Dynamic Isotherms of Dye in Activated Carbon

Gleisy Kelly Lopes Matta[a]*, *Maria Angélica Simões Dornelas Barros*[a]*, *Rafael Lambrecht*[a]*,

Edison Antonio da Silva[b]*, *Oswaldo Curty da Motta Lima*[a]*

[a]*Depto. de Engenharia Química, Universidade Estadual de Maringá – UEM,*
Av. Colombo 5790, Bl. D-90, 97020-900 Maringá - PR, Brazil
[b]*Depto. de Engenharia Química, Campus de Toledo,*
Universidade Estadual do Oeste do Paraná – UNIOESTE,
Toledo - PR, Brazil

Textile industrial wastewaters have significant quantities of dyes. Adsorption processes using industrials rejects may help in the treatment of these effluents. In this context, uptake of Reactive Blue 5G dye by babassu coconut shell activated carbon was studied with upstream flow fixed-bed experiments. First, the minimum flow rate that minimizes the diffusion effects of 4 mL/min was chosen within the range investigated (2-10 mL/min). Then, the breakthrough curves were obtained for this flow rate for different initial dye concentrations (13.15-102.0 mg/L) and temperature of 30 °C. The mass retained until bed saturation in each experiment was used to obtain the dynamic isotherms, which showed a favorable dye uptake behavior with a maximum adsorption capacity of 12.9 mg.g^{-1}. The irreversible model fitted the experimental data well when compared to Langmuir and Freundlich models. A LDF model simulated the experimental breakthrough curves, and the bed axial dispersion and mass transfer coefficients were estimated.

1. Introduction

With the urban and mainly the industrial activity growth, environmental problems have become more frequent and more critical. The textile industries stand out among the industries that produce effluents with high polluting load. In this sector, industrial laundries, which count 1200 installed units in the whole Brazil, play a major role[1]. The environmental problems caused by laundry effluents are even more serious when the discharge of dyes not fixed or not degraded by conventional treatment processes is taken into account. It has a potentially high environmental impact in terms of toxicity and interference with photosynthesis in water resources[2]. Activated carbon adsorption processes are largely used, particularly due to their versatility, efficiency, and low operating costs. Many activated carbon precursors may be obtained from industrial wastes. In Brazil, babassu coconut shell activated carbon is trade rather common.

The objective of the present work was to evaluate the adsorption mechanism of dyes on babassu coconut shell activated carbon granted by Tobasa Bioindustrial de Babassu S.A.

For such, commercial dye Reactive Blue 5G was chosen as an adsorbate because it is the main dye used with jeans-type fabrics. To achieve this goal, the following specific objectives have been set:
- Evaluation of the optimal column operating conditions;
- Isotherm plotting and breakthrough curve modeling; and
- Evaluation of process thermodynamic parameters.

2. Materials and Methods

2.1. Characterization of babassu coconut shell activated carbon

Samples of the commercial babassu coconut shell activated carbon was donated by Tobasa Bioindustrial de Babaçu S.A. located in Tocantinópolis-TO-Brazil. For surface area, pore size, and chemical characterization of babassu coconut shell activated carbon, it was used the N_2 adsorption technique at 77 K, zero point charge (ZPC), FTIR spectroscopy, and scanning electron microscopy (SEM). Adsorbent particle size was determined by sieving[3].

2.2. Dye characterization

The Reactive Blue 5G dye molecule was submitted to semi-empirical calculation (AM1) with GAUSSIAN 03 package at the Chemistry Department of State University of Maringá. The AM1 method is semi-empirical as empirical data (experimental) are included in this type of calculation besides the integrals generated by the Quantum Mechanics principle.

2.3. Analytical methodology

The dye solutions were prepared from commercial Reactive Blue 5G from Texpal Química. Sample concentrations were determined by UV-Vis spectroscopy in a Shimadzu UV-Visible Spectrophotometer UV - 1601PC apparatus.

2.4. Fixed-bed experiments

The adsorption module consists in a solution container and a deionized water container used to homogenize the bed and stabilize the flow rate. A Cole Parmer peristaltic pump fed the packed bed with internal diameter of 1.01 cm and a thermostatized bath was used to keep the column temperature constant at 30 °C.

