent particles.

Other objectives:

- ✓ Know the adsorption process.
- ✓ Study and development of equations that define the adsorption model.
- ✓ Acquisition of knowledge of the Mathematica® program.
- ✓ Validate the results using experimental data.

3. DEVELOPMENT: MATHEMATICAL MODEL

The dynamic of adsorption process is based in a model developed by Chatzopoulos and Varma (*Chatzopoulos, D., Arvind Varna, 1994.*). They carried out a process of toluene adsorption and desorption in the aqueous phase using F-300 activated carbon as the adsorbent.

The study that is presented is based in an individual adsorption of three compounds that are benzene, toluene and o-xylene (BTX) in aqueous phase using coconut shell activated carbon as the adsorbent. The numeric methodology is based on two adsorbate mass balances in liquid and solid phase. These balances are developed and then discretized using the Integration Over Control Volume method with the CDS formulation.

The numerical simulation describes the variation in the adsorbate concentration in the column and surface the adsorbent (includes the pore and the external surface of the particle) as a function of time and position.

The mathematical model that is used is the of homogeneous particle and it is considered two resistances to mass transfer

- External-film resistance.
- Surface diffusion resistance in the adsorbent particle.

The diffusion coefficient (Ds) is not considered to be constant as it depends on the solute solid-phase concentration. The diffusion coefficient increases exponentially with adsorbent surface coverage of the adsorbent surface. The equation 1 describes this increase.

$$D_s(q) = D_0 \left[e^{k\left(\frac{q}{q_{sat}}\right)} \right] \qquad (1)$$

Where D_0 is the surface diffusion coefficient when the adsorbate mass fraction in solid phase (q) is equal to zero (q = 0) [cm^2/s], k is the experimental parameter of eq.1 [-] and q_{sat} is the adsorbate saturation mass fraction in solid phase [mg/g].

3.1. 1ST ADSORBATE MASS BALANCE FOR THE SOLID PHASE

Mass balance for one chemical specie in one differential volume (See eq. 2) contains four terms: term of non-stationary regime, convective term, dispersion term and generation term.

For the study of the adsorbent particle, three conditions are supposed that are the following:

- Isothermal process.
- Adsorbent particle whit spherical geometrical.
- Fast adsorption kinetic.

$$\frac{\partial \rho_s\, q}{\partial t} + \nabla . [\rho_s\, q\, \vec{v}] = \nabla . \rho_s\, D_s\, \nabla q + R \qquad (2)$$

Where q is the adsorbate mass fraction [mg/g], D_s is the surface diffusion coefficient [cm^2/s], ρ_s is the apparent particle density [g/cm^3] and R is the generation term of the species [$mg/(s \cdot m^3)$].

Adsorbate mass balance for the solid phase contains the non-stationary term and the diffusion term (see Eq. 3). So, the equation 3 allows the study of the variation in the solute concentration in function of the radial position of the particle and the time.

$$\frac{\partial \rho_s\, q}{\partial t} = \nabla . \rho_s\, D_s \nabla q \qquad (3)$$

Equation 1 was incorporated in mas balance (see eq. 3) to take account the variation of the diffusion coefficient at the surface (Ds).

$$\frac{\partial q}{\partial t} = \nabla . D_0 \left[e^{k\left(\frac{q}{q_{sat}}\right)} \right] \nabla q \qquad (4)$$

Finally, the definition of convergence and divergence in the field of orthogonal spherical coordinates applies. Considering that the adsorbate concentration only depends on the radial position (r), the terms related to theta and phi do not contribute. The final balance is described by Eq. 5.

$$\frac{\partial q}{\partial t} = \frac{D_0}{r^2} \frac{\partial}{\partial r} \left\{ r^2 e^{[k(q/q_{sat})]} \frac{\partial q}{\partial r} \right\} \qquad (5)$$

In q is done a change of variable to work with units of concentration [mg/cm^3]. This leads to the following relation:

$$q\left[\frac{\text{mg of adsorbate}}{\text{g of adsorbent}}\right]\rightarrow C_p\left[\frac{\text{mg of adsorbate}}{\text{cm}^3}\right]$$

The Langmuir isotherm relates the concentrations (See eq. 6) and the variation of q with respect to Cp (See eq. 6.1).

$$q=\frac{q_{sat}\,b_L\,C_p}{1+b_L\,C_p} \qquad (6)$$

$$\frac{\partial q}{\partial C_p}=\frac{b_L\,q_{sat}}{\left(1+b_L\,C_p\right)^2} \qquad (6.1)$$

Equations 6 and 6.1 was incorporated in mass balance (see eq. 5) gives:

$$\frac{b_L\,q_{sat}}{\left(1+b_L\,C_p\right)^2}\frac{\partial C_p}{\partial t}=\frac{D_0}{r^2}\frac{\partial}{\partial r}\left\{r^2 e^{\left[k\left(\frac{\frac{b_L\,q_{sat}\,C_p}{1+b_L\,C_p}}{q_{sat}}\right)\right]}\frac{b_L\,q_{sat}}{\left(1+b_L\,C_p\right)^2}\frac{\partial C_p}{\partial r}\right\} \qquad (7)$$

3.1.1. 2nd Initial and boundary conditions

For the study of momentum, heat or mass, there are 3 types of boundary conditions.

Type 1: The value of the dependent variable is known on the boundary. The dependent variable in this case is the adsorbate concentration.

Type 2: The flow that penetrates through the boundary is known. In this case the flow is of mass.

Type 3: The transfer coefficient is known. The coefficient in this case is of external mass transfer.

Equation 7 has to be solved with following initial and boundary conditions. The conditions that are shown are for the adsorption and desorption processes.

3.1.1.1. 3rd Initial condition

At time zero, at all radius of the particle (r) and at all axial length of the bed (z), the adsorbate concentration remains at a fixed value.

$t = 0, \quad 0 \le r \le R, \quad 0 \le z \le L$

For adsorption: The concentration is equal to zero.

$$C_p = 0 \qquad (7.1)$$

For desorption: The concentration is equal to adsorbate initial concentration in liquid-phase.

$$C_p = C_{p,in} \qquad (7.2)$$

3.1.1.2. 3rd Boundary conditions

Type 2: All the time, at all axial length of the bed (z), there is not diffusion at r = 0.

$t > 0, \quad 0 \le z \le L, \quad r = 0$

$$\frac{\partial C_p}{\partial r}\Big|_{r=0} = 0 \qquad (7.3)$$

Type 3: All the time and at all axial length of the bed (z), the external mass transfer coefficient (k_f) is known. The following equality applies for r = R.

The flux density at the particle surface = The flux density at the fluid film

3.2. 1ST ADSORBATE MASS BALANCE FOR THE LIQUID PHASE

Initially, mass balance for one chemical specie in one differential volume (See Eq. 2) is studied to describe the variation of the adsorbate concentration in the axial position (z) and the time (t). The balance is given by eq. 8.

$$\varepsilon_L \frac{\partial C}{\partial t} + \varepsilon_L v_S \frac{\partial C}{\partial z} = \varepsilon_L D_{eff} \frac{\partial^2 C}{\partial z^2} - (1 - \varepsilon_L) \frac{\partial q\, \rho_s}{\partial t} \qquad (8)$$

Where C is the solute liquid-phase concentration [mg/cm^3], D_{eff} is the dispersion coefficient [cm/s], v_s is the superficial liquid velocity in bed [cm/s], ε_L is the bed void fraction [-] and (1- ε_L) is the bed fraction [-].

In the absence of axial dispersion of the adsorbate in the bed, the dispersion term is removed of equation 8. This is possible when the relationship between the bed length and the particle diameter is greater than 20.

$$\varepsilon_L \frac{\partial C}{\partial t} + \varepsilon_L v_S \frac{\partial C}{\partial z} = - (1 - \varepsilon_L) \frac{\partial q \rho_s}{\partial t} \qquad (9)$$

Generation term can be related through the adsorbate flow (See eq.10), where the driving force is the difference between the adsorbate concentration in liquid-phase and the equilibrium concentration in the solid-liquid interface. This relation is applied in equation 9 (See eq. 11).

$$\frac{\partial q \rho_s}{\partial t} = a\, k_f (C - C_s) \qquad (10)$$

Where Cs is the equilibrium concentration in the solid-liquid interface [mg/cm^3] and a is the specific area [m^2/m^3].

$$\varepsilon_L \frac{\partial C}{\partial t} + \frac{v_S}{\varepsilon_L} \frac{\partial C}{\partial z} = - (1 - \varepsilon_L) \frac{3}{R}\, k_f (C - C_s) \qquad (11)$$

3.2.1. 2nd Initial and boundary conditions

Equation 11 has to be solved with the following initial and boundary conditions. The conditions that are shown are for the adsorption and desorption processes.

3.2.1.1. 3rd Initial condition

At time zero, at all radius of the particle (r) and at all axial length of the bed (z), the adsorbate concentration remains at a fixed value.

$t = 0, \quad 0 \leq r \leq R, \quad 0 \leq z \leq L$

For adsorption: The concentration is equal to zero.

$$C_p = 0 \qquad (11.1)$$

For desorption: The concentration is equal to adsorbate initial concentration in liquid phase.

$$C = C_{in} \qquad (11.2)$$

3.2.1.2. 3rd Boundary conditions

Type 1: At all the time and at all radius of the particle (r), the adsorbate concentration is equal to adsorbate initial concentration in liquid-phase, at z = 0.

$t > 0, \quad z = 0, \quad 0 \leq r \leq R$

$$C = C_{in} \qquad (11.3)$$

Type 2: At all the time and at all axial length of the bed (z), there is not adsorbate diffusion at z = L.

$t > 0, \quad z = L, \quad 0 \leq r \leq R$

$$\frac{\partial C}{\partial z}\Big|_{z=L} = 0 \qquad (11.4)$$

4. DIMENSIONLESS MATHEMATICAL MODEL

The mathematical model is presented with its initials and boundary conditions using the following dimensionless quantities:

$$A=\frac{v_s\,R^2}{L\,D_0},\quad B=\frac{3\,R\,(1\text{-}\varepsilon)\,k_f}{\varepsilon\,D_0},\quad L=\frac{R\,k_f\,C_{ref}}{\rho_s\,D_0\,q_{ref}},\quad p=\frac{q_{ref}}{q_{sat}},\quad ra=b_L\,C_{ref},\quad w=\frac{C}{C_{ref}},\quad w_p=\frac{C_p}{C_{ref}},\quad w_{p,MM}=\frac{C_{p,MM}}{C_{ref}},$$

$$Z=\frac{z}{L},\quad \rho=\frac{r}{R},\quad \tau=\frac{D_0\,t}{R^2}$$

Where w is the dimensionless concentration in liquid-phase, w_p and $w_{p,MM}$ are the dimensionless concentrations in solid-phase, Z and ρ are the dimensionless lengths, τ is the dimensionless time and A, B, L and ra are the dimensionless groups.

Dimensionless adsorbate mass balance for the solid-phase

$$\frac{ra}{\left(1+ra\,w_p\right)^2}\,\frac{\partial w_p}{\partial \tau}=\frac{1}{\rho^2}\,\frac{\partial}{\partial \rho}\left\{\rho^2\,e^{\left[k\left(\frac{ra\,w_p}{1+ra\,w_p}\right)\right]}\,\frac{ra}{\left(1+ra\,w_p\right)^2}\,\frac{\partial w_p}{\partial \rho}\right\} \qquad (12)$$

Dimensionless initial condition

$\tau = 0,\quad 0 \le \rho \le 1,\quad 0 \le Z \le 1$

For adsorption:

$$w_p = 0; \qquad (12.1)$$

For desorption:

$$w_p = w_{p,in}; \qquad (12.2)$$

Dimensionless boundary conditions

Type 2: $\tau > 0,\quad 0 \le Z \le 1,\quad \rho = 0$

$$\frac{\partial w_p}{\partial \rho}\Big|_{\rho=0}=0 \qquad (12.3)$$

Type 3: $\tau > 0, \quad 0 \le Z \le 1, \quad \rho = 1$

$$AE\left(\frac{\frac{ra}{p}\,w_{p,MM}}{1 + ra\,w_{p,MM}} - \frac{\frac{ra}{p}\,w_{p,MM-1}}{1 + ra\,w_{p,MM-1}}\right) = L\,\Delta\tau\left(w_i - w_{p,MM}\right) \qquad (12.4)$$

Where AE is the dimensionless matter flow entering from the right (The value is shown in the discretization section).

Dimensionless adsorbate mass balance for the liquid phase

$$\frac{\partial w}{\partial \tau} + A\frac{\partial w}{\partial Z} = -B\left(w - w_{p,s}\right) \qquad (13)$$

Dimensionless initial and boundary conditions

Dimensionless initial condition

$\tau = 0, \quad 0 \le Z \le 1, \quad 0 \le \rho \le 1$

For adsorption:

$$w = 0 \qquad (13.1)$$

For desorption:

$$w = w_{in} \qquad (13.2)$$

Dimensionless boundary conditions

Type 1: $\tau > 0, \quad 0 \le \rho \le 1, \quad Z = 0$

$$w = 1 \qquad (13.3)$$

Type 2: $\tau > 0, \quad 0 \le \rho \le 1, \quad Z = 0$

$$\frac{\partial w}{\partial Z}\Big|_{Z=0} = 0 \qquad (13.4)$$

5. DISCRETIZATION

The behaviour of fluids (in motion or in rest) is studied through fluid mechanics. One of the most important fields in this science is the computational fluid dynamics (CFD).

CFD allows to simulate, analyse and solve problems that involve fluid flows. This is possible through numerical analysis (contains the equations that describe fluid motion, interaction of fluid with solid and the boundary conditions) and the computer programming to solve and analyse the results.

