MODELING OF THE PACKED THREAD DYEING PROCESS

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Abstract. *A mathematical model for the simulation of the thread dyeing process in bobbins is proposed. This model is based on the laws of mass and chemical species conservation, being utilized the Method of Volume Averaging. The model is developed in the microscale, where are found the textile fibers in contact with the dyeing bath contained into the micropores. The obtained equation in the microscale has all the relevant information, which allows carrying these information to the upper scales modeling. In this work the closure problem is also modeled, making possible to calculate the effective diffusion coefficient, without the necessity of correlations or empirical data.*

***Keywords**. The Method of Volume Averaging, Modeling, Dyeing, Textile, Closure Problem.*

1. Introduction

The textile dyeing can be made directly in the fabric or in the threads. The dyeing of threads before weaving provides higher quality to the final product, when compared to the traditional process.

The threads dyeing process in bobbins is characterized by the continuous flow of the dyeing bath through the bobbins until the exhaustion of the dye, as presented by Cegarra (1992).

Dyeing equipments have been designed for short runs and even so the quality specifications must be the same or higher with a low cost. With the recent increase in worldwide environmental issues, the environmental protection regulations for textile processing and ecological demands on dyeing system are growing, so, developments in equipments, dye chemistry, and a review of processing, techniques and procedures can lead to a successful solution of the problems faced by the current dyeing industry, as discussed by Hyde et al. (1996).

In this work a study of the packed thread dyeing process in bobbins is made, with several types of dyes, such as acid, basic, direct, reactive and other dyes. A mathematical model for the simulation of the thread dyeing process is the main objective of this work, where the model is based on the laws of mass and chemical species conservation. The Method of Volume Averaging, described by Whitaker (1985) is utilized for the development of the model from the microscale, where the textile fibers are in contact with the dyeing bath contained into the micropores, to the macroscale, that is the dyeing equipment with thread bobbins and the dyeing bath.

The effective transport properties in two-phase periodic media are of considerable interest, because of this, theoretical derivations of the effective parameters have also appeared in many ways. The Method of Volume Averaging has been applied to diffusion problems. Numerical values for the effective diffusivity in two-dimensional periodic medium have been derived in literature using this approach.

Theoretical derivations of the effective diffusivity in thread bobbins are developed in this work, these theoretical equations are called the closure problem. The closure problem as well as the effective diffusivity depend on the geometric parameters and physical properties.

2. Description of the thread dyeing process in bobbins

The mathematical model developed in this work simulates the thread dyeing process in bobbins in a dyeing equipment of a textile industry.

The dyeing equipment is shown in Fig. (1) where the dyeing bath is pumped through the bobbins. After the fluid reaches the support it is recycled, and then pumped again. This process is repeated until dye exhaustion, and then the dyeing process is finished, Perkins (1997). The flow direction can be inside to outside (I-O) or outside to inside (O-I).

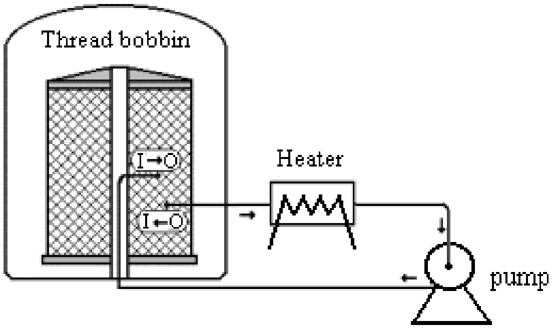

Figure (1). Equipment for thread bobbin dyeing.

3. Matematical Modeling

The Method of Volume Averaging, presented by Whitaker (1985), was utilized to develop the mathematical model in this work. This method allows modeling the problem in different scales, as presented by Revello (2002). In this paper only the mathematical modeling in the microscale will be shown, where the textile fibers are in contact with the dyeing bath contained into the porous of the thread, but in future works the modeling of the intermediary scale will be presented, which is the area where are the bobbins thread along with the dyeing bath, and the macroscale, formed by the thread bobbins immersed in the dyeing bath inside the equipment.

