

# Application of Diffusion Model for Adsorption of Azo Reactive Dye on Pumice

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## Abstract

In this work, adsorption of reactive azo dye on pumice has been studied by using batch techniques. The influence of agitation, initial dye concentration, and adsorbent mass has been studied. The equilibrium adsorption capacity of pumice for dye was obtained by using linear Freundlich isotherm. It was found that pumice could be an appropriate adsorbent in removal of dye from wastewater. In order to explain the adsorption mechanism, a diffusion model was applied, and calculations were made for solid diffusivity ( $D_s$ ) and external mass-transfer coefficient ( $k_f$ ). The applied diffusion model showed that  $k_f$  was constant for all initial dye concentrations ( $c_0$ ), and  $D_s$  increased as  $c_0$  did. Furthermore,  $D_s$  was found to decrease with increasing adsorbent mass.

**Keywords:** Azo reactive dye, pumice, diffusion model, adsorption isotherm

## Introduction

The textile industry constitutes one of the most important industrial branches in Turkey and it has a rather distinct place for its employment capacity and contribution to the national economy.

Wastewater from textile plants contains suspending solid particles, solvent organics and a high proportion of colored compounds. Many of these substances except dye can be eliminated through physical processes [1].

Color usually originates from the use of dyes in high concentrations. Azo dyes are the most common and constitute 20 to 40% of all dyes used for coloring [2, 3]. Azo dyes have hetero-cyclical structure and one or more azo rings (-N=N-) [4, 5].

Colored compounds in wastewater lead to aesthetic pollution at their points of discharge. Discharged wastewater containing dyes reduces the conductivity of light necessary for the photosynthesis of primary producers

living in water and thus seriously harms ecosystems [6].

Hence, treatment of dye-containing wastewater from textile and dye manufacturing plants has recently drawn significant interest. Since methods used in this treatment differ in their effect depending on the nature of dye in wastewater, it becomes difficult to choose the right one. For example, since reactive dyes have high levels of solubility in water, it is difficult to obtain effective results from such methods as conventional coagulation and active sludge [7]. Consequently, oxidation and adsorption systems come to the fore as two major technologies in the treatment of textile wastewater [8]. The adsorption method is commonly used in the elimination of both colored and uncolored organic pollutants [9]. It should be noted, however, that the applicability of the adsorption process is largely dependent on the availability of cheap adsorbents and thus recent initiatives in adsorption process have targeted reaching economically reasonable adsorbents. Alternative adsorbents tested for this purpose include the following: volatile ash [10], sawdust [11], turf [12], chromium sludge [13], zeolite [14],

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active sludge [15], clay [16,17], mashed sugar beet [18], processed olive derivatives [19], fruit wastes [20], palm seed [21], bamboo [22], prune pit [23], chitosan [24], calcite alunite [25] and cellulose-based wastes [26].

A common feature of adsorbent materials is their large specific surface area. Structurally, adsorbent pellets are inevitably microporous and adsorption takes place almost exclusively in the pellets internal void surface (pore space). Consequently, uptake of adsorbates requires their molecules to diffuse into the interior of the pellets. Intrapellet mass transfer, therefore, needs to be considered as part of the uptake process.

Concerning the mechanisms by which intrapellet mass transfer is affected, since pellets are microporous and their void is occupied by the fluid to be treated by adsorption, adsorbate may diffuse through the pore fluid because of the presence of the radial concentration gradient. The presence of concentration gradient implies the existence of a similar concentration gradient in the adsorbed phase, which, in turn, causes the diffusion of the adsorbed molecules.

Both pore diffusion and molecular diffusion involve the migration of adsorbate molecules in fluid phases. Superficially, they may appear to be the same. There are, however, significant differences between them. Generally speaking, diffusion in the fluid phase results from collisions among molecules and with surfaces [27].