In this study the development of the CFD code is done through the Mathematica® program to simulate an adsorption column.

5.1. 1ST MESHING

Two different meshes are created. One for the column and other for the particle in each node (point) of the column. These are two-dimensional (time-space) structured meshes to store the discrete points that are used. The nomenclature that is used in each mesh is the next:

Mesh in the column

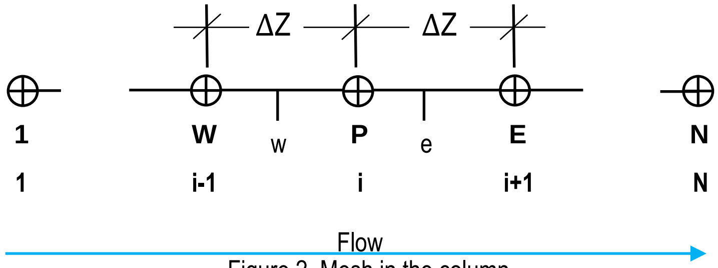


Figure 2. Mesh in the column

Where 1 is the first node, N is the last, P or i is the node to study, W or i-1 is the west node respect to P, E or i+1 is the east node respect P and ΔZ is a dimensionless length increment.

Mesh in the particle

For each node of i, all the values of j are studied.

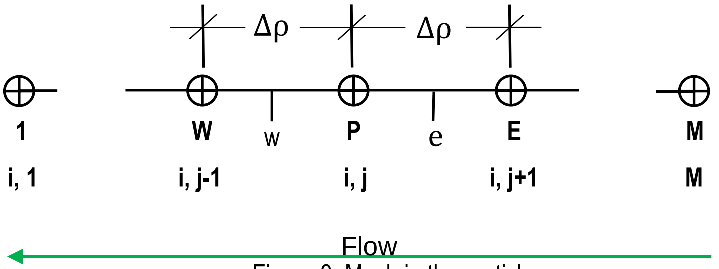


Figure 3. Mash in the particle

Where i is each node of the column, 1 is the first node referred to the particle, M is the last, P or j is the node to study, W or j-1 is the west node respect to P, E or j+1 is the east node respect to P and Δρ is a dimensionless length increase.

5.2. 1ST DISCRETIZED EQUATIONS

The discretization is done by the Integration Over Control Volume method (IOCV). The data are stored in the centre of the control volumes. The method of calculation that is used is the Explicit. This method works with small increments of time to do that the solutions do not depend on the increment value. The new node at each phase depends on three previous values (See figure 4) that are:

Liquid phase: w^n_i depends on w^o_i, w^o_{i+1} y w^o_{i-1}.

Solid phase: wp^n_i depends on $wp^o_{i,j}$, $wp^o_{I,j+1}$ y $wp^o_{I,j-1}$.

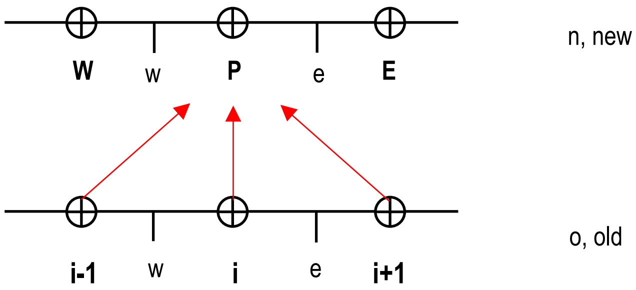


Figure 4. Calculation of P from the previous nodes.

The development of differential equations with their corresponding boundary conditions can be seen in Appendix 1. Equations that are obtained are shown below.

Discretized adsorbate mass balance for the liquid phase (See eq. 13).

$$eq[i]:= (Sp + AW)\ w_i[\tau] == AW\ w_{i-1}[\tau] + Su \qquad (14)$$

Where:

$Sp = 1 + \Delta\tau\ B$, $AW = A\ \frac{\Delta\tau}{\Delta Z}$, $Su = \Delta\tau\ B\ w_{p\ i,MM}[\tau] + w_i[\tau-\Delta\tau]$

Boundary conditions

Type 1: In node 1 (entry of the column) the dimensionless concentration is 1, at all the time.

$$w_1[\tau] = 1 \quad \tau > 0 \qquad (14.1)$$

Type 2: The condition of flow density (Ds = 0) affects the node NN and N-1(end of the column).

$$eq[NN]= w_{NN}[\tau] == w_{NN-1}[\tau] \qquad (14.2)$$

AE = 0

$$eq[NN-1] = (Sp + AW)\ w_{NN-1}[\tau] == AWw_{NN-2}[\tau] + Su \qquad (14.3)$$

Discretized adsorbate mass balance for the solid phase (See eq. 12).

$$eq[i,j]:= (Sp + AW + AE)\ w_{p\ i,j}[\tau] == AW\ w_{p\ i,j-1}[\tau] + AE\ w_{p\ i,j+1}[\tau] + Su \qquad (15)$$

Where:

$$Sp = \Delta\rho,\ \ AW = AE = \frac{\Delta\tau}{\Delta\rho} e^{\left[k\left(\frac{ra\ w_{p\ i,j}[\tau-\Delta\tau]}{1 + ra\ w_{p\ i,j}[\tau-\Delta\tau]}\right)\right]},\ \ Su = w_{p\ i,j}[\tau-\Delta\tau]$$

Boundary conditions

Type 2: Flow density equal to zero affects the node 1 and 2 (center of the particle).

$$eq[i, 1]:= w_{p\ i,1}[\tau] == w_{p\ i,2}[\tau] \qquad (15.1)$$

AW = 0

$$eq[i, 2]:= (Sp + AE)\ w_{p\ i,2}[\tau] == AE\ w_{p\ i,3}[\tau] + Su \qquad (15.2)$$

Type 3: The fact that the external mass transfer coefficient is known is the condition that affects the node MM and MM-1 (surface of the particle).

$$eq[i, MM]:= w_{p,MM}[\tau] == \frac{\dfrac{AE\ \frac{ra}{p}\ w_{p\ i,MM-1}[\tau]}{1 + ra\ w_{p\ i,MM-1}[\tau-\Delta\tau]} + \dfrac{L\ \Delta\tau}{\Delta\rho}\ w_{i}[\tau-\Delta\tau]}{\dfrac{AE\ \frac{ra}{p}}{1 + ra\ w_{p\ i,MM}[\tau-\Delta\tau]} + \dfrac{L\ \Delta\tau}{\Delta\rho}} \qquad (15.3)$$

$$eq[i, MM-1]:= \left(Sp + AW_{MM-1} + \frac{1}{\dfrac{ra}{p\ L\ \Delta\tau\ (1 + ra\ w_{p\ i,MM}[\tau-\Delta\tau])} + \dfrac{1}{AE_{MM-1}}} \right)$$
$$w_{p\ i,MM-1}[\tau] == AW_{MM-1}\ w_{p\ i,MM-2}[\tau] + \frac{1}{\dfrac{ra}{p\ L\ \Delta\tau\ (1 + ra\ w_{p\ i,MM}[\tau-\Delta\tau])} + \dfrac{1}{AE_{MM-1}}} w_i[\tau-\Delta\tau] + Su \quad (15.4)$$

6. RESULTS

From the mathematical model that is proposed, we proceed to validate the numerical methodology that has been developed. For this, the results obtained from the numerical simulation for each component through the Mathematica® program are compared with the experimental results made by Adriana Luz and others (*Dervanoski Luz, A. et al., 2013.*).

The input parameters for simulation of each component (benzene, toluene, o-xylene) are given in Table 3 and the code in the Mathematica is shown in appendix 2.

Table 3. Parameters used to simulation (*Dervanoski Luz, A. et al., 2013.*).

Parameters	**Units**	**Benzene**	**Toluene**	**O-xylene**
B	cm^3/mg	49	49,7	40,5
C_{in}	mg/cm^3	0,15	0,15	0,15
D_o	cm^2/s	$8,12\cdot10^{-09}$	$7,17\cdot10^{-08}$	$2,40\cdot10^{-08}$
D_c	cm	1,2	1,2	1,2
d_p	cm	0,085	0,085	0,085
***k**	adm.	3,2	3	3,4
k_f	cm/s	$6,31\cdot10^{-03}$	$6,31\cdot10^{-03}$	$6,31\cdot10^{-03}$
L	cm	10	10	10
Q	cm^3/s	0,67	0,67	0,67
q_{sat}	mg/g	124,77	150,42	165,07
vs	cm/s	1,44	0,59	0,59
ε_L	adim.	0,41	0,41	0,41
ρs	g/cm^3	0,49	0,49	0,49

*The values of k are the are best adjusted to the experimental results, since the article does not give that data.

The number of nodes used for each meshes are given table 4.

Table 4. The number of nodes for each mesh

Number of nodes	Benzene	Toluene	O-xylene
In the time	128	128	128
In the axial direction	28	30	30
In the radial position	58	21	28

Figures 5, 6, and 7 show the experimental and simulated (new and old) dimensionless breakthrough curves for benzene, toluene and o-xylene, respectively. The data of dimensionless concentrations that are shown are taken at the exit of the column.

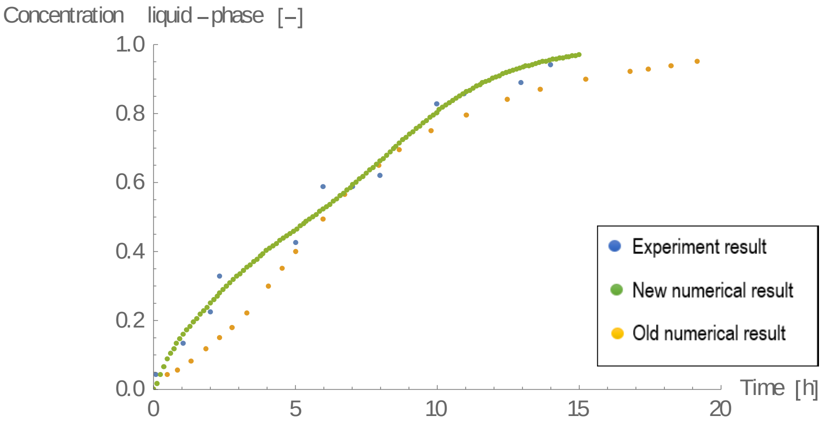


Figure 5. Experimental and simulated dimensionless breakthrough curves for benzene.

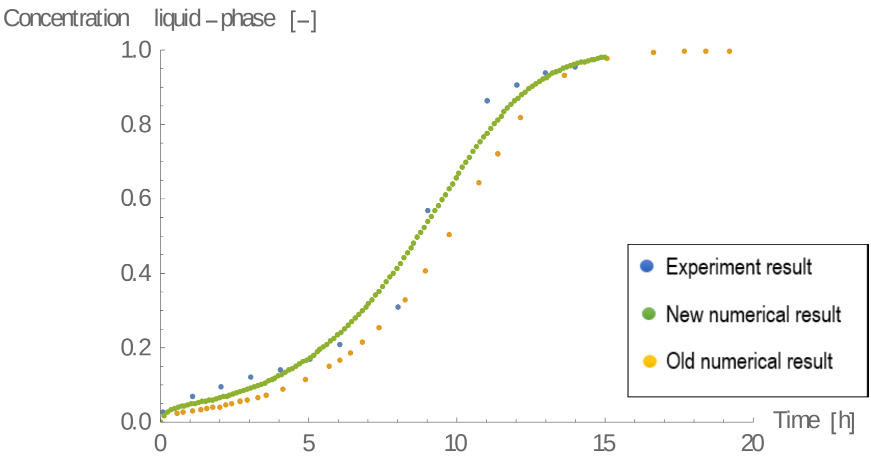


Figure 6. Experimental and simulated dimensionless breakthrough curves for toluene.

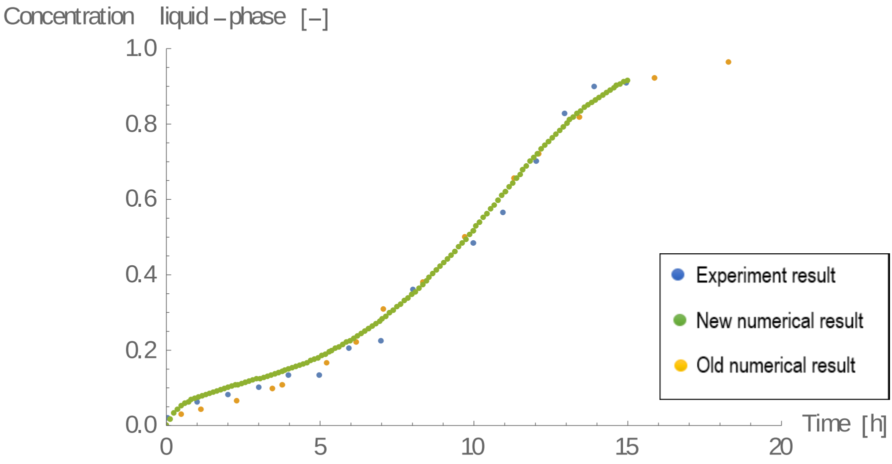


Figure 7. Experimental and simulated dimensionless breakthrough curves for o-xylene.

Comparing the dimensionless breakthrough curves in each graph (See figure 5, 6, and 7) it can be observed that the results obtained from the new simulation shows a better agreement with experimental values. Table 5 shows the maximum errors obtained between the numerical result (new and old) and the experimental one.

Table 5. Maximum errors between the numerical result (new and old) and the experimental.

Components	**New maximum error**	**Old maximum error**
Benzene	1,68%	10,05%
Toluene	3,78%	10,49%
O-xylene	0,78%	1,84%

The results are adjusted with a small error to the experimental results and the new maximum error < old maximum error. With this it is verified that the development of the numerical methodology and the development of the program have been made out correctly.