Figure (2) shows the problem scales of this study. The *k*-phase represents the textile fibers in contact with a dyeing bath, which is identified as the γ-phase. The *k*-phase is assumed to be a rigid and impermeable solid in this modeling.

The dye is the chemical species of interest in this work. It is transferred from the dyeing bath to the γ-k interface during the dyeing process.

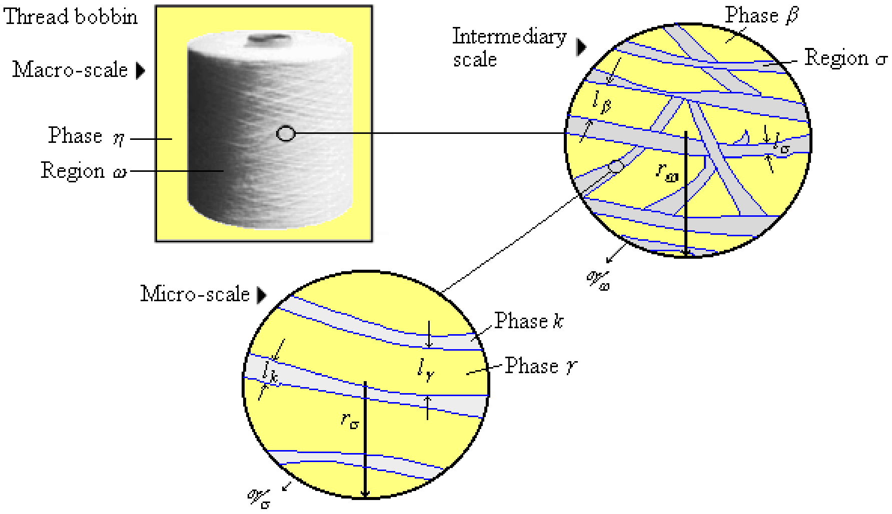

Figure 2. Thread bobbin in different scales.

3.1. Mathematical Modeling in the Microscale

The mathematical modeling presented in this section includes the k and γ phases, which represent the microscale. The microscale is formed by the textile fibers (solid phase) denominated of *k*-phase and by the dyeing bath (fluid phase or γ-phase), as shown in Fig. (2).

The microscale can be interpreted as an enlarged image of the thread in the microscope. The γ-k interface is a fiber surface where chemical reactions can take place, so the hypothesis that dyeing occurs just in the fiber surface will be assumed.

The textile fibers can be natural or synthetic. The most utilized fiber among the natural ones is cotton. Polyester and acrylic are increasingly becoming more important in the textile industry, among the synthetic ones.

The chemical reaction in the fiber surface results in the textile dyeing, so a good reaction will result in a better quality of the product. Some factors have interference in this reaction, but the most important is the interaction among dyes and fibers, due to that, some types of dyes can be just used with some specific fibers. For example, cotton fibers are dyed with reactive dyes on the other hand acrylic fibers can not, so it is used a basic dye instead.

Aiming to develop a general mathematical model, where different dye classes and textile fibers could be utilized, the equations and their boundary conditions in the microscale will be written with two reactions terms, the first one in Eq. (2) is the reactive and the second one is the adsorptive. The mechanism of the alkaline hydrolysis competes with the formation of covalent bonds between dye and fiber. Therefore, the hydrolysis rate of reactive dyes is also an indirect measurement of the reactivity of the dye to cellulose at a given temperature and pH value, as discussed by Klancnik and Gorensek (1997).