The beds were packed as follows for each experiment: first, it was added a layer of glass beads, followed by a small cotton wool piece to ensure that the adsorbent did not penetrate between the beads. Next, the adsorbent was added to the column and deionized water was run

*e-mail: gleisynha@gmail.com, angelica@deq.uem.br, lambrecht10@pop.com.br, edsondeq@unioeste.br, oswaldo@deq.uem.br

to remove any air. Another piece of cotton wool was placed on the column top and it was filled up with glass beads. Next, flow rate and temperature were adjusted and experiments started by closing the water valve and opening the solution valve simultaneously.

Feed solution flowed upwards and samples were collected in pre-defined time intervals until the bed saturation. The analysis of the dye concentration of each sample allowed plotting the breakthrough curves (C/C_0 vs. time).

2.5. Optimization of fixed-bed flow rate

The optimal column operating flow rate is that which minimized the diffusion effects. Runs were carried out at 30 °C, $C_0 = 35$ mg.L^{-1}, 5.639 g of babassu coconut shell activated carbon (bed height of 15.5 cm). It was investigated the flow rates of de 2.0, 4.0, 6.0, 8.0, and 10.0 mL/min.

Mass transfer parameters: mass transfer zone length (MTZ), operating ratio (R_o), nondimensional variance (σ^2) and amount retained up to breakthrough point (q_{tu}) were used in the analysis of the optimal flow rate[4].

2.6. Dynamic isotherm plotting

Runs were carried out under optimal operating flow rate with different concentrations in the range 13.15-102.00 mg.L^{-1} and pH range of 5.5-6.5. Plots of dye retained in the bed up to saturation and the concentration of the feed solution is called dynamic isotherm, as described elsewhere[5].

2.7. LDF model proposed by Silva[6]

The model proposed by Silva[6] considers the process isothermal and isobaric with constant porosity and physical properties and negligible radial dispersion. The differential mass balance of a component in the fluid phase is given by:

$$\frac{\partial C}{\partial \iota} + \rho_b \frac{1}{\varepsilon} \frac{\partial q}{\partial \iota} = -\frac{\partial C}{\partial \xi} + \frac{1}{Pe_b} \frac{\partial^2 C}{\partial \xi^2} \tag{1}$$

with the following initial condition:

$$C(\xi, 0) = C_0 \tag{2}$$

and the boundary conditions:

$$\frac{\partial C}{\partial \xi} = Pe_b \left(C(\tau, 0) - C^F \right) \text{ for } \xi = 0 \tag{3}$$

$$\frac{\partial C}{\partial \xi} = 0 \text{ for } \xi = 1 \tag{4}$$

where:

C^F - Feed concentration;
q - Dye concentration in the adsorbent;
v - Surface velocity;
Pe_b - Peclet number for the bed (Hv/DL);
ε - Fraction of bed voids;
P_b - Bed density;
ι - Nondimensional time coordinate (tu/H); and
ξ - Nondimensional axial coordinate (H/H$_t$).

Considering the intraparticle diffusion as the rate controlling step, C = C*, (C* is the concentration on the particle external surface):

$$\frac{\partial q}{\partial t} = -K_C(q - q^*) \tag{5}$$

where $Kc = K_{c\,int}a$ and:

$K_{c\,int}$ - intraparticle mass transfer coefficient;
a - transfer area per bed volume unit.

It was used the line method in the solution of the equation model with sub routine DASSL developed for algebraic-differential equation systems (source code in FORTRAN). Thus, the equations were described in the form:

$$\frac{dy_k}{dt} = \sum_{i=1}^{nt} A_{k,i} y_i + f\left(y_1, y_2, \ldots, y_{nt}\right), \text{ for } k = 1, \ldots nt \tag{6}$$

The DASSL code requires a consistent set of values for y_k variables and for their respective derivatives in relation to time, dy_k/dt. Therefore, it was necessary to modify the representation of concentration at the column inlet by transforming it into a continual function by means of the following expression:

$$C_0 = C_0 \left(1 - e^{-st}\right) + C_0^F e^{-st} \tag{7}$$

where s = 10^{10}, C^F is the feed dye concentration, C_0^F is the initial dye concentration in the fluid phase, and τ is the nondimensional time coordinate.