Two dimensionless concentration profiles are studied, for different times.

- The dimensionless adsorbate concentration profile in liquid phase is studied along the bed and for each compound. These profiles may be observed in figures 8, 9 and 10.
- The dimensionless adsorbate concentration profile in solid phase is studied along the radius and for each compound. The concentration values are obtained at the end of the bed. These profiles may be observed in figures 11, 12 and 13.

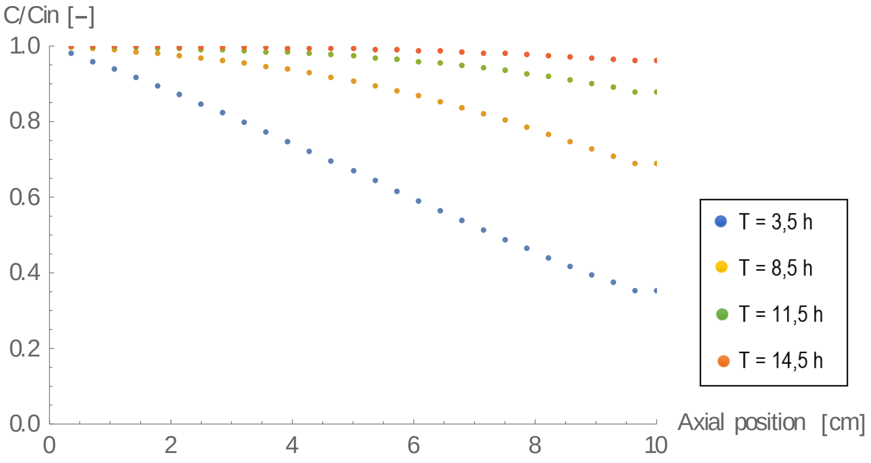


Figure 8. Dimensionless concentration profiles in liquid-phase, along the bed for the benzene.

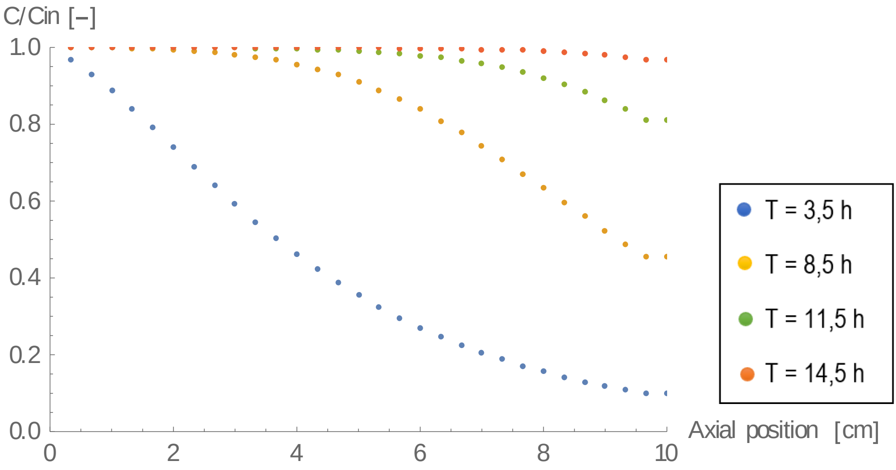


Figure 9. Dimensionless concentration profiles in liquid-phase, along the bed for the toluene.

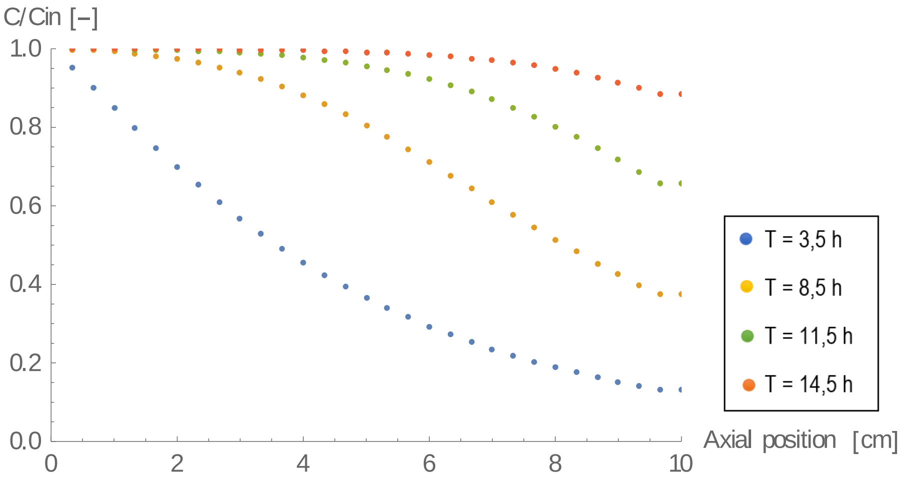


Figure 10. Dimensionless concentration profiles in liquid-phase, along the bed for the o-xylene.

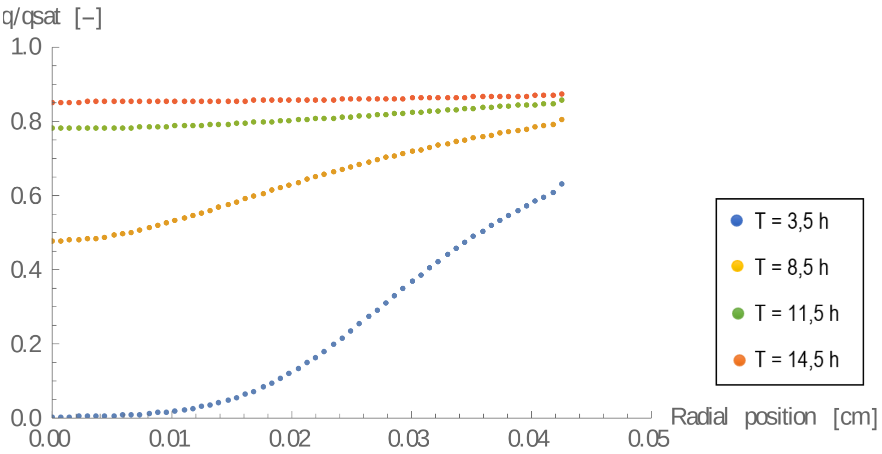


Figure 11. Dimensionless concentration profiles in solid-phase, along the particle radius for the benzene.

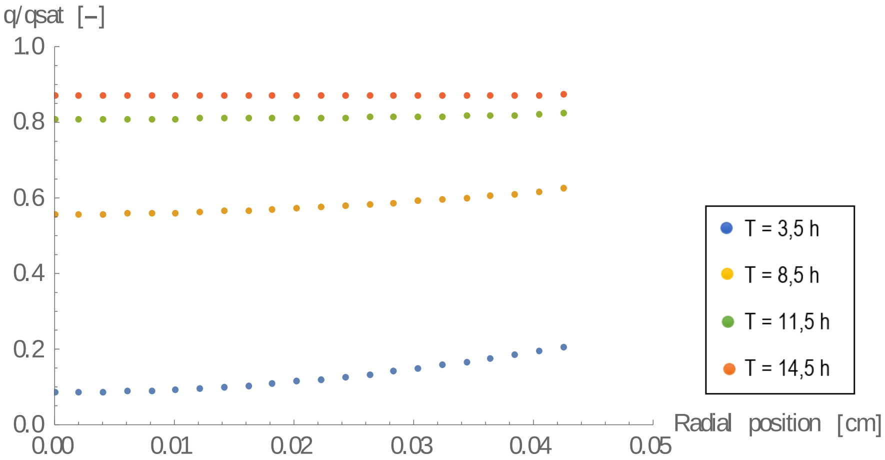


Figure 12. Dimensionless concentration profiles in solid-phase, along the particle radius for the toluene.

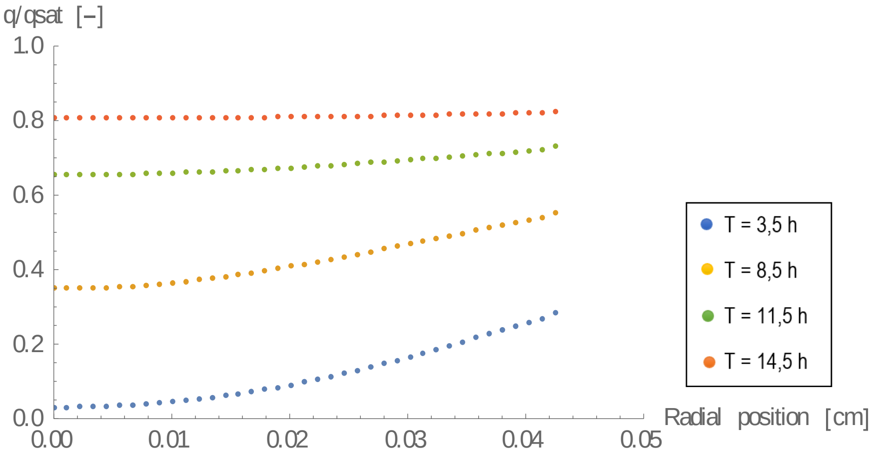


Figure 13. Dimensionless concentration profiles in solid-phase, along the particle radius for the o-xylene.

In the figures 8, 9 and 10 it can be observed that as the adsorption time increase the concentration in liquid-phase also increases until arrive to the initial concentration in the whole column.

For the three compounds in an adsorption time of 14.5 h the bed doesn't get completely saturated.

In the figures 11, 12 and 13 the profiles have an exponential tendency (mainly in small adsorption times), this tendency is related to the variation of the diffusion coefficient (See eq. 1). It is also observed that concentration of the adsorbate increases with time, but the increases decreases when the particle is practically saturated.

N. CONCLUSIONS

Comparing the experimental results of benzene, toluene and o-xylene we can conclude that the numerical results obtained from simulation program are consistent, because the profiles of adsorbate concentration show a good agreement with experimental values and the maximum error obtained is less than 4%.

This leads us to say that through a simulation program we can predict the behaviour of a real system.

Finally, the time used for the simulation is not greater because an explicit method is used (implies small time increments) and the power of the processor is not enough to calculate a mesh with more nodes of time (the resolution time is very slow). If the time was greater, it could be seen that the concentration at the exit of the column would be equal to the initial concentration and that all the particles would be completely saturated.

PROPOSALS

As the work was being carried out, the following proposals emerged.

- ✓ Realization of the experimental part, since some erroneous data was found (due to the units or some data that are incorrect copied of another article).
- ✓ To use a better processor to study a greater adsorption time using small intervals of time (increasing the numbers of nodes).
- ✓ Simulate a desorption column.

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SYMBOLS

a: adsorbent specific area [cm^2/cm^3]

A: dimensionless group, $A=\frac{v_s R^2}{L D_0}$ [-]

AE: dimensionless mass flow entering from the right [-]

AW: dimensionless mass flow entering from the left [-]

B: dimensionless group, $B=\frac{3 R (1-\varepsilon) k_f}{\varepsilon D_0}$ [-]

C: adsorbate liquid phase concentration [mg/cm^3]

$C_{ref} = C_{in}$: adsorbate initial concentration in liquid phase [mg/cm^3].

C_p: adsorbate concentration in solid phase [mg/cm^3]

C_s: equilibrium concentration in the solid-liquid interface [mg/cm^3]

d_p: particle diameter [cm]

D_{eff}: dispersion coefficient [cm^2/s]

D_0: surface diffusion coefficient at $C_p = 0$ or $q = 0$ [cm^2/s]

D_s: surface diffusion coefficient [cm^2/s]

k: dimensionless parameter in eq.1 [-]

k_f: external mass transfer coefficient [cm/s]

L: dimensionless group, $L=\frac{R k_f C_{ref}}{\rho_s D_0 q_{ref}}$ [-]

L_o: bed length [cm]

q: adsorbate mass fraction in solid phase [mg/g]

q_{ref}: adsorbate mass fraction in equilibrium with C_{ref} [mg/g]

q_{sat}: adsorbate saturation mass fraction in solid phase [mg/g]

Q: flowrate [cm^3/s]

p: dimensionless group, $p=\frac{q_{ref}}{q_{sat}}$ [-]

r: radial position inside the adsorbent particle [cm] ra: dimensionless group, ra=b_L C_{ref} [-]

R: adsorbent particle radius [cm]

t: time [s]

v: superficial liquid velocity in bed [cm/s]

w: dimensionless concentration in liquid phase [-]

w_p: dimensionless concentration in solid phase [-]

$w_{p, MM}$: dimensionless equilibrium concentration in the solid-liquid interface [-]

z: axial position in bed [cm]

Z: dimensionless axial position in bed [-]

Greek letters

ε_L: bed void fraction [-]

(1-ε_L): bed fraction [-]

ρ: dimensionless radial position inside the adsorbent particle [-]

ρ_s: apparent particle density [g/cm^3]

τ: dimensionless time [-]

Letters for mesh

P: Node to study

W: west node respect to P

E: east node respect to P

i: node of the column

j: node of the particle

APPENDICES

APPENDIX 1: THE DEVELOPMENT OF DIFFERENTIAL EQUATIONS WITH THEIR BOUNDARY CONDITIONS

Discretization of the dimensionless adsorbate mass balance in the liquid-phase.