The reactive term will be utilized when reactive dyes are applied, so in this situation the coefficient Ψ is 1 and Ω is 0. When another dye is utilized the adsorptive term is necessary, so Ψ is 0 and Ω is 1.

$$\frac{\partial C_A}{\partial t} = \nabla\cdot(\mathrm{D}_\gamma \nabla C_A) + \Psi\, r_A''' , \qquad \text{in the } \gamma\text{- phase} \tag{1}$$

$$\text{C.C.1} \qquad -\boldsymbol{n}_{\gamma\kappa}\cdot \mathrm{D}_\gamma \nabla C_A = \Psi\, k C_A + \Omega \frac{\partial C_{As}}{\partial t} , \qquad \text{at } \mathscr{A}_{\gamma k} \tag{2}$$

$$\text{C.C.2} \qquad C_A = \mathscr{F}(r,t) , \qquad \text{at } \mathscr{A}_{\gamma e} \tag{3}$$

$$\text{C.I} \qquad C_A = \mathscr{G}(r) \qquad \text{at } t = 0 \tag{4}$$

The variable C_A is the molar concentration, C_{As} is the surface molar concentration, t is the time, D_γ is the molecular diffusivity in the γ- phase, r_A''' is the molar rate of the hydrolysis chemical reaction, $n_{\gamma k}$ represents the unit normal vector pointing from the γ- phase toward the k - phase, k is the reaction rate constant, $\mathscr{A}_{\gamma k}$ represents the interfacial area γ- k and $\mathscr{A}_{\gamma e}$ represents the entrances and exits of the γ- phase at the boundary of the intermediary scale region, as shown in Fig. (4).

The chemical species conservation equation is written according to Eq. (1), where the convective term is neglected in this scale because the velocity is zero into the thread. Equation (2) is the first boundary condition, and represents that every molar flux arriving in the γ- k interface is reacted or adsorbed in the same interface, following a given kinetic. When the problem has homogeneous and heterogeneous reaction, the constant Ψ will be 1 and Ω will be 0. When just adsorption occurs, Ψ will be 0 and Ω will be 1.

The functions in the second condition and initial condition represented by Eq. (3) and (4), respectively, are not known, so it is impossible to solve Eq. (1) to (4). To solve this problem the Method of Volume Averaging will be applied in these equations. It will allow determining the average concentration, which is sufficient because there is no need to have the point concentration.

In the Method of Volume Averaging the superficial average concentration is given by Eq. (5).

$$\langle C_A \rangle = \frac{1}{\mathrm{V}_\sigma} \int_{V_\gamma} C_A \, dV \tag{5}$$

The intrinsic average concentration, defined by Eq. (6), is a preferred form to represent the average concentration for the development of the mathematical modeling. Because of this, the final equation will be written with intrinsic average concentration.

$$\langle C_A \rangle^\gamma = \frac{1}{V_\gamma} \int_{V_\gamma} C_A \, dV \tag{6}$$

These two concentrations are related by Eq. (7), where the ε_γ is the porosity in the γ- phase given by Eq. (8).

$$\langle C_A \rangle = \varepsilon_\gamma \langle C_A \rangle^\gamma \tag{7}$$

$$\varepsilon_\gamma = \frac{V_\gamma}{\mathrm{V}_\sigma} \tag{8}$$

Equation (1) is integrated over the domain V_γ and divided by V_σ to obtain Eq. (9). Since V_γ is not a function of time, the left hand side of Eq. (9) becomes Eq. (10).

$$\frac{1}{V_\sigma}\int_{V_\gamma}\frac{\partial C_A}{\partial t}dV = \frac{1}{V_\sigma}\int_{V_\gamma}\nabla\cdot(\mathrm{D}_\gamma\nabla C_A)dV + \frac{1}{V_\sigma}\int_{V_\gamma}\Psi\, r_A^{'''}\,dV \tag{9}$$

$$\varepsilon_\gamma\frac{\partial\langle C_A\rangle^\gamma}{\partial t} = \left\langle\nabla\cdot\left(\mathrm{D}_\gamma\nabla C_A\right)\right\rangle + \Psi\left\langle r_A^{'''}\right\rangle \tag{10}$$

Application of the spatial averaging theorem, presented by Howes and Whitaker (1985), in the diffusive term give us

$$\varepsilon_\gamma\frac{\partial\langle C_A\rangle^\gamma}{\partial t} = \nabla\cdot\left(\nabla\left\langle \mathrm{D}_\gamma C_A\right\rangle + \frac{1}{\mathrm{V}_\sigma}\int_{A_{\gamma\kappa}}\boldsymbol{n}_{\gamma\kappa}\mathrm{D}_\gamma C_A\,dA\right) + \frac{1}{\mathrm{V}_\sigma}\int_{A_{\gamma\kappa}}\boldsymbol{n}_{\gamma\kappa}\cdot\mathrm{D}_\gamma\nabla C_A dA + \Psi\left\langle r_A^{'''}\right\rangle \tag{11}$$

and application of the boundary condition given by Eq. (2) leads to a new equation with heterogeneous reaction terms in the principal equation.