Silva[6] recommends that the model parameters, that is, axial dispersion coefficients (D_L) and the mass transfer (K_c), should be estimated from the experimental breakthrough curves and the minimization of the following objective function:

$$F = \sum_{i=1}^{n\exp} \left(C_{out}^{EXP} - C_{out}^{MOD}\right)^2 \tag{8}$$

where:

C_{out}^{EXP} - adsorbate concentration experimentally determined at the column outlet;

C_{out}^{MOD} - adsorbate concentration determined through the solution of the model at the column outlet;

n_exp - experimental points of the breakthrough curve.

3. Discussion and Results

3.1. Adsorbent characterization

Babassu coconut shell activated carbons was predominantly microporous with micropore area of 1160 m^2.g^{-1} and mean pore diameter of 20.64 nm. ZPC occurs at pH 7.7, a value higher than those of the dye solutions. Therefore, it is believed that adsorption occurs by the attraction of dye anionic groups in relation to the positive surface charge of the solid material with a high percentage of removal of dye[7].

The FTIR spectra suggest the presence of hydroxyl groups such as carboxylic groups, C = O bonds (aldehydes, ketones, carboxylic acids), phenols, ethers or lactones, and negligible amounts of nitrate complexes and aromatic ring bonds.

The SEM micrograph shown in Figure 1 displays some flaws and some apparently cylindrical macropores in the babassu coconut shell activated carbon.

Finally, the mean particle diameter determined by sieving was in the order of 0.56 mm.

3.2. Adsorbate characterization

The longitudinal size of the Reactive Blue 5G dye molecule was obtained with the GAUSSIAN 03 software package, as shown in Figure 2. The mean pore diameter is in the order of 22.35 nm. Therefore, one can suppose that dye adsorption meets significant diffusion resistance.

Reactive Blue 5G dye present variations in the maximum wavelength (624 nm) for different solution concentrations, indicating that the increase in dye concentration results in dye aggregation, at least dimmers, which may make adsorption on carbon with relatively small

pore diameter difficult. Alterations in the molecule aggregation state had already been observed for other dyes[8].

### 3.3. Effect of flow rate variation

The experimental breakthrough curves obtained by flow rate variation are given in Figure 3.

The saturation of some curves is not given so that their slopes may be evaluated in more detail. The saturation for the flow rate run at 2 mL/min occurred in 22,000 minutes, while for flow rates of 4, 6, 8, and 10 mL/min, saturation occurred in 7,000, 5,300, 2,800, and 1,800 minutes, respectively.

Therefore, the increase in feed flow rate led to a faster saturation of the adsorbent, as expected and in agreement with the results of[10,11]. Anyway, the saturation time is rather long and a consequence of the diffusion effects.
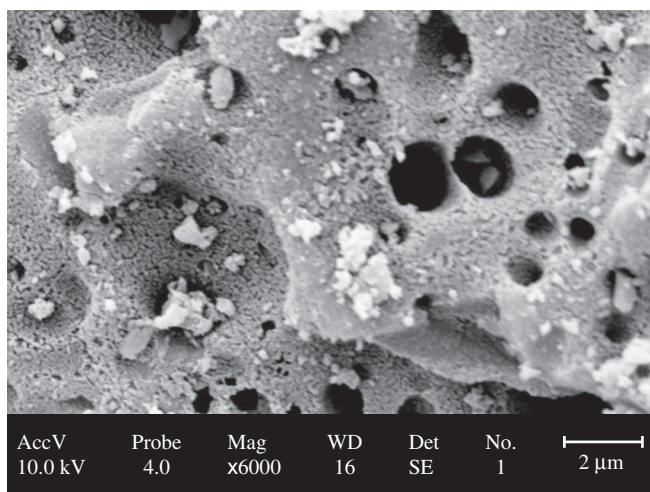
Figure 1. Micrograph of babassu coconut shell activated carbon enlarged 6000x.
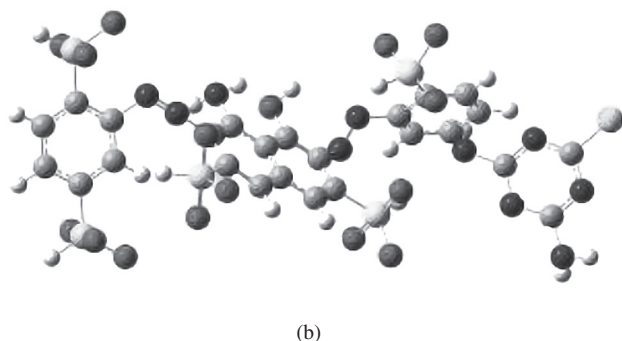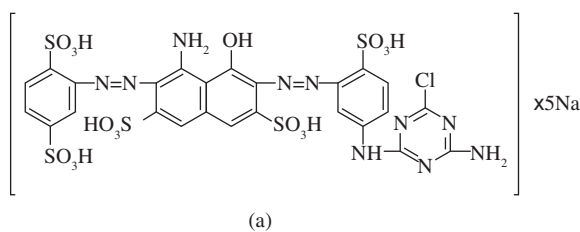
Figure 2. a) Representation of Reactive Blue 5G molecule[9], and b) three-dimensional structure of the dye molecule.