$$\frac{\partial w}{\partial \tau} + A\frac{\partial w}{\partial Z} = -B\left(w - w_{p,MM}\right)$$

$$\frac{\partial w}{\partial \tau} = -A\frac{\partial w}{\partial Z} - B\left(w - w_{p,MM}\right)$$

$$\int_{w}^{e}\int_{\tau-\Delta\tau}^{\tau}\frac{\partial w}{\partial \tau}\,d\tau\,dZ = \Delta Z\,(w_P^n - w_P^o) = \Delta Z\,w_i^n - \Delta Z\,w_i^o$$

$$\int_{\tau-\Delta\tau}^{\tau}\int_{w}^{e} A\,\frac{\partial w}{\partial Z}\,dZ\,d\tau = \Delta\tau\left[\left(A\,w^n\right)_e - (A\,w^n)_w\right] = \Delta\tau\left[A\left(\frac{w_{i+1}^n + w_i^n}{2}\right) - A\left(\frac{w_i^n + w_{i-1}^n}{2}\right)\right] =$$

$$\Delta\tau\left[A\left(\frac{w_{i+1}^n - w_{i-1}^n}{2}\right)\right] = \Delta\tau\left[A\left(\frac{2\,\Delta w}{2}\right)\right] = \Delta\tau\,A\,\Delta w = \Delta\tau\,A\,(w_i^n - w_{i-1}^n)$$

$$\int_{\tau-\Delta\tau}^{\tau}\int_{w}^{e} B\left(w - w_{p,MM}\right)dZ\,d\tau = \Delta\tau\,\Delta Z\;B\left(w_i^n - w_{p,MM}^n\right)$$

$$\Delta Z\,w_i^n - \Delta Z\,w_i^o = -\Delta\tau\,A\,(w_i^n - w_{i-1}^n) - \Delta\tau\,\Delta Z\,B\left(w_i^n - w_{p,MM}^n\right)$$

$$\Delta Z\,w_i^n + \Delta\tau\,\Delta Z\,B\,w_i^n + \Delta\tau\,A\,w_i^n = \Delta\tau\,A\,w_{i-1}^n + \Delta\tau\,\Delta Z\,B\,w_{p,MM}^n + \Delta Z\,w_i^o$$

$$(\Delta Z + \Delta\tau\,\Delta Z\,B + \Delta\tau\,A)\;w_i^n = \Delta\tau\,A\,w_{i-1}^n + \Delta\tau\,\Delta Z\,B\,w_{p,MM}^n + \Delta Z\,w_i^o$$

$$\left(1 + \Delta\tau\,B + \frac{\Delta\tau}{\Delta Z}\,A\right)\;w_i^n = \frac{\Delta\tau}{\Delta Z}\,A\,w_{i-1}^n + \Delta\tau\,B\,w_{p,MM}^n + w_i^o$$

$$(Sp + AW)\;w_i^n = AW\,w_{i-1}^n + Su$$

$$\boxed{eq[i] := (Sp + AW)\;w_i[\tau] == AW\;w_{i-1}[\tau] + Su}$$

Where:

$Sp = 1 + \Delta\tau\, B$, $AW = A\, \frac{\Delta\tau}{\Delta Z}$, $Su = \Delta\tau\, B\, w^{n}_{p,MM} + w^{o}_{i}$

Boundary conditions

Type 1:

$$w_i[\tau] = 1 \qquad \tau > 0$$

Type 2:

$$\boxed{eq[NN] = w_{NN}[\tau] = w_{NN-1}[\tau]}$$

AE = 0

$$\boxed{eq[NN-1] = (Sp + AE)\, w_{NN-1}[\tau] = AW\, w_{NN-2}[\tau] + Su}$$

Discretization of the dimensionless adsorbate mass balance for the solid phase.

$$\frac{ra}{(1+ra\, w_p)^2}\, \frac{\partial w_p}{\partial \tau} = \frac{1}{\rho^2}\, \frac{\partial}{\partial \rho}\left\{\rho^2\, e^{\left[k\left(\frac{ra\, w_p}{1 + ra\, w_p}\right)\right]}\, \frac{ra}{(1 + ra\, w_p)^2}\, \frac{\partial w_p}{\partial \rho}\right\}$$

$$\int_{w}^{e} \int_{\tau-\Delta\tau}^{\tau} \frac{ra}{(1 + ra\, w_{p\, i,j})^2}\, \frac{\partial w_{p\, i,j}}{\partial \tau}\, d\tau\, d\rho = \Delta\rho\, \frac{ra}{(1 + ra\, w^{o}_{p\, i,j})^2}\, (w^{n}_{p\, i,j} - w^{o}_{p\, i,j})$$

$$\int_{\tau-\Delta\tau}^{\tau} \int_{e}^{w} = \frac{1}{\rho^2}\, \frac{\partial}{\partial \rho}\left\{\rho^2\, e^{\left[k\left(\frac{ra\, w^{o}_{p\, i,j}}{1 + ra\, w^{o}_{p\, i,j}}\right)\right]}\, \frac{ra}{(1 + ra\, w_{p\, i,j})^2}\, \frac{\partial w_{p\, i,j}}{\partial \rho}\right\} d\rho\, d\tau =$$

$$\Delta\tau\, e^{\left[k\left(\frac{ra\, w^{o}_{p\, i,j}}{1 + ra\, w^{o}_{p,i}}\right)\right]}\, \frac{ra}{(1 + ra\, w^{o}_{p\, i,j})^2}\left[\left(\frac{\partial w_{p\, i,j}}{\partial \rho}\right)_{w} - \left(\frac{\partial w_{p\, i,j}}{\partial \rho}\right)_{e}\right] =$$

$$\Delta\tau\, e^{\left[k\left(\frac{ra\, w^{o}_{p\, i,j}}{1 + ra\, w^{o}_{p\, i,j}}\right)\right]}\, \frac{ra}{(1 + ra\, w^{o}_{p\, i,j})^2}\left[\left(\frac{\Delta w_{p\, i,j}}{\Delta \rho}\right)_{w} - \left(\frac{\Delta w_{p\, i,j}}{\Delta \rho}\right)_{e}\right] =$$

$$\Delta\tau\, e^{\left[k\left(\frac{ra\, w^{o}_{p\, i,j}}{1 + ra\, w^{o}_{p\, i,j}}\right)\right]}\, \frac{ra}{(1 + ra\, w^{o}_{p\, i,j})^2}\left(\frac{(w^{n}_{p\, i,j-1} - w^{n}_{p\, i,j})}{\Delta\rho} - \frac{(w^{n}_{p\, i,j} - w^{n}_{p\, i,j+1})}{\Delta\rho}\right) =$$

$$\frac{\Delta\tau}{\Delta\rho}\, e^{\left[k\left(\frac{ra\, w^{o}_{p\, i,j}}{1 + ra\, w^{o}_{p\, i,j}}\right)\right]}\, \frac{ra}{(1+ ra\, w^{o}_{p\, i,j})^2}\, (w^{n}_{p\, i,j-1} - w^{n}_{p\, i,j}) + \frac{\Delta\tau}{\Delta\rho}\, e^{\left[k\left(\frac{ra\, w^{o}_{p\, i,j}}{1 + ra\, w^{o}_{p\, i,j}}\right)\right]}\, \frac{ra}{(1+ra\, w^{o}_{p\, i,j})^2}\, (-w^{n}_{p\, i,j} + w^{n}_{p\, i,j+1})$$

$$\Delta\rho\,\frac{ra}{\left(1+ra\,w^{o}_{p\,i,j}\right)^{2}}\left(w^{n}_{p,i}-w^{o}_{p,i}\right)=\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}\frac{ra}{\left(1+ra\,w^{o}_{p\,i,j}\right)^{2}}\left(w^{n}_{p\,i,j-1}-w^{n}_{p\,i,j}\right)+$$

$$\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}\frac{ra}{\left(1+ra\,w^{o}_{p\,i,j}\right)^{2}}\left(-w^{n}_{p\,i,j}+w^{n}_{p\,i,j+1}\right)$$

$$\Delta\rho\left(w^{n}_{p\,i,j}-w^{o}_{p\,i,j}\right)=\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}\left(w^{n}_{p\,i,j-1}-w^{n}_{p\,i,j}\right)+\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}\left(-w^{n}_{p\,i,j}+w^{n}_{p\,i,j+1}\right)$$

$$\Delta\rho\,w^{n}_{p\,i,j}+\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}w^{n}_{p\,i,j}+\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}w^{n}_{p\,i,j}=$$

$$\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}w^{n}_{p\,i,j-1}+\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}w^{n}_{p\,i,j+1}+\Delta\rho\,w^{o}_{p\,i,j}$$

$$\left(\Delta\rho+\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}+\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}\right)w^{n}_{p\,i,j}=$$

$$\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}w^{n}_{p\,i,j-1}+\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}w^{n}_{p\,i,j+1}+\Delta\rho\,w^{o}_{p\,i,j}$$

$$(Sp+AW+AE)\,w^{n}_{p\,i,j}=AW\,w^{n}_{p\,i,j-1}+AE\,w^{n}_{p\,i,j+1}+Su$$

$$\boxed{eq[i,j]:=(Sp+AW+AE)\,w_{p,i}[\tau]==AW\,w_{p,i-1}[\tau]+AE\,w_{p,i+1}[\tau]+Su}$$

Where:

$Sp=\Delta\rho$, $AW=AE=\frac{\Delta\tau}{\Delta\rho}\,e^{\left[k\left(\frac{ra\,w^{o}_{p\,i,j}}{1+ra\,w^{o}_{p\,i,j}}\right)\right]}$, $Su=\Delta\rho\,w^{o}_{p\,i,j}$

Boundary conditions

Type 2:

$$\boxed{eq[i,1] := w_{p\,i,1}[\tau] = w_{p\,i,2}[\tau]}$$

$AW_2 = 0$

$$eq[i,2] := (Sp + AE)\, w_{p\,i,2}[\tau] = AE\, w_{p\,i,3}[\tau] + Su$$

Type 3:

$$AE\left(-\frac{\frac{ra}{p}\, w^{n}_{p\,i,MM}}{1 + ra\, w^{o}_{p\,i,MM}} + \frac{\frac{ra}{p}\, w^{n}_{p\,i,MM-1}}{1 + ra\, w^{o}_{p\,i,MM-1}}\right) = L\,\Delta\tau\left(-\, w^{o}_{i} + w^{n}_{p\,i,MM}\right)$$

$$-AE\,\frac{\frac{ra}{p}\, w^{n}_{p\,i,MM}}{1 + ra\, w^{o}_{p\,i,MM}} + AE\,\frac{\frac{ra}{p}\, w^{n}_{p\,i,MM-1}}{1 + ra\, w^{o}_{p\,i,MM-1}} = -\,L\,\Delta\tau\, w^{o}_{i} + L\,\Delta\tau\, w^{n}_{p\,i,MM}$$

$$AE\,\frac{\frac{ra}{p}\, w^{n}_{p\,i,MM}}{1 + ra\, w^{o}_{p\,i,MM}} + L\,\Delta\tau\, w^{n}_{p\,i,MM} = AE\,\frac{\frac{ra}{p}\, w^{n}_{p\,i,MM-1}}{1 + ra\, w^{o}_{p\,i,MM-1}} + L\,\Delta\tau\, w^{o}_{i}$$

$$w^{n}_{p\,i,MM}\left(AE\,\frac{\frac{ra}{p}}{1 + ra\, w^{o}_{p\,i,MM}} + L\,\Delta\tau\right) = AE\,\frac{\frac{ra}{p}\, w^{n}_{p\,i,MM-1}}{1 + ra\, w^{o}_{p\,i,MM-1}} + L\,\Delta\tau\, w^{o}_{i}$$

$$w^{n}_{p\,i,MM} = \frac{AE_{MM-1}\,\frac{\frac{ra}{p}\, w^{n}_{p\,i,MM-1}}{1 + ra\, w^{o}_{p\,i,MM-1}} + L\,\Delta\tau\, w^{o}_{i}}{AE_{MM-1}\,\frac{\frac{ra}{p}}{1 + ra\, w^{o}_{p\,i,MM}} + L\,\Delta\tau}$$

$$\boxed{eq[MM] := w_{p\,i,MM}[\tau] = \frac{AE_{MM-1}\,\frac{\frac{ra}{p}\, w_{p\,i,MM-1}[\tau]}{1 + ra\, w_{p\,i,MM-1}[\tau-\Delta\tau]} + L\,\Delta\tau\;\; w_{i}[\tau-\Delta\tau]}{AE_{MM-1}\,\frac{\frac{ra}{p}}{1 + ra\, w_{p\,i,MM}[\tau-\Delta\tau]} + L\,\Delta\tau}}$$

$$\mathrm{AE}\left(-\frac{\frac{\mathrm{ra}}{\mathrm{p}}\,w^{n}_{p\,i,MM}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM}}+\frac{\frac{\mathrm{ra}}{\mathrm{p}}\,w^{n}_{p\,i,MM-1}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM-1}}\right)=\mathrm{L}\,\Delta\tau\left(-w^{o}_{i}+w^{n}_{p\,i,MM}\right)$$

$$-\mathrm{AE}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}\,w^{n}_{p\,i,MM}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM}}+\mathrm{AE}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}\,w^{n}_{p\,i,MM-1}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM-1}}=-\,\mathrm{L}\,\Delta\tau\,w^{o}_{i}+\mathrm{L}\,\Delta\tau$$

$$w^{n}_{p\,i,MM}=\frac{-w^{o}_{i}+w^{n}_{p\,i,MM}}{\frac{1}{\mathrm{L}\,\Delta\tau}}=\frac{-w^{o}_{i}+\dfrac{\mathrm{AE}_{MM-1}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}\,w^{n}_{p\,i,MM-1}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM-1}}+\mathrm{L}\,\Delta\tau\,w^{o}_{i}}{\mathrm{AE}_{MM-1}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM}}+\mathrm{L}\,\Delta\tau}}{\frac{1}{\mathrm{L}\,\Delta\tau}}=$$