The hydrolysis reaction of reactive dyes in an aqueous alkaline solution can be represented by Eq. (12), as presented by Ruiz and Hoechst (1987).

$$r_A^{'''} = -k_h C_A \tag{12}$$

In which k_h is the pseudo-first-order rate constant of hydrolysis. This constant changes with the variation of temperature, pH and dyes.

The process of spatially smoothing Eq. (12) is given by Eq. (13).

$$\left\langle r_A^{'''}\right\rangle = -\langle k_h C_A\rangle = -k_h\langle C_A\rangle = -k_h\varepsilon_\gamma\langle C_A\rangle^\gamma \tag{13}$$

Substituting Eq. (13) in Eq. (11) and neglecting variations of the molecular diffusivity within the averaging volume, it is possible to use the spatial averaging theorem a second time to obtain

$$\varepsilon_\gamma\frac{\partial\langle C_A\rangle^\gamma}{\partial t} = \nabla\cdot\left[\mathrm{D}_\gamma\left(\nabla\langle C_A\rangle + \frac{1}{\mathrm{V}_\sigma}\int_{A_{\gamma\kappa}}\boldsymbol{n}_{\gamma\kappa}C_A\,dA\right)\right] + \frac{1}{\mathrm{V}_\sigma}\int_{A_{\gamma\kappa}} -\left(\Psi\,kC_A + \Omega\frac{\partial C_{As}}{\partial t}\right)dA - \Psi\,k_h\varepsilon_\gamma\langle C_A\rangle^\gamma \tag{14}$$

The reaction constant k is considered constant in the *γ-k* interface, and we are using a rigid porous medium, which allows us writing that *γ-k* interface does not change with time.

The Nernst linear isotherm, given by Eq. (15), can represent the equilibrium between surface molar concentration and bulk molar concentration.

$$C_{As} = K_{eq}C_A \tag{15}$$

Equations (16) and (17) represent the surface area per unit volume $a_v|_{\gamma\kappa}$ and area average concentration $\langle C_A\rangle_{\gamma k}$, respectively.

$$a_v|_{\gamma\kappa} = \frac{A_{\gamma\kappa}}{\mathrm{V}_\sigma} \tag{16}$$

$$\langle C_A\rangle_{\gamma\kappa} = \frac{1}{A_{\gamma\kappa}}\int_{A_{\gamma\kappa}}C_A dA \tag{17}$$

Applying the definitions above and substituting Eq. (7) into Eq. (14), it is possible to obtain

$$\varepsilon_\gamma \frac{\partial \langle C_A \rangle^\gamma}{\partial t} = \nabla \cdot \left[\mathrm{D}_\gamma \left(\varepsilon_\gamma \nabla \langle C_A \rangle^\gamma + \langle C_A \rangle^\gamma \nabla \varepsilon_\gamma + \frac{1}{\mathrm{V}_\sigma} \int_{A_{\gamma\kappa}} \boldsymbol{n}_{\gamma\kappa} C_A \, dA \right) \right] - \\ - \Psi \left(a_v\big|_{\gamma\kappa} k \langle C_A \rangle_{\gamma k} + \varepsilon_\gamma k_h \langle C_A \rangle^\gamma \right) - \Omega \, a_v\big|_{\gamma\kappa} \frac{\partial}{\partial t}\left(K_{eq} \langle C_A \rangle_{\gamma k} \right) \tag{18}$$

Our goal is to obtain the governing equation for intrinsic average concentration, so it is necessary to eliminate the point concentration from Eq. (18). We decompose the point concentration, according to Gray (1975), which is analogous to the temporal decomposition used in turbulent transport study.

$$C_A = \langle C_A \rangle^\gamma + \tilde{C}_A \tag{19}$$

where $\tilde{C}_A$ is the spatial derivation concentration.