It is worth pointing out that longitudinal diameter of the dye molecule is in the order of the mean pore diameter, which inhibits transversal diffusion. Diffusion is made easier only when the molecule tries to diffuse through one of the ends, through the activated carbon pores, as the monomer radial diameter is estimated at 9 nm. When dimmers are present, one may suppose that specie may be qualitatively represented by a cylinder with the same longitudinal size (22.35 nm); however, with a diameter two-fold as large, around 18 nm. In this condition, the diffusion and consequently adsorption are even more affected by significant steric effects.

It is also observed that the breakthrough points of each run decreased with the increase in flow rate. Sometimes, this phenomenon does not occur. In fact, when the adsorbent has pore that cause diffusion problems at the very channel opening, the breakthrough points for distinct flow rates are very close to each other[12].

More accurate conclusions may be drawn from the mass transfer parameter values given in Table 1. Within the flow rate studied, it is observed that the flow rate of 4 mL/min afforded the lowest MTZ, the largest amount of retained dye up to t_u (q_{tu}), the smallest operational ratio, and a high degree of dispersion on the bed. At this flow rate, the diffusion resistance is probably minimized due to the large degree of dispersion of the dye in the column. Thus, the flow rate of 4 mL/min was considered the optimal operating condition for this system and all the other data were obtained at this flow rate.

3.4. Dynamic isotherm

Figure 4 displays the dynamic isotherm. It can be observed a gradual decrease in the retained amount of dye due to progressive
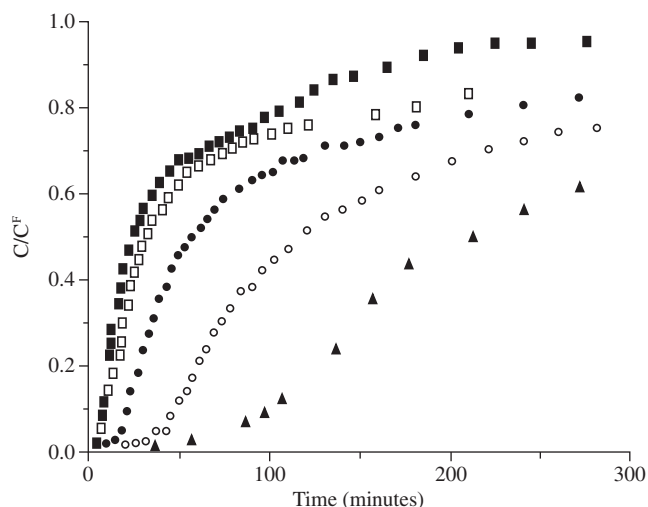
Figure 3. Breakthrough curves for different flow rates using babassu coconut shell activated carbon with concentration of 35 mg/L (■ 10 mL/min, □ 8 mL/min, ● 6 mL/min, ○ 4 mL/min, and ▲ 2 mL/min)

Table 1. Mass transfer parameters.