$$\frac{\dfrac{-\,\mathrm{AE}_{MM-1}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}\,w^{o}_{i}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM}}-\mathrm{L}\,\Delta\tau\,w^{o}_{i}+\mathrm{AE}_{MM-1}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}\,w^{n}_{p\,i,MM-1}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM-1}}+\mathrm{L}\,\Delta\tau\,w^{o}_{i}}{\mathrm{AE}_{MM-1}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM}}+\mathrm{L}\,\Delta\tau}}{\frac{1}{\mathrm{L}\,\Delta\tau}}=$$

$$\frac{\dfrac{-\,\mathrm{AE}_{MM-1}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}\,w^{o}_{i}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM}}+\mathrm{AE}_{MM-1}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}\,w^{n}_{p\,i,MM-1}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM-1}}}{\mathrm{AE}_{MM-1}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM}}+\mathrm{L}\,\Delta\tau}}{\frac{1}{\mathrm{L}\,\Delta\tau}}=$$

$$\frac{-\,\mathrm{AE}_{MM-1}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}\,w^{o}_{i}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM}}\,\mathrm{L}\,\Delta\tau+\mathrm{AE}_{MM-1}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}\,w^{n}_{p\,i,MM-1}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM-1}}\,\mathrm{L}\,\Delta\tau}{\mathrm{AE}_{MM-1}\,\frac{\frac{\mathrm{ra}}{\mathrm{p}}}{1+\mathrm{ra}\,w^{o}_{p\,i,MM}}+\mathrm{L}\,\Delta\tau}=$$

$$\frac{-\frac{w_i^o}{1+ra\,w^o_{p\,i,MM}}+\frac{w^n_{p\,i,MM-1}}{1+ra\,w^o_{p\,i,MM-1}}}{\frac{1}{AE_{MM-1}\,\frac{ra}{p}\,L\,\Delta\tau}\left(AE_{MM-1}\,\frac{\frac{ra}{p}}{1+ra\,w^o_{p\,i,MM}}+L\,\Delta\tau\right)}=\frac{-\frac{w_i^o}{1+ra\,w^o_{p\,i,MM}}+\frac{w^n_{p\,i,MM-1}}{1+ra\,w^o_{p\,i,MM-1}}}{\frac{1}{L\,\Delta\tau\left(1+ra\,w^o_{p\,i,MM}\right)}+\frac{1}{AE_{MM-1}\,\frac{ra}{p}}}=$$

$$\frac{-\frac{w_i^o}{1+ra\,w^o_{p\,i,MM}}}{\frac{1}{L\,\Delta\tau\left(1+ra\,w^o_{p\,i,MM}\right)}+\frac{1}{AE_{MM-1}\,\frac{ra}{p}}}+\frac{\frac{w^n_{p\,i,MM-1}}{1+ra\,w^o_{p\,i,MM-1}}}{\frac{1}{L\,\Delta\tau\left(1+ra\,w^o_{p\,i,MM}\right)}+\frac{1}{AE_{MM-1}\,\frac{ra}{p}}}$$

$$-AE_{MM-1}\,\frac{\frac{ra}{p}\,w^n_{p\,i,MM}}{1+ra\,w^o_{p\,i,MM}}+AE_{MM-1}\,\frac{\frac{ra}{p}\,w^n_{p\,i,MM-1}}{1+ra\,w^o_{p\,i,MM-1}}=$$

$$\frac{-\frac{w_i^o}{1+ra\,w^o_{p\,i,MM}}}{\frac{1}{L\,\Delta\tau\left(1+ra\,w^o_{p\,i,MM}\right)}+\frac{1}{AE_{MM-1}\,\frac{ra}{p}}}+\frac{\frac{w^n_{p\,i,MM-1}}{1+ra\,w^o_{p\,i,MM-1}}}{\frac{1}{L\,\Delta\tau\left(1+ra\,w^o_{p\,i,MM}\right)}+\frac{1}{AE_{MM-1}\,\frac{ra}{p}}}$$

$$-AE_{MM-1}\,\frac{\frac{ra}{p}\,w^n_{p\,i,MM}}{1+ra\,w^o_{p\,i,MM}}=\frac{-\frac{w_i^o}{1+ra\,w^o_{p\,i,MM}}}{\frac{1}{L\,\Delta\tau\left(1+ra\,w^o_{p\,i,MM}\right)}+\frac{1}{AE_{MM-1}\,\frac{ra}{p}}}$$

$$AE_{MM-1}\,\frac{ra}{p}\,w^n_{p\,i,MM}=\frac{w_i^o}{\frac{1}{L\,\Delta\tau\left(1+ra\,w^o_{p\,i,MM}\right)}+\frac{1}{AE_{MM-1}\,\frac{ra}{p}}}$$

$$AE_{MM-1}\,w^n_{p\,i,MM}=\frac{w_i^o}{\frac{ra}{p}\left(\frac{1}{L\,\Delta\tau\left(1+ra\,w^o_{p\,i,MM}\right)}+\frac{1}{AE_{MM-1}\,\frac{ra}{p}}\right)}=\frac{w_i^o}{\frac{ra}{p\,L\,\Delta\tau\left(1+ra\,w^o_{p\,i,MM}\right)}+\frac{1}{AE_{MM-1}}}$$

$$AE_{MM-1}\,\frac{\frac{ra}{p}\,w^n_{p\,i,MM-1}}{1+ra\,w^o_{p\,i,MM-1}}=\frac{\frac{w^n_{p\,i,MM-1}}{1+ra\,w^o_{p\,i,MM-1}}}{\frac{1}{L\,\Delta\tau\left(1+ra\,w^o_{p\,i,MM}\right)}+\frac{1}{AE_{MM-1}\,\frac{ra}{p}}}$$

$$\mathrm{AE}_{\mathrm{MM\text{-}1}}\,\frac{\mathrm{ra}}{\mathrm{p}}\,\mathrm{w}^{\mathrm{n}}_{\mathrm{p\,i,MM\text{-}1}} = \frac{\mathrm{w}^{\mathrm{n}}_{\mathrm{p\,i,MM\text{-}1}}}{\dfrac{1}{\mathrm{L}\,\Delta\tau\left(1+\mathrm{ra}\,\mathrm{w}^{\mathrm{o}}_{\mathrm{p\,i,MM}}\right)}+\dfrac{1}{\mathrm{AE}_{\mathrm{MM\text{-}1}}\,\dfrac{\mathrm{ra}}{\mathrm{p}}}}$$

$$\mathrm{AE}_{\mathrm{MM\text{-}1}}\,\mathrm{w}^{\mathrm{n}}_{\mathrm{p\,i,MM\text{-}1}} = \frac{\mathrm{w}^{\mathrm{n}}_{\mathrm{p\,i,MM\text{-}1}}}{\dfrac{\mathrm{ra}}{\mathrm{p}}\left(\dfrac{1}{\mathrm{L}\,\Delta\tau\left(1+\mathrm{ra}\,\mathrm{w}^{\mathrm{o}}_{\mathrm{p\,i,MM}}\right)}+\dfrac{1}{\mathrm{AE}_{\mathrm{MM\text{-}1}}\,\dfrac{\mathrm{ra}}{\mathrm{p}}}\right)} = \frac{\mathrm{w}^{\mathrm{n}}_{\mathrm{p\,i,MM\text{-}1}}}{\dfrac{\mathrm{ra}}{\mathrm{p}\,\mathrm{L}\,\Delta\tau\left(1+\mathrm{ra}\,\mathrm{w}^{\mathrm{o}}_{\mathrm{p\,i,MM}}\right)}+\dfrac{1}{\mathrm{AE}_{\mathrm{MM\text{-}1}}}}$$

$$\left(\mathrm{Sp}+\mathrm{AW}_{\mathrm{MM\text{-}1}}+\mathrm{AE}_{\mathrm{MM\text{-}1}}\right)\mathrm{w}^{\mathrm{n}}_{\mathrm{p\,i,MM\text{-}1}} = \mathrm{AW}_{\mathrm{MM\text{-}1}}\,\mathrm{w}^{\mathrm{n}}_{\mathrm{p\,i,MM\text{-}2}}+\mathrm{AE}_{\mathrm{MM\text{-}1}}\,\mathrm{w}^{\mathrm{n}}_{\mathrm{p\,i,MM}}+\mathrm{Su}$$

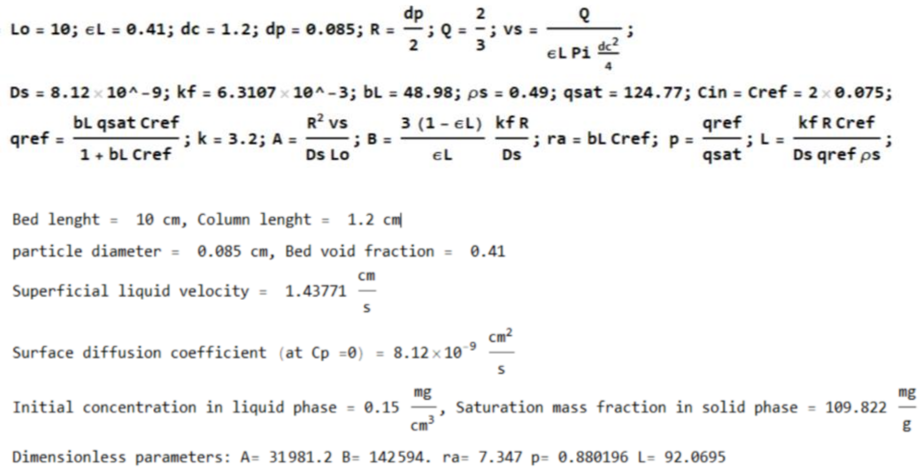
$$\left(\mathrm{Sp}+\mathrm{AW}_{\mathrm{MM\text{-}1}}+\frac{1}{\dfrac{\mathrm{ra}}{\mathrm{p}\,\mathrm{L}\,\Delta\tau\left(1+\mathrm{ra}\,\mathrm{w}^{\mathrm{o}}_{\mathrm{p\,i,MM}}\right)}+\dfrac{1}{\mathrm{AE}_{\mathrm{MM\text{-}1}}}}\right)\mathrm{w}^{\mathrm{n}}_{\mathrm{p\,i,MM\text{-}1}} = \mathrm{AW}_{\mathrm{MM\text{-}1}}\,\mathrm{w}^{\mathrm{n}}_{\mathrm{p\,i,MM\text{-}2}} + \frac{1}{\dfrac{\mathrm{ra}}{\mathrm{p}\,\mathrm{L}\,\Delta\tau\left(1+\mathrm{ra}\,\mathrm{w}^{\mathrm{o}}_{\mathrm{p\,i,MM}}\right)}+\dfrac{1}{\mathrm{AE}_{\mathrm{MM\text{-}1}}}}\,\mathrm{w}^{\mathrm{o}}_{\mathrm{i}}+\mathrm{Su}$$

$$\mathrm{eq[i,MM\text{-}1]{:=}}\left(\mathrm{Sp}+\mathrm{AW}_{\mathrm{MM\text{-}1}}+\frac{1}{\dfrac{\mathrm{ra}}{\mathrm{p}\,\mathrm{L}\,\Delta\tau\left(1+\mathrm{ra}\,\mathrm{w}_{\mathrm{p\,i,MM}}[\tau\text{-}\Delta\tau]\right)}+\dfrac{1}{\mathrm{AE}_{\mathrm{MM\text{-}1}}}}\right)\mathrm{w}_{\mathrm{p\,i,MM\text{-}1}}[\tau] == \mathrm{AW}_{\mathrm{MM\text{-}1}}\,\mathrm{w}_{\mathrm{p\,i,MM\text{-}2}}[\tau] + \frac{1}{\dfrac{\mathrm{ra}}{\mathrm{p}\,\mathrm{L}\,\Delta\tau\left(1+\mathrm{ra}\,\mathrm{w}_{\mathrm{p\,i,MM}}[\tau\text{-}\Delta\tau]\right)}+\dfrac{1}{\mathrm{AE}_{\mathrm{MM\text{-}1}}}}\,\mathrm{w}_{\mathrm{i}}[\tau\text{-}\Delta\tau]+\mathrm{Su}$$

APPENDIX 2: CODE IN THE MATHEMATICA® PROGRAM

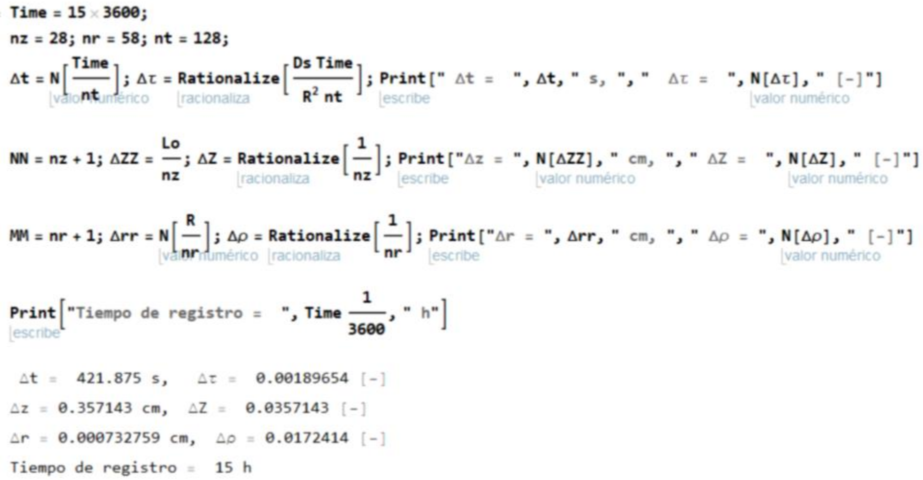
Code in the Mathematica® program for the benzene.