Substitution of decomposition into Eq. (18) allows us writing Eq. (20), as Brandão (2002).

$$\varepsilon_\gamma \frac{\partial \langle C_A \rangle^\gamma}{\partial t} = \nabla . \left[\mathrm{D}_\gamma \left(\varepsilon_\gamma \nabla \langle C_A \rangle^\gamma + \frac{1}{\mathrm{V}_\sigma} \int_{A_{\gamma\kappa}} \boldsymbol{n}_{\gamma\kappa} \tilde{C}_A \, dA \right) \right] - \Psi \left(a_v\big|_{\gamma\kappa} k \langle C_A \rangle_{\gamma k} + \varepsilon_\gamma k_h \langle C_A \rangle^\gamma \right) - \Omega \, a_v\big|_{\gamma\kappa} \frac{\partial}{\partial t}\left(K_{eq} \langle C_A \rangle_{\gamma k} \right) \tag{20}$$

For all the practical problems of fluid diffusion in porous we can affirm that intrinsic average concentration is equal to the area average concentration $\langle C_A \rangle_{\gamma k}$, as presented by Whitaker (1999). If the constraint given in Eq. (21) is satisfied, this affirmation can be proved.

$$\left(\frac{r_o}{L_c} \right) << 1 \ \text{e} \ \left(\frac{r_o^2}{L_{c1} L_c} \right) << 1 \tag{21}$$

in which r_o is the radius of the average volume in the microscale, L_c represents a characteristic length associated with the averaging concentration and L_{c1} is a characteristic length associated with the first derivative of $\langle C_A \rangle^\gamma$.

$$\varepsilon_\gamma \frac{\partial \langle C_A \rangle^\gamma}{\partial t} = \nabla \cdot \left[\mathrm{D}_\gamma \left(\varepsilon_\gamma \nabla \langle C_A \rangle^\gamma + \frac{1}{\mathrm{V}_\sigma} \int_{A_{\gamma\kappa}} \boldsymbol{n}_{\gamma\kappa} \tilde{C}_A \, dA \right) \right] - \Psi \left(a_v\big|_{\gamma\kappa} k + \varepsilon_\gamma k_h \right) \langle C_A \rangle^\gamma - \Omega \, a_v\big|_{\gamma\kappa} \frac{\partial}{\partial t}\left(K_{eq} \langle C_A \rangle^\gamma \right) \tag{22}$$

To obtain the governing equation for intrinsic averaging concentration it is necessary to develop the closure problem for $\tilde{C}_A$ and this is done in the next section.

3.2. Closure problem in the microscale

In this section our problem has been reduced to the determination of spatial deviations, $\tilde{C}_A$. To obtain a governing differential equation for $\tilde{C}_A$ we can subtract Eq. (1) from Eq. (22) using the decomposition given by Eq. (19).

$$\frac{\partial \tilde{C}_A}{\partial t} = \nabla \cdot \left(\mathrm{D}_\gamma \nabla \tilde{C}_A \right) - \varepsilon_\gamma^{-1} \left(\nabla \varepsilon_\gamma \right) \cdot \left(\mathrm{D}_\gamma \nabla \langle C_A \rangle^\gamma \right) - \Psi \, k_h \tilde{C}_A - \\ - \varepsilon_\gamma^{-1} \nabla \cdot \left[\frac{D_\gamma}{\mathrm{V}_\sigma} \int_{A_{\gamma\kappa}} \boldsymbol{n}_{\gamma\kappa} \tilde{C}_A \, dA \right] + \Psi \, \varepsilon_\gamma^{-1} a_v\big|_{\gamma\kappa} k \langle C_A \rangle^\gamma + \Omega \, \varepsilon_\gamma^{-1} a_v\big|_{\gamma\kappa} \frac{\partial}{\partial t}\left(K_{eq} \langle C_A \rangle^\gamma \right) \tag{23}$$