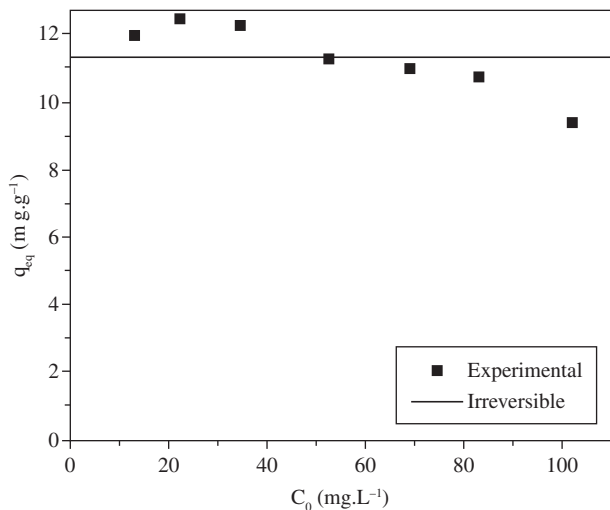| Flow rate (mL/min)	MTZ (cm)	q_{tu} (mg.g^{-1})	R_0	σ^2
2	14.35	0.77	0.96	6.38
4	13.94	0.88	0.92	8.6
6	14.21	0.57	0.95	7.6
8	14.43	0.31	0.97	1.98
10	14.07	0.39	0.94	6.43

Figure 4. Dynamic isotherm at 30 °C.

diffusion effects. As the feed concentration becomes more concentrated, there is an increase in the dye and thus, the larger the steric effects are. The isotherm was considered irreversible and described as $q_{eq} = 11.3014$ mg.g^{-1} for modeling.

3.5. Fitting of the LDF model proposed by Silva[6]

The breakthrough curves are given in Figure 5. As can be observed, Silva's[6] model fitted well to the breakthrough curve experimental data, confirming the intraparticle as the controlling stage. This model allows estimating the intraparticle mass transfer coefficient (K_C) and the bed axial dispersion (D_L). These results are given in Table 2.

It can be observed that K_C is influenced by the initial concentration, as previously observed by[6,12]. Possibly, the dye retention process driving force is the increase in the number of molecules in the system, that is, the more concentrated the solution is, apparently, the more strongly the molecules are pushed to the adsorption sites, which favors the adsorption process. D_L values are little sensitive under analysis in Silva's[6] model, as been evidenced in other works[5,4].
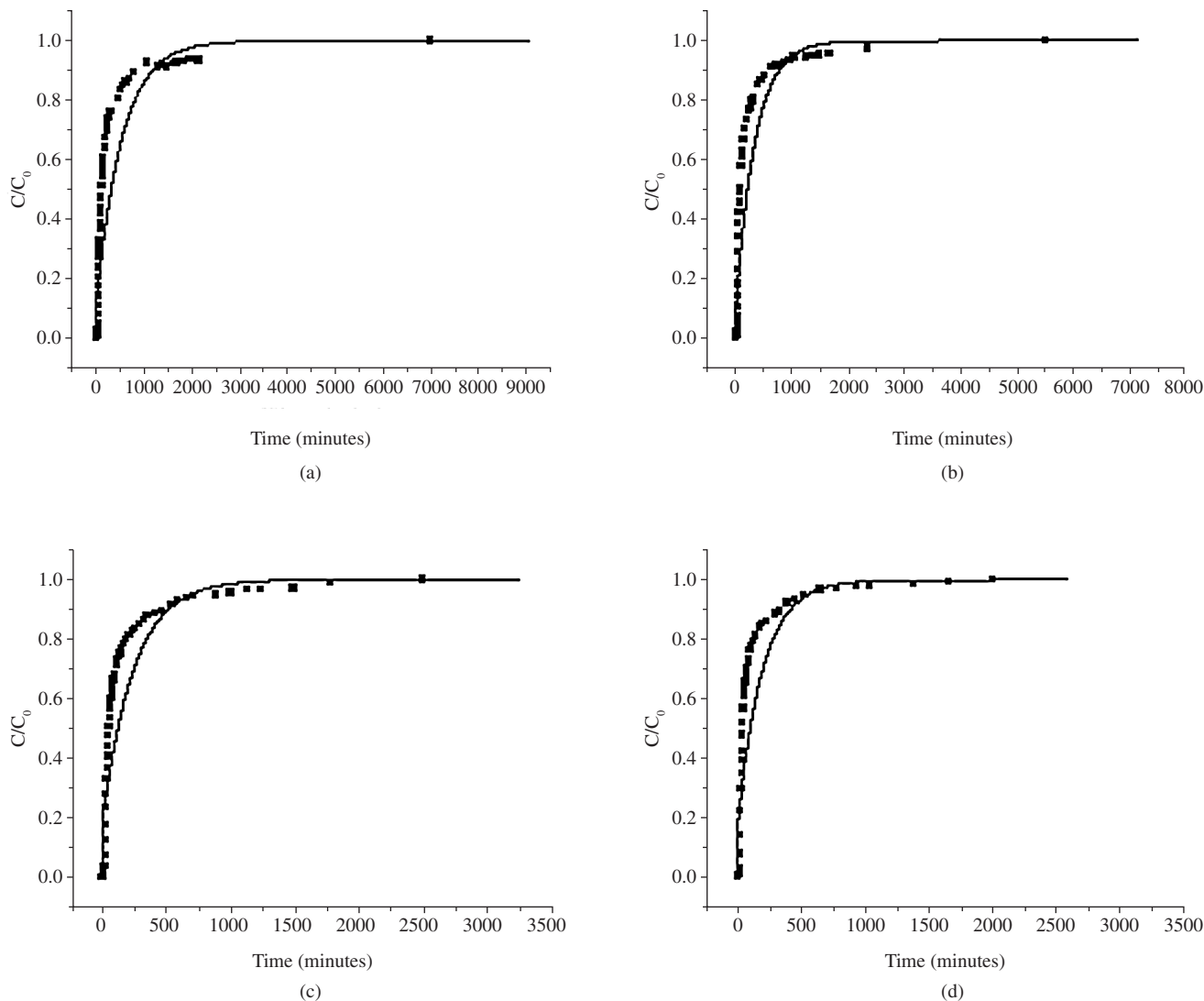