Data



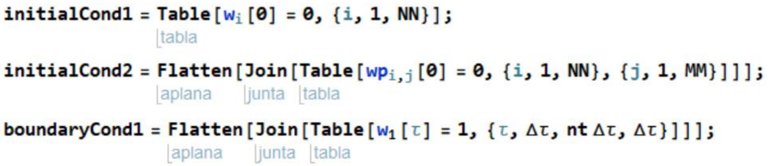
```
Lo = 10; ϵL = 0.41; dc = 1.2; dp = 0.085; R = dp/2; Q = 2/3; vs = Q/(ϵL Pi dc^2/4);

Ds = 8.12 × 10^-9; kf = 6.3107 × 10^-3; bL = 48.98; ρs = 0.49; qsat = 124.77; Cin = Cref = 2 × 0.075;
qref = (bL qsat Cref)/(1 + bL Cref); k = 3.2; A = (R^2 vs)/(Ds Lo); B = (3 (1 - ϵL))/ϵL (kf R)/Ds; ra = bL Cref; p = qref/qsat; L = (kf R Cref)/(Ds qref ρs);

Bed lenght =  10 cm, Column lenght =  1.2 cm
particle diameter =  0.085 cm, Bed void fraction =  0.41
Superficial liquid velocity =  1.43771 cm/s
Surface diffusion coefficient (at Cp =0) = 8.12×10^-9 cm^2/s
Initial concentration in liquid phase = 0.15 mg/cm^3, Saturation mass fraction in solid phase = 109.822 mg/g
Dimensionless parameters: A= 31981.2 B= 142594. ra= 7.347 p= 0.880196 L= 92.0695
```

Meshing



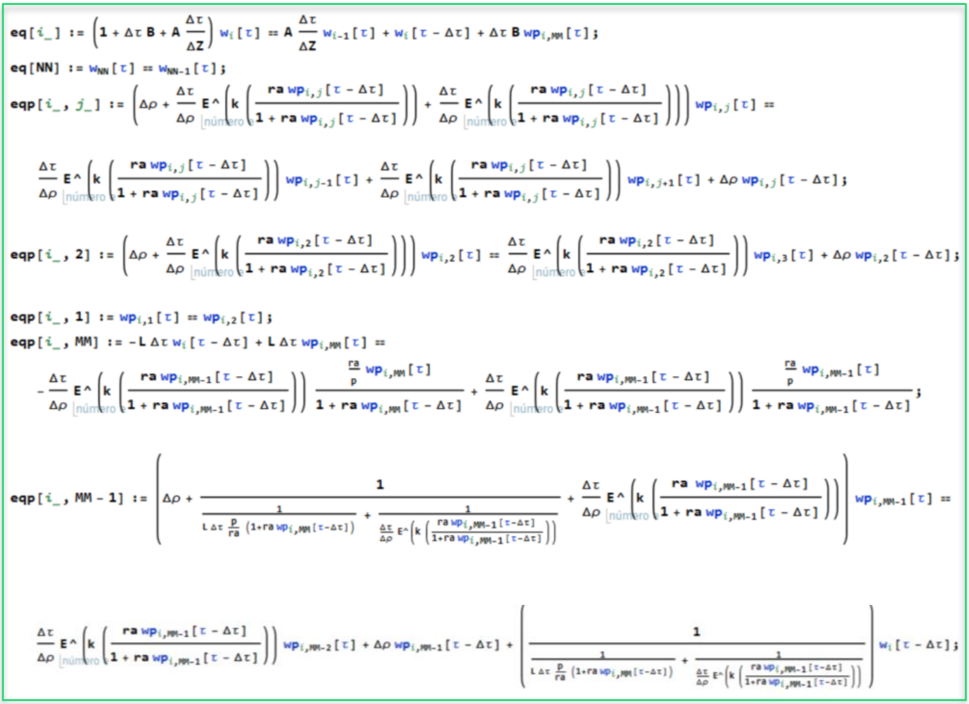
```
Time = 15 × 3600;
nz = 28; nr = 58; nt = 128;
Δt = N[Time/nt]; Δτ = Rationalize[(Ds Time)/(R^2 nt)]; Print[" Δt =  ", Δt, " s, ", "  Δτ =  ", N[Δτ], " [-]"]

NN = nz + 1; ΔZZ = Lo/nz; ΔZ = Rationalize[1/nz]; Print["Δz = ", N[ΔZZ], " cm, ", " ΔZ =  ", N[ΔZ], " [-]"]

MM = nr + 1; Δrr = N[R/nr]; Δρ = Rationalize[1/nr]; Print["Δr = ", Δrr, " cm, ", " Δρ = ", N[Δρ], " [-]"]

Print["Tiempo de registro =  ", Time 1/3600, " h"]

 Δt =  421.875 s,   Δτ =  0.00189654 [-]
Δz = 0.357143 cm,  ΔZ =  0.0357143 [-]
Δr = 0.000732759 cm,  Δρ = 0.0172414 [-]
Tiempo de registro =  15 h
```

Initial and boundary conditions



```
initialCond1 = Table[w_i[0] = 0, {i, 1, NN}];
               [tabla
initialCond2 = Flatten[Join[Table[wp_{i,j}[0] = 0, {i, 1, NN}, {j, 1, MM}]]];
               [aplana   [junta  [tabla
boundaryCond1 = Flatten[Join[Table[w_1[τ] = 1, {τ, Δτ, nt Δτ, Δτ}]]];
                [aplana   [junta  [tabla
```

Discretization



$$\mathrm{eq}[i\_] := \left(1 + \Delta\tau\, B + A\,\frac{\Delta\tau}{\Delta Z}\right) w_i[\tau] == A\,\frac{\Delta\tau}{\Delta Z}\, w_{i-1}[\tau] + w_i[\tau - \Delta\tau] + \Delta\tau\, B\, wp_{i,MM}[\tau];$$

$$\mathrm{eq}[NN] := w_{NN}[\tau] == w_{NN-1}[\tau];$$

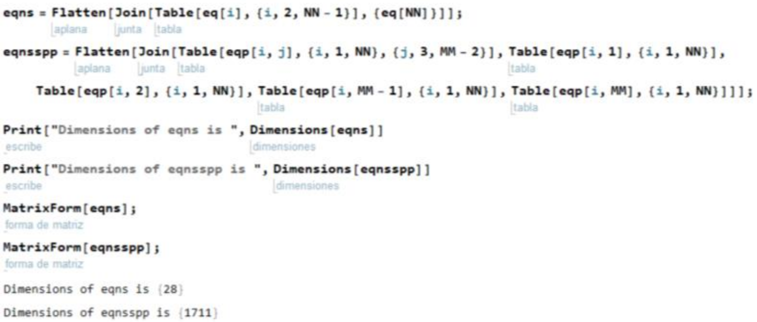
$$\mathrm{eqp}[i\_, j\_] := \left(\Delta\rho + \frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,j}[\tau - \Delta\tau]}{1 + ra\, wp_{i,j}[\tau - \Delta\tau]}\right)\right) + \frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,j}[\tau - \Delta\tau]}{1 + ra\, wp_{i,j}[\tau - \Delta\tau]}\right)\right)\right) wp_{i,j}[\tau] ==$$
$$\frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,j}[\tau - \Delta\tau]}{1 + ra\, wp_{i,j}[\tau - \Delta\tau]}\right)\right) wp_{i,j-1}[\tau] + \frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,j}[\tau - \Delta\tau]}{1 + ra\, wp_{i,j}[\tau - \Delta\tau]}\right)\right) wp_{i,j+1}[\tau] + \Delta\rho\, wp_{i,j}[\tau - \Delta\tau];$$

$$\mathrm{eqp}[i\_, 2] := \left(\Delta\rho + \frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,2}[\tau - \Delta\tau]}{1 + ra\, wp_{i,2}[\tau - \Delta\tau]}\right)\right)\right) wp_{i,2}[\tau] == \frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,2}[\tau - \Delta\tau]}{1 + ra\, wp_{i,2}[\tau - \Delta\tau]}\right)\right) wp_{i,3}[\tau] + \Delta\rho\, wp_{i,2}[\tau - \Delta\tau];$$

$$\mathrm{eqp}[i\_, 1] := wp_{i,1}[\tau] == wp_{i,2}[\tau];$$

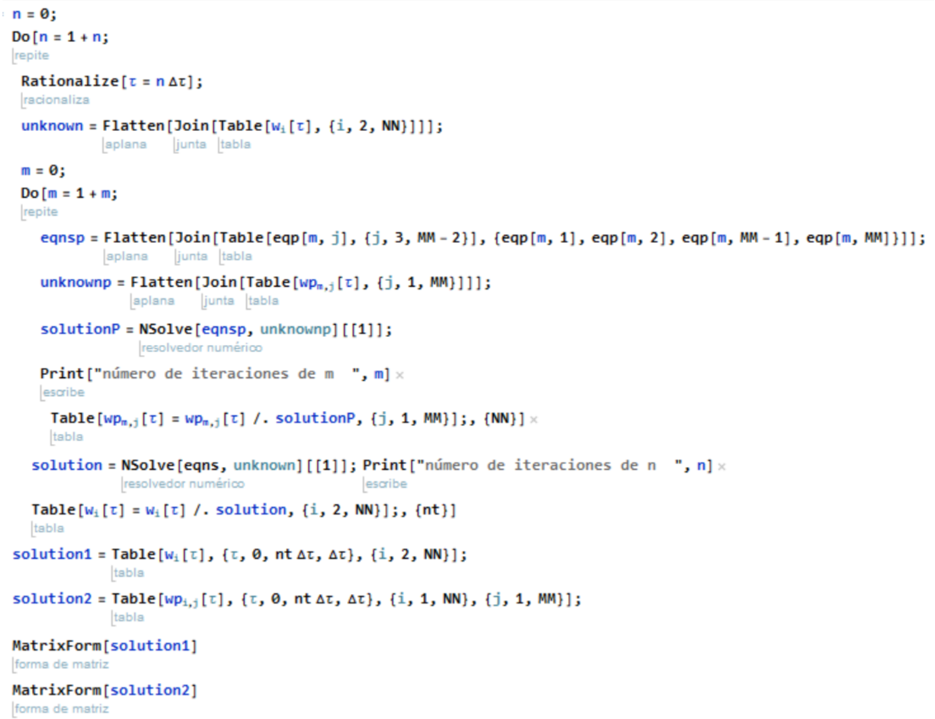
$$\mathrm{eqp}[i\_, MM] := -L\,\Delta\tau\, w_i[\tau - \Delta\tau] + L\,\Delta\tau\, wp_{i,MM}[\tau] ==$$
$$-\frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau - \Delta\tau]}{1 + ra\, wp_{i,MM-1}[\tau - \Delta\tau]}\right)\right) \frac{\frac{ra}{p}\, wp_{i,MM}[\tau]}{1 + ra\, wp_{i,MM}[\tau - \Delta\tau]} + \frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau - \Delta\tau]}{1 + ra\, wp_{i,MM-1}[\tau - \Delta\tau]}\right)\right) \frac{\frac{ra}{p}\, wp_{i,MM-1}[\tau]}{1 + ra\, wp_{i,MM-1}[\tau - \Delta\tau]};$$

$$\mathrm{eqp}[i\_, MM - 1] := \left(\Delta\rho + \frac{1}{\frac{1}{L\,\Delta\tau\,\frac{p}{ra}\,(1 + ra\, wp_{i,MM}[\tau - \Delta\tau])} + \frac{1}{\frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau - \Delta\tau]}{1 + ra\, wp_{i,MM-1}[\tau - \Delta\tau]}\right)\right)}} + \frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau - \Delta\tau]}{1 + ra\, wp_{i,MM-1}[\tau - \Delta\tau]}\right)\right)\right) wp_{i,MM-1}[\tau] ==$$
$$\frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau - \Delta\tau]}{1 + ra\, wp_{i,MM-1}[\tau - \Delta\tau]}\right)\right) wp_{i,MM-2}[\tau] + \Delta\rho\, wp_{i,MM-1}[\tau - \Delta\tau] + \left(\frac{1}{\frac{1}{L\,\Delta\tau\,\frac{p}{ra}\,(1 + ra\, wp_{i,MM}[\tau - \Delta\tau])} + \frac{1}{\frac{\Delta\tau}{\Delta\rho}\,\mathrm{E}^\wedge\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau - \Delta\tau]}{1 + ra\, wp_{i,MM-1}[\tau - \Delta\tau]}\right)\right)}}\right) w_i[\tau - \Delta\tau];$$



```
eqns = Flatten[Join[Table[eq[i], {i, 2, NN - 1}], {eq[NN]}]];
       [aplana  [junta [tabla
eqnsspp = Flatten[Join[Table[eqp[i, j], {i, 1, NN}, {j, 3, MM - 2}], Table[eqp[i, 1], {i, 1, NN}],
          [aplana  [junta [tabla                                          [tabla
    Table[eqp[i, 2], {i, 1, NN}], Table[eqp[i, MM - 1], {i, 1, NN}], Table[eqp[i, MM], {i, 1, NN}]]];
                                  [tabla                                [tabla
Print["Dimensions of eqns is ", Dimensions[eqns]]
[escribe                        [dimensiones
Print["Dimensions of eqnsspp is ", Dimensions[eqnsspp]]
[escribe                           [dimensiones
MatrixForm[eqns];
[forma de matriz
MatrixForm[eqnsspp];
[forma de matriz

Dimensions of eqns is {28}
Dimensions of eqnsspp is {1711}
```