The boundary condition can be obtained in the same form with the substitution of Eq. (19) by Eq. (2), which we express as

C.C.1 $$-\boldsymbol{n}_{\gamma\kappa}\cdot \mathrm{D}_\gamma \nabla \tilde{C}_A - \Psi k\, \tilde{C}_A - \Omega \frac{\partial (K_{eq}\, \tilde{C}_A)}{\partial t} = \boldsymbol{n}_{\gamma\kappa}\cdot \mathrm{D}_\gamma \nabla \langle C_A \rangle^\gamma + \Psi k \,\langle C_A\rangle^\gamma + \Omega \frac{\partial \left(K_{eq} \langle C_A \rangle^\gamma \right)}{\partial t}, \quad \text{in the } \mathscr{A}_{\gamma k} \tag{24}$$

Equation (23) is much complex with non-homogeneous terms, so it is necessary to simplify terms by estimating of magnitude order.

It is obvious that the textile dyeing process is transient. Although, we must retain the transient term in the intrinsic average concentration equation given by Eq. (22), in the closure problem we can eliminate the transient term if the constraint in Eq. (25) is satisfied.

$$\frac{\mathrm{D}_\gamma t^*}{\ell_\gamma^2} >> 1 \tag{25}$$

where t^* is the characteristic time.

The second term to be analyzed is the non-local term written below

$$\varepsilon_\gamma^{-1}\ \nabla \cdot \left[\frac{D_\gamma}{\mathrm{V}_\sigma} \int_{A_{\gamma\kappa}} n_{\gamma\kappa}\, \tilde{C}_A \, dA \right] = \boldsymbol{O}\left(\frac{\varepsilon_\gamma^{-1} \mathrm{D}_\gamma\, \tilde{C}_A}{\ell_\gamma L} \right) \tag{26}$$

The magnitude order of diffusive term into Eq. (23) is estimated in Eq. (27).

$$\nabla \cdot \left(\mathrm{D}_\gamma \nabla \tilde{C}_A \right) = \boldsymbol{O}\left(\frac{\mathrm{D}_\gamma\, \tilde{C}_A}{\ell_\gamma^2} \right) \tag{27}$$

The length scale ℓ_γ is so small compared to L, and ε_γ is in the order of 1. Due to this, it is possibly to write Eq. (28).

$$\varepsilon_\gamma^{-1}\ \nabla \cdot \left[\frac{D_\gamma}{\mathrm{V}_\sigma} \int_{A_{\gamma\kappa}} \boldsymbol{n}_{\gamma\kappa}\, \tilde{C}_A \, dA \right] << \nabla \cdot \left(\mathrm{D}_\gamma \nabla \tilde{C}_A \right) \tag{28}$$

We can neglect the second term of the right hand side of Eq. (23) using the method of Quintard and Whitaker (1994) to obtain the following closure problem:

$$\nabla^2 \tilde{C}_A = \frac{\Psi\, k_h}{\mathrm{D}_\gamma} \tilde{C}_A - \Psi \frac{a_v|_{\gamma\kappa}\, k}{\varepsilon_\gamma \mathrm{D}_\gamma} \langle C_A \rangle^\gamma - \Omega \frac{a_v|_{\gamma\kappa} K_{eq}}{\varepsilon_\gamma \mathrm{D}_\gamma} \frac{\partial \langle C_A \rangle^\gamma}{\partial t} \tag{29}$$

C.C.1 $$-\boldsymbol{n}_{\gamma\kappa}\cdot \mathrm{D}_\gamma \nabla \tilde{C}_A = \boldsymbol{n}_{\gamma\kappa}\cdot \mathrm{D}_\gamma \nabla \langle C_A\rangle^\gamma + \Psi k\,\langle C_A \rangle^\gamma + \Omega K_{eq} \frac{\partial \langle C_A \rangle^\gamma}{\partial t}, \quad \text{in the } \mathscr{A}_{\gamma k} \tag{30}$$

C.C.2 $$\tilde{C}_A(\boldsymbol{r} + \ell_i) = \tilde{C}_A(\boldsymbol{r}), \quad i = 1, 2, 3, \tag{31}$$

Equation (31) is the periodicity condition. This condition can be written if the geometry of the representative region is spatially periodic. The problem in study is the packed thread in bobbins, these threads are packed in a region spatially periodic.