(a)

(b)

(c)

(d)

Figure 5. Experimental (■) and simulated (—) breakthrough curves for the adsorption of dye on babassu coconut shell activated carbon a) C_0 = 34.5 mg/L, b) C_0 = 52.5 mg/L, c) C_0 = 83 mg/L, and d) C_0 = 102 mg/L.

Table 2. Intraparticle mass transfer coefficients for babassu coconut shell activated carbon.

C_0 (mg/L)	K_C (per minute)	$D_e \times 10^{11}$ (m^2/min)
13.15	0.0007	0.73
22.30	0.0012	1.25
34.50	0.0018	1.88
52.50	0.0028	2.93
69.00	0.0033	3.45
83.00	0.0041	4.29
102.00	0.0051	5.33

Thus, it can be adopted a mean D_L. The mean axial dispersion value of dye Reactive Blue 5G in activated carbon at 30 °C was 0.01057 cm^2/min. The K_C parameter sensitivity was analyzed based on the modeling results for the babassu coconut shell activated carbon data. It can be noticed that the mass transfer coefficient is very sensitive to the data simulation. Any variation in K_C leads to noticeable variations in the breakthrough curve modeling.

4. Conclusions

From the surface characterization results obtained, it can be observed that the babassu coconut shell activated carbon used in this work is predominantly microporous and has a large surface area, with the presence of acidic, carboxylic, lactone, and phenolic groups.

The dye molecule longitudinal size is in the order of 22.35 nm with a diameter of around 9 nm. These characteristics indicate the transversal approximation of the molecule to the activated carbon pores as a result of the high diffusion resistance.

Runs carried out in fixed-bed column to determine the optimal adsorption operating conditions demonstrated that flow rate influenced the dye retention process and that, in the investigated conditions, the optimal flow rate was 4 mL/min.

The equilibrium experimental data obtained in the fixed-bed runs showed a decrease in the amount of retained dye, possibly due to a diffusion effect resulting from the increase in the number of dimmers with the feed concentration. However, the isotherm was modeled by the irreversible model satisfactorily.

Silva's[6] model simulated the experimental curves adequately. The mass transfer coefficient was dependent on the concentration, while the axial dispersion coefficient was little sensitive to these alterations, leading to a mean value of 0.01057 cm^2/min.

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