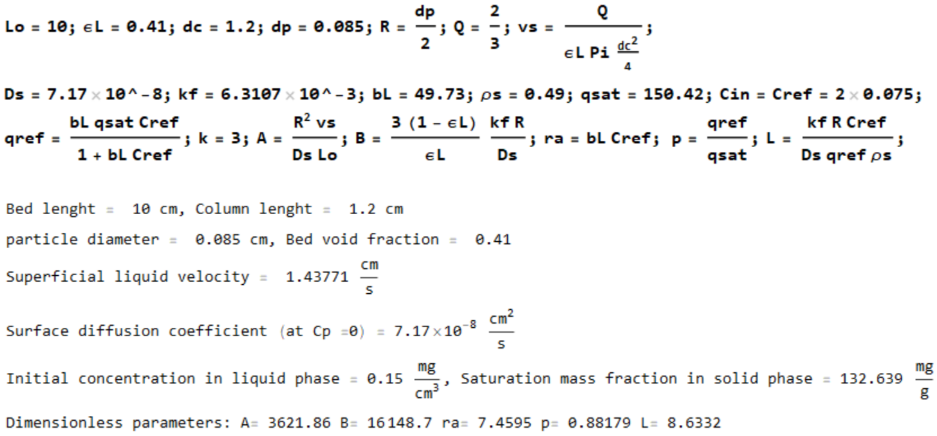
Solution



```
n = 0;
Do[n = 1 + n;
 Rationalize[τ = n Δτ];
 unknown = Flatten[Join[Table[w_i[τ], {i, 2, NN}]]];
 m = 0;
 Do[m = 1 + m;
   eqnsp = Flatten[Join[Table[eqp[m, j], {j, 3, MM - 2}], {eqp[m, 1], eqp[m, 2], eqp[m, MM - 1], eqp[m, MM]}]];
   unknownp = Flatten[Join[Table[wp_{m,j}[τ], {j, 1, MM}]]];
   solutionP = NSolve[eqnsp, unknownp][[1]];
   Print["número de iteraciones de m  ", m]
    Table[wp_{m,j}[τ] = wp_{m,j}[τ] /. solutionP, {j, 1, MM}];, {NN}]
  solution = NSolve[eqns, unknown][[1]]; Print["número de iteraciones de n  ", n]
  Table[w_i[τ] = w_i[τ] /. solution, {i, 2, NN}];, {nt}]
solution1 = Table[w_i[τ], {τ, 0, nt Δτ, Δτ}, {i, 2, NN}];
solution2 = Table[wp_{i,j}[τ], {τ, 0, nt Δτ, Δτ}, {i, 1, NN}, {j, 1, MM}];
MatrixForm[solution1]
MatrixForm[solution2]
```

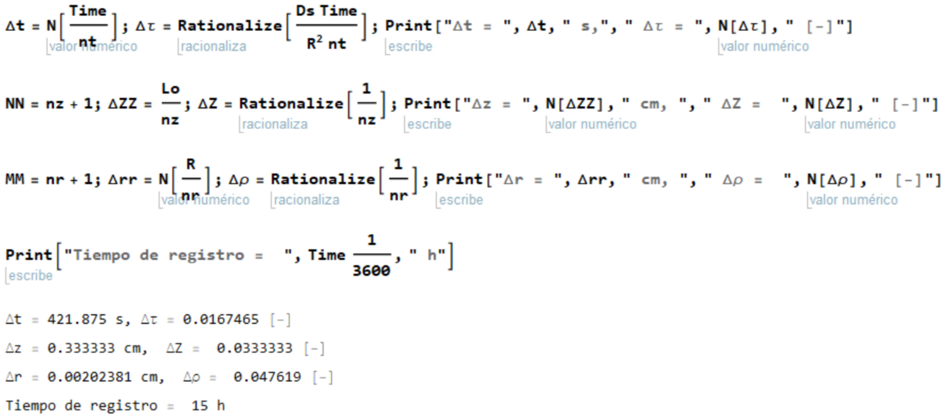
Code in the Mathematica® program for the toluene.

Data



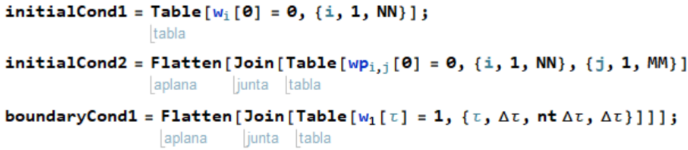
```
Lo = 10; ϵL = 0.41; dc = 1.2; dp = 0.085; R = dp/2; Q = 2/3; vs = Q/(ϵL Pi dc^2/4);

Ds = 7.17 × 10^-8; kf = 6.3107 × 10^-3; bL = 49.73; ρs = 0.49; qsat = 150.42; Cin = Cref = 2 × 0.075;
qref = bL qsat Cref/(1 + bL Cref); k = 3; A = R^2 vs/(Ds Lo); B = 3 (1 - ϵL)/ϵL kf R/Ds; ra = bL Cref; p = qref/qsat; L = kf R Cref/(Ds qref ρs);

Bed lenght = 10 cm, Column lenght = 1.2 cm
particle diameter = 0.085 cm, Bed void fraction = 0.41
Superficial liquid velocity = 1.43771 cm/s
Surface diffusion coefficient (at Cp =0) = 7.17×10^-8 cm^2/s
Initial concentration in liquid phase = 0.15 mg/cm^3, Saturation mass fraction in solid phase = 132.639 mg/g
Dimensionless parameters: A= 3621.86 B= 16148.7 ra= 7.4595 p= 0.88179 L= 8.6332
```

Meshing



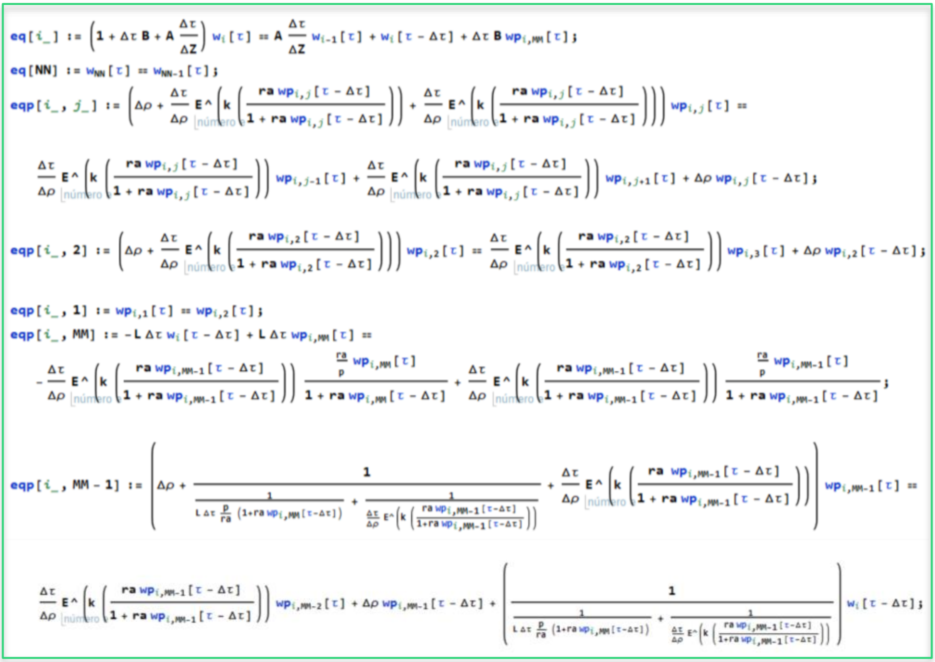
```
Time = 15 × 3600;
nz = 30; nr = 21; nt = 128;
Δt = N[Time/nt]; Δτ = Rationalize[Ds Time/(R^2 nt)]; Print["Δt = ", Δt, " s,", " Δτ = ", N[Δτ], " [-]"]

NN = nz + 1; ΔZZ = Lo/nz; ΔZ = Rationalize[1/nz]; Print["Δz = ", N[ΔZZ], " cm, ", " ΔZ = ", N[ΔZ], " [-]"]

MM = nr + 1; Δrr = N[R/nr]; Δρ = Rationalize[1/nr]; Print["Δr = ", Δrr, " cm, ", " Δρ = ", N[Δρ], " [-]"]

Print["Tiempo de registro = ", Time 1/3600, " h"]

Δt = 421.875 s, Δτ = 0.0167465 [-]
Δz = 0.333333 cm, ΔZ = 0.0333333 [-]
Δr = 0.00202381 cm, Δρ = 0.047619 [-]
Tiempo de registro = 15 h
```

Initial and boundary conditions

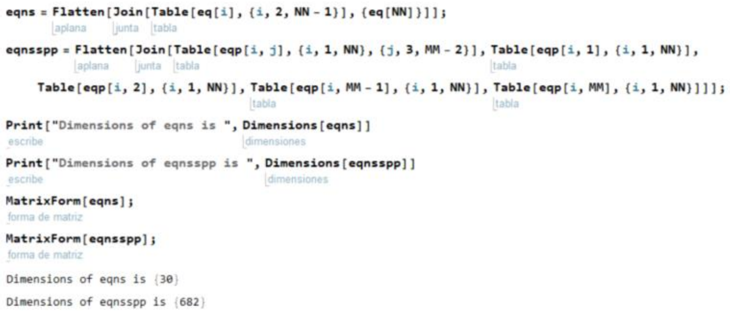


```
initialCond1 = Table[w_i[0] = 0, {i, 1, NN}];

initialCond2 = Flatten[Join[Table[wp_{i,j}[0] = 0, {i, 1, NN}, {j, 1, MM}]]];

boundaryCond1 = Flatten[Join[Table[w_1[τ] = 1, {τ, Δτ, nt Δτ, Δτ}]]];
```

Discretization



```
eq[i_] := (1 + Δτ B + A Δτ/ΔZ) w_i[τ] == A Δτ/ΔZ w_{i-1}[τ] + w_i[τ - Δτ] + Δτ B wp_{i,MM}[τ];
eq[NN] := w_NN[τ] == w_{NN-1}[τ];
eqp[i_, j_] := (Δρ + Δτ/Δρ E^(k ((ra wp_{i,j}[τ - Δτ])/(1 + ra wp_{i,j}[τ - Δτ]))) + Δτ/Δρ E^(k ((ra wp_{i,j}[τ - Δτ])/(1 + ra wp_{i,j}[τ - Δτ])))) wp_{i,j}[τ] ==

   Δτ/Δρ E^(k ((ra wp_{i,j}[τ - Δτ])/(1 + ra wp_{i,j}[τ - Δτ]))) wp_{i,j-1}[τ] + Δτ/Δρ E^(k ((ra wp_{i,j}[τ - Δτ])/(1 + ra wp_{i,j}[τ - Δτ]))) wp_{i,j+1}[τ] + Δρ wp_{i,j}[τ - Δτ];

eqp[i_, 2] := (Δρ + Δτ/Δρ E^(k ((ra wp_{i,2}[τ - Δτ])/(1 + ra wp_{i,2}[τ - Δτ])))) wp_{i,2}[τ] == Δτ/Δρ E^(k ((ra wp_{i,2}[τ - Δτ])/(1 + ra wp_{i,2}[τ - Δτ]))) wp_{i,3}[τ] + Δρ wp_{i,2}[τ - Δτ];

eqp[i_, 1] := wp_{i,1}[τ] == wp_{i,2}[τ];
eqp[i_, MM] := -L Δτ w_i[τ - Δτ] + L Δτ wp_{i,MM}[τ] ==
   -Δτ/Δρ E^(k ((ra wp_{i,MM-1}[τ - Δτ])/(1 + ra wp_{i,MM-1}[τ - Δτ]))) (ra/p wp_{i,MM}[τ])/(1 + ra wp_{i,MM}[τ - Δτ]) + Δτ/Δρ E^(k ((ra wp_{i,MM-1}[τ - Δτ])/(1 + ra wp_{i,MM-1}[τ - Δτ]))) (ra/p wp_{i,MM-1}[τ])/(1 + ra wp_{i,MM-1}[τ - Δτ]);

eqp[i_, MM - 1] := (Δρ + 1/(1/(L Δτ p/ra (1+ra wp_{i,MM}[τ-Δτ])) + 1/(Δτ/Δρ E^(k ((ra wp_{i,MM-1}[τ-Δτ])/(1+ra wp_{i,MM-1}[τ-Δτ]))))) + Δτ/Δρ E^(k ((ra wp_{i,MM-1}[τ - Δτ])/(1 + ra wp_{i,MM-1}[τ - Δτ])))) wp_{i,MM-1}[τ] ==

   Δτ/Δρ E^(k ((ra wp_{i,MM-1}[τ - Δτ])/(1 + ra wp_{i,MM-1}[τ - Δτ]))) wp_{i,MM-2}[τ] + Δρ wp_{i,MM-1}[τ - Δτ] + (1/(1/(L Δτ p/ra (1+ra wp_{i,MM}[τ-Δτ])) + 1/(Δτ/Δρ E^(k ((ra wp_{i,MM-1}[τ-Δτ])/(1+ra wp_{i,MM-1}[τ-Δτ])))))) w_i[τ - Δτ];
```