To solve the closure problem equations the method of superposition will be applied. The solution proposed is expressed as

$$\tilde{C}_A = \boldsymbol{b}\cdot \nabla \langle C_A \rangle^\gamma \Big|_{\boldsymbol{x}} + s\Psi \langle C_A \rangle^\gamma \Big|_{\boldsymbol{x}} + p\Omega \frac{\partial \langle C_A \rangle^\gamma \Big|_{\boldsymbol{x}}}{\partial t} + \psi \tag{32}$$

In which $\boldsymbol{b}$ is a vector and s , p e ψ are scalar closure variables. When Eq. (32) is substituted into Eqs. (29) to (31), we obtain four new problems given as

Problem I

$$\nabla^2 \boldsymbol{b} - \frac{\Psi\, k_h}{\mathrm{D}_\gamma}\boldsymbol{b} = 0 \tag{33}$$

$$\text{B.C.1} \qquad -\boldsymbol{n}_{\gamma\kappa}\cdot\nabla\boldsymbol{b} = \boldsymbol{n}_{\gamma\kappa}, \qquad \text{at } \mathscr{A}_{\gamma\kappa} \tag{34}$$

$$\text{Periodicity:} \qquad \boldsymbol{b}(\boldsymbol{r}+\ell_i) = \boldsymbol{b}(\boldsymbol{r}), \qquad \mathrm{i} = 1, 2, 3 \tag{35}$$

Problem II

$$\nabla^2 s + \frac{\Psi\, k_h}{\mathrm{D}_\gamma} s = -\left(\frac{a_v\big|_{\gamma\kappa} k}{\varepsilon_\gamma \mathrm{D}_\gamma}\right) \tag{36}$$

$$\text{B.C.1} \qquad -\boldsymbol{n}_{\gamma\kappa}\cdot\nabla s = \left(\frac{k}{\mathrm{D}_\gamma}\right), \qquad \text{at } \mathscr{A}_{\gamma\kappa} \tag{37}$$

$$\text{Periodicity:} \qquad s(\boldsymbol{r}+\ell_i) = s(\boldsymbol{r}), \qquad \mathrm{i} = 1, 2, 3 \tag{38}$$

Problem III

$$\nabla^2 p = -\left(\frac{a_v\big|_{\gamma\kappa} K_{eq}}{\varepsilon_\gamma \mathrm{D}_\gamma}\right) \tag{39}$$

$$\text{B.C.1} \qquad -\boldsymbol{n}_{\gamma\kappa}\cdot\nabla p = \left(\frac{K_{eq}}{\mathrm{D}_\gamma}\right), \qquad \text{at } \mathscr{A}_{\gamma\kappa} \tag{40}$$

$$\text{Periodicity:} \qquad p(\boldsymbol{r}+\ell_i) = p(\boldsymbol{r}), \qquad \mathrm{i} = 1, 2, 3 \tag{41}$$

Problem IV

$$\nabla^2 \psi + \frac{\Psi\, k_h}{\mathrm{D}_\gamma}\psi = 0 \tag{42}$$

$$\text{B.C.1} \qquad -\boldsymbol{n}_{\gamma\kappa}\cdot\nabla\psi = 0, \qquad \text{at } \mathscr{A}_{\gamma\kappa} \tag{43}$$

$$\text{Periodicity:} \qquad \psi(\boldsymbol{r}+\ell_i) = \psi(\boldsymbol{r}), \qquad \mathrm{i} = 1, 2, 3 \tag{44}$$

The problems I, II and III have to be solved by computational methods, Ochoa (1993). The problem IV has analytical solution and certainly Ψ is constant, but it is not necessary to solve this problem because Ψ will not pass through the filter in Eq. (22).