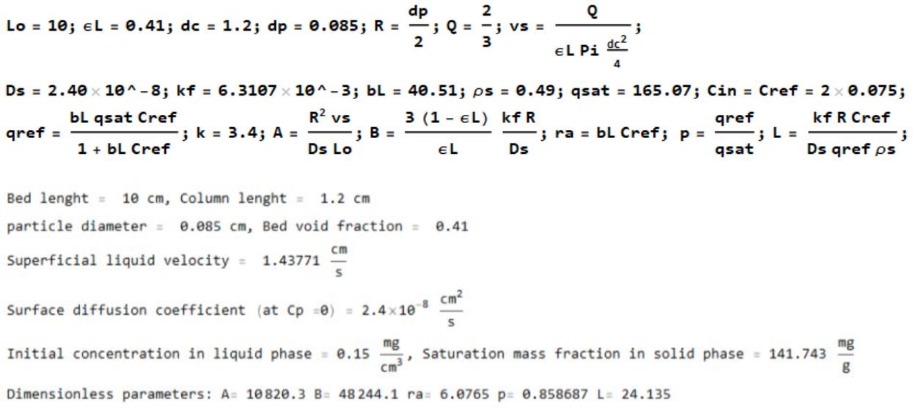
```
eqns = Flatten[Join[Table[eq[i], {i, 2, NN - 1}], {eq[NN]}]];

eqnsspp = Flatten[Join[Table[eqp[i, j], {i, 1, NN}, {j, 3, MM - 2}], Table[eqp[i, 1], {i, 1, NN}],
    Table[eqp[i, 2], {i, 1, NN}], Table[eqp[i, MM - 1], {i, 1, NN}], Table[eqp[i, MM], {i, 1, NN}]]];

Print["Dimensions of eqns is ", Dimensions[eqns]]

Print["Dimensions of eqnsspp is ", Dimensions[eqnsspp]]

MatrixForm[eqns];

MatrixForm[eqnsspp];

Dimensions of eqns is {30}

Dimensions of eqnsspp is {682}
```

Solution

```
n = 0;
Do[n = 1 + n;
|repite
 Rationalize[τ = n Δτ];
 |racionaliza
 unknown = Flatten[Join[Table[wᵢ[τ], {i, 2, NN}]]];
           |aplana    |junta |tabla
 m = 0;
 Do[m = 1 + m;
 |repite
   eqnsp = Flatten[Join[Table[eqp[m, j], {j, 3, MM - 2}], {eqp[m, 1], eqp[m, 2], eqp[m, MM - 1], eqp[m, MM]}]];
           |aplana    |junta |tabla
   unknownp = Flatten[Join[Table[wpₘ,ⱼ[τ], {j, 1, MM}]]];
              |aplana    |junta |tabla
   solutionP = NSolve[eqnsp, unknownp][[1]];
               |resolvedor numérico
   Print["número de iteraciones de m  ", m] ×
   |escribe
    Table[wpₘ,ⱼ[τ] = wpₘ,ⱼ[τ] /. solutionP, {j, 1, MM}];, {NN}] ×
    |tabla
  solution = NSolve[eqns, unknown][[1]]; Print["número de iteraciones de n  ", n] ×
             |resolvedor numérico          |escribe
  Table[wᵢ[τ] = wᵢ[τ] /. solution, {i, 2, NN}];, {nt}]
  |tabla
solution1 = Table[wᵢ[τ], {τ, 0, nt Δτ, Δτ}, {i, 2, NN}];
            |tabla
solution2 = Table[wpᵢ,ⱼ[τ], {τ, 0, nt Δτ, Δτ}, {i, 1, NN}, {j, 1, MM}];
            |tabla
MatrixForm[solution1]
|forma de matriz
MatrixForm[solution2]
|forma de matriz
```

Code in the Mathematica® program for the o-xylene.

Data



$$Lo = 10;\ \epsilon L = 0.41;\ dc = 1.2;\ dp = 0.085;\ R = \frac{dp}{2};\ Q = \frac{2}{3};\ vs = \frac{Q}{\epsilon L\ Pi\ \frac{dc^2}{4}};$$

$$Ds = 2.40 \times 10\text{^}-8;\ kf = 6.3107 \times 10\text{^}-3;\ bL = 40.51;\ \rho s = 0.49;\ qsat = 165.07;\ Cin = Cref = 2 \times 0.075;$$

$$qref = \frac{bL\ qsat\ Cref}{1 + bL\ Cref};\ k = 3.4;\ A = \frac{R^2\ vs}{Ds\ Lo};\ B = \frac{3\ (1 - \epsilon L)}{\epsilon L}\ \frac{kf\ R}{Ds};\ ra = bL\ Cref;\ p = \frac{qref}{qsat};\ L = \frac{kf\ R\ Cref}{Ds\ qref\ \rho s};$$

Bed lenght = 10 cm, Column lenght = 1.2 cm

particle diameter = 0.085 cm, Bed void fraction = 0.41

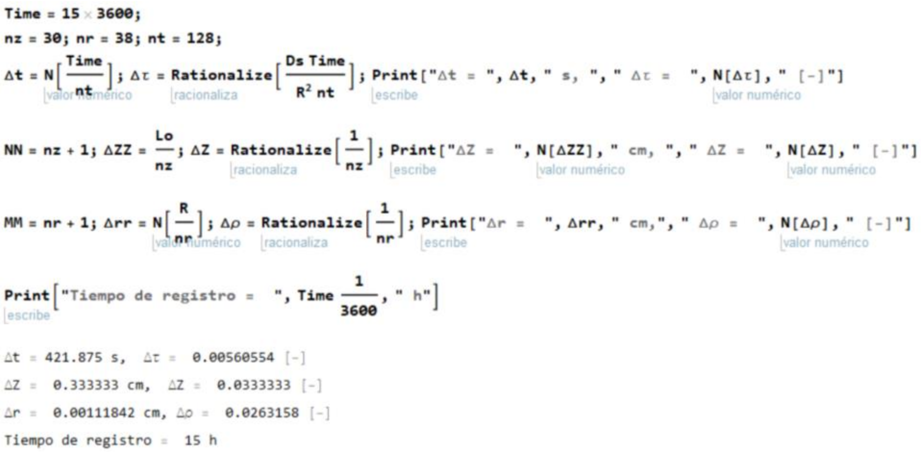
Superficial liquid velocity = 1.43771 $\frac{cm}{s}$

Surface diffusion coefficient (at Cp = 0) = 2.4×10^{-8} $\frac{cm^2}{s}$

Initial concentration in liquid phase = 0.15 $\frac{mg}{cm^3}$, Saturation mass fraction in solid phase = 141.743 $\frac{mg}{g}$

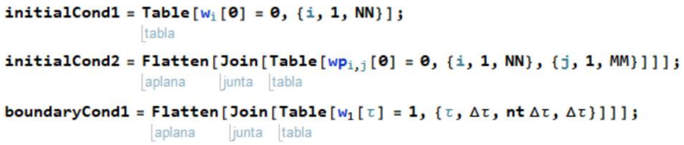
Dimensionless parameters: A= 10820.3 B= 48244.1 ra= 6.0765 p= 0.858687 L= 24.135

Meshing



```
Time = 15 × 3600;
nz = 30; nr = 38; nt = 128;
Δt = N[Time/nt]; Δτ = Rationalize[Ds Time/(R^2 nt)]; Print["Δt = ", Δt, " s, ", " Δτ = ", N[Δτ], " [-]"]

NN = nz + 1; ΔZZ = Lo/nz; ΔZ = Rationalize[1/nz]; Print["ΔZ = ", N[ΔZZ], " cm, ", " ΔZ = ", N[ΔZ], " [-]"]

MM = nr + 1; Δrr = N[R/nr]; Δρ = Rationalize[1/nr]; Print["Δr = ", Δrr, " cm,", " Δρ = ", N[Δρ], " [-]"]

Print["Tiempo de registro = ", Time 1/3600, " h"]

Δt = 421.875 s,  Δτ = 0.00560554 [-]
ΔZ = 0.333333 cm,  ΔZ = 0.0333333 [-]
Δr = 0.00111842 cm, Δρ = 0.0263158 [-]
Tiempo de registro = 15 h
```

Initial and boundary conditions



```
initialCond1 = Table[w_i[0] = 0, {i, 1, NN}];
initialCond2 = Flatten[Join[Table[wp_{i,j}[0] = 0, {i, 1, NN}, {j, 1, MM}]]];
boundaryCond1 = Flatten[Join[Table[w_1[τ] = 1, {τ, Δτ, nt Δτ, Δτ}]]];
```

Discretization

$$eq[i\_] := \left(1 + \Delta\tau\, B + A\,\frac{\Delta\tau}{\Delta Z}\right) w_i[\tau] == A\,\frac{\Delta\tau}{\Delta Z}\, w_{i-1}[\tau] + w_i[\tau - \Delta\tau] + \Delta\tau\, B\, wp_{i,MM}[\tau];$$

$$eq[NN] := w_{NN}[\tau] == w_{NN-1}[\tau];$$

$$eqp[i\_, j\_] := \left(\Delta\rho + \frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,j}[\tau-\Delta\tau]}{1 + ra\, wp_{i,j}[\tau-\Delta\tau]}\right)\right) + \frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,j}[\tau-\Delta\tau]}{1 + ra\, wp_{i,j}[\tau-\Delta\tau]}\right)\right)\right) wp_{i,j}[\tau] ==$$

$$\frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,j}[\tau-\Delta\tau]}{1 + ra\, wp_{i,j}[\tau-\Delta\tau]}\right)\right) wp_{i,j-1}[\tau] + \frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,j}[\tau-\Delta\tau]}{1 + ra\, wp_{i,j}[\tau-\Delta\tau]}\right)\right) wp_{i,j+1}[\tau] + \Delta\rho\, wp_{i,j}[\tau-\Delta\tau];$$

$$eqp[i\_, 2] := \left(\Delta\rho + \frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,2}[\tau-\Delta\tau]}{1 + ra\, wp_{i,2}[\tau-\Delta\tau]}\right)\right)\right) wp_{i,2}[\tau] == \frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,2}[\tau-\Delta\tau]}{1 + ra\, wp_{i,2}[\tau-\Delta\tau]}\right)\right) wp_{i,3}[\tau] + \Delta\rho\, wp_{i,2}[\tau-\Delta\tau];$$

$$eqp[i\_, 1] := wp_{i,1}[\tau] == wp_{i,2}[\tau];$$

$$eqp[i\_, MM] := -L\,\Delta\tau\, w_i[\tau-\Delta\tau] + L\,\Delta\tau\, wp_{i,MM}[\tau] ==$$

$$-\frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau-\Delta\tau]}{1 + ra\, wp_{i,MM-1}[\tau-\Delta\tau]}\right)\right) \frac{\frac{ra}{p}\, wp_{i,MM}[\tau]}{1 + ra\, wp_{i,MM}[\tau-\Delta\tau]} + \frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau-\Delta\tau]}{1 + ra\, wp_{i,MM-1}[\tau-\Delta\tau]}\right)\right) \frac{\frac{ra}{p}\, wp_{i,MM-1}[\tau]}{1 + ra\, wp_{i,MM-1}[\tau-\Delta\tau]};$$

$$eqp[i\_, MM-1] := \left(\Delta\rho + \frac{1}{\frac{1}{L\,\Delta\tau\,\frac{p}{ra}\,(1+ra\, wp_{i,MM}[\tau-\Delta\tau])} + \frac{1}{\frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau-\Delta\tau]}{1+ra\, wp_{i,MM-1}[\tau-\Delta\tau]}\right)\right)}} + \frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau-\Delta\tau]}{1 + ra\, wp_{i,MM-1}[\tau-\Delta\tau]}\right)\right)\right) wp_{i,MM-1}[\tau] ==$$

$$\frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau-\Delta\tau]}{1 + ra\, wp_{i,MM-1}[\tau-\Delta\tau]}\right)\right) wp_{i,MM-2}[\tau] + \Delta\rho\, wp_{i,MM-1}[\tau-\Delta\tau] + \left(\frac{1}{\frac{1}{L\,\Delta\tau\,\frac{p}{ra}\,(1+ra\, wp_{i,MM}[\tau-\Delta\tau])} + \frac{1}{\frac{\Delta\tau}{\Delta\rho}\,E\hat{}\left(k\left(\frac{ra\, wp_{i,MM-1}[\tau-\Delta\tau]}{1+ra\, wp_{i,MM-1}[\tau-\Delta\tau]}\right)\right)}}\right) w_i[\tau-\Delta\tau];$$

```
eqns = Flatten[Join[Table[eq[i], {i, 2, NN - 1}], {eq[NN]}]];

eqnsspp = Flatten[Join[Table[eqp[i, j], {i, 1, NN}, {j, 3, MM - 2}], Table[eqp[i, 1], {i, 1, NN}],
    Table[eqp[i, 2], {i, 1, NN}], Table[eqp[i, MM - 1], {i, 1, NN}], Table[eqp[i, MM], {i, 1, NN}]]];

Print["Dimensions of eqns is ", Dimensions[eqns]]

Print["Dimensions of eqnsspp is ", Dimensions[eqnsspp]]

MatrixForm[eqns];

MatrixForm[eqnsspp];

Dimensions of eqns is {30}

Dimensions of eqnsspp is {1209}
```

Solution

```
n = 0;
Do[n = 1 + n;
 Rationalize[τ = n Δτ];
 unknown = Flatten[Join[Table[w_i[τ], {i, 2, NN}]]];
 m = 0;
 Do[m = 1 + m;
   eqnsp = Flatten[Join[Table[eqp[m, j], {j, 3, MM - 2}], {eqp[m, 1], eqp[m, 2], eqp[m, MM - 1], eqp[m, MM]}]];
   unknownp = Flatten[Join[Table[wp_m,j[τ], {j, 1, MM}]]];
   solutionP = NSolve[eqnsp, unknownp][[1]];
   Print["número de iteraciones de m  ", m]
    Table[wp_m,j[τ] = wp_m,j[τ] /. solutionP, {j, 1, MM}];, {NN}]
  solution = NSolve[eqns, unknown][[1]]; Print["número de iteraciones de n  ", n]
  Table[w_i[τ] = w_i[τ] /. solution, {i, 2, NN}];, {nt}]
solution1 = Table[w_i[τ], {τ, 0, nt Δτ, Δτ}, {i, 2, NN}];
solution2 = Table[wp_i,j[τ], {τ, 0, nt Δτ, Δτ}, {i, 1, NN}, {j, 1, MM}];
MatrixForm[solution1]
MatrixForm[solution2]
```