Substituting Eq. (32) into the intrinsic average concentration equation, Eq. (22), we obtain the closed differential equation to $\langle C_A\rangle^\gamma$.

$$\begin{aligned} \varepsilon_\gamma \frac{\partial\langle C_A\rangle^\gamma}{\partial t} &= \nabla\cdot\left(\varepsilon_\gamma\, \boldsymbol{Deff}\big|_{\gamma\kappa}\cdot\nabla\langle C_A\rangle^\gamma\right) + \Psi\,\nabla\cdot\left(\varepsilon_\gamma\, \boldsymbol{u}\, k\langle C_A\rangle^\gamma\right) + \Omega\,\nabla\cdot\left(\varepsilon_\gamma\, \boldsymbol{v}\, K_{eq}\frac{\partial\langle C_A\rangle^\gamma}{\partial t}\right) - \\ &- \Psi\left(a_v\big|_{\gamma\kappa} k + \varepsilon_\gamma k_h\right)\langle C_A\rangle^\gamma - \Omega\, a_v\big|_{\gamma\kappa}\frac{\partial}{\partial t}\left(K_{eq}\langle C_A\rangle^\gamma\right) \end{aligned} \tag{45}$$

The effective diffusivity term is defined by

$$\boldsymbol{Deff}\big|_{\gamma\kappa} = \mathrm{D}_\gamma \left(\boldsymbol{I} + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \boldsymbol{n}_{\gamma\kappa}\, \boldsymbol{b}\, dA \right) \qquad (46)$$

and the vectors $\boldsymbol{u}$ e $\boldsymbol{v}$, represented by Eqs. (47) and (48) are associated with heterogeneous chemical reaction and adsorption, respectively.

$$\boldsymbol{u} = \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \boldsymbol{n}_{\gamma\kappa} \left(\frac{\mathrm{D}_\gamma\, s}{k} \right) dA \qquad (47)$$

$$\boldsymbol{v} = \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \boldsymbol{n}_{\gamma\kappa} \left(\frac{\mathrm{D}_\gamma\, p}{K_{eq}} \right) dA \qquad (48)$$

The vectors $\boldsymbol{u}$ e $\boldsymbol{v}$ are the convective transport terms generated by a heterogeneous reaction and adsorption in the fibers surface. The contribution of this convective term can be negligible in the microscale, because it has not velocity and the diffusion is much more important than the convective term. Therefore, the vectors $\boldsymbol{u}$ e $\boldsymbol{v}$ can be zero, as Quintard e Whitaker (1993).

From this analysis we can write the closed dye transport equation in the fluid phase microscale, given by Eq. (49).

$$\varepsilon_\gamma \frac{\partial \langle C_A \rangle^\gamma}{\partial t} = \nabla \cdot \left(\varepsilon_\gamma\, \boldsymbol{Deff}\big|_{\gamma\kappa} \cdot \nabla \langle C_A \rangle^\gamma \right) - \Psi \left(a_v\big|_{\gamma\kappa}\, k + \varepsilon_\gamma k_h \right) \langle C_A \rangle^\gamma - \Omega\, a_v\big|_{\gamma\kappa} \frac{\partial}{\partial t} \left(K_{eq} \langle C_A \rangle^\gamma \right) \qquad (49)$$

4. Conclusion

The present study contains the modeling of the packed thread dyeing process in the microscale region, where this region is formed by textile fibers in contact with the dyeing bath contained into the thread.

A theory of diffusion in two-phase systems has been presented based on the method of volume averaging. This method allows developing the mathematical modeling from the microscale to the macroscale problem. Due to that, in general, the model becomes more accurate than classical ones. The developed model in this work allows simulating the dyeing process with any type of dyes.

The method of closure has been developed for spatially periodic porous media. The solution of closure problem allows calculating the theoretical effective diffusivity tensor, without empirical correlations.

The analysis of the closure problem makes possible to affirm that the dye hydrolysis reaction affects the effective diffusivity tensor. In the next work, the solution of the closure problem is presented as well as the effect of hydrolysis reaction in the effective diffusivity tensor.

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