In order to explain the adsorption mechanism, various models have been proposed [27, 28, 14]. The aim of these models is to predict adsorption uptake rates by adsorbent pellets. The uptake of adsorbents from adsorption-treated solutions by adsorbent pellets involves several steps that transfer the adsorbent from the bulk of the fluid phase to the specific sites within the interior of the pellets as well as steps in the adsorption process itself [27].

Some of the investigators have applied the pore diffusion model with [28, 29] and without film resistance [30, 28]. McKay et al. [31] has developed "homogeneous solid phase diffusion" models to describe the adsorption of dyes on bagasse pith.

Meshko et al. [14], combining homogeneous diffusion models with external mass transfer resistance proposed a new approach for the kinetic investigation of the adsorption process.

Pumice, which is commonly found in Turkey and thus is easily and cheaply accessible, was used in this study as an alternative adsorbent to remove reactive azo dye from watery decompositions. Pumice is a volcanic stone, which can have an acidic or basic character. Due to its microporous structure, it has a high specific surface area. Pumice has been found to be effective for the removal of phosphate ion and also used as a support material for metal catalysts in biological treatments [32]. While assessing pumice in its dye-removing properties, the present study focused on the impact of such parameters as initial dye concentration, stirring speed, and adsorbent mass. The Freundlich adsorption isotherm was adopted. To explain the outcomes of the experiment, the diffusion method developed by Meshko et al. [14] was used as a model. The equation, describing the adsorption process, cannot be solved analytically because of its non-linearity and

the complicated boundary condition on the surface of the adsorbent particle. The Crank-Nicholson method was adopted to solve the partial differential equations. The dependency of both solid diffusivity ( $D_s$ ) and external mass transfer coefficient ( $k_f$ ) to different parameters was examined. The model showed good agreement with experimental data. It was finally concluded that pumice has high adsorption capacity and may therefore be used as an adsorbent.

## Mathematical Model

Pumice is a volcanic stone and pumice pellets are formed by binding large numbers of small microporous crystals with microporous material. Since resistances to mass transfer within the crystals and those through the binding material are different, they require different treatment in formulating the overall intrapellet diffusion process.

The pumice of pellet has a radius of  $R$  and is composed of many spherical microporous crystals of  $r_c$  with  $r_c \ll R$ . For diffusion within the crystals, since the intracrystalline pores are small, the diffusing molecules are always within the force field of the adsorbing surface, and their transport takes place in the form of "molecule hopping" between adsorption sites. Thus, the process is more similar to surface diffusion than to ordinary pore (or macropore) diffusion, except that the domain through which diffusing molecules migrate is not a two-dimensional surface but rather a three-dimensional space [27].

Following Meshko et al. [14] the diffusion process is described by the following partial differential equation:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ D_s r^2 \frac{\partial q}{\partial r} \right], \quad 0 < r < R, t > 0 \quad (1)$$

the boundary conditions are:

$$\frac{\partial q}{\partial r} = 0, \quad r = 0, t > 0 \quad (2)$$

$$D_s \rho_p \frac{\partial q}{\partial r} = k_f (c - c_s), \quad r = R, t > 0 \quad (3)$$

$$q_s = A c_s^{1/n}, \quad r = R, t > 0 \quad (4)$$

and the initial condition is:

$$q = 0, \quad 0 \leq r \leq R, t = 0 \quad (5)$$

In equation (3) we postulate that the uptake rate of adsorbate by a pellet is linearly proportional to  $(c - c_s)$ . Initial condition (Equation 5), shows that adsorption begins from  $t=0$ .

The overall mass balance for the closed batch experiment is given by:

$$V(c_0 - c) = M\bar{q}, \quad (6)$$

where the average concentration throughout the adsorbent particle is defined as:

$$\bar{q} = \frac{3}{R^3} \int_0^R qr^2 dr \quad (7)$$

The system of Equations (1) through (6) cannot be solved analytically because of its non-linearity and the complicated boundary conditions on the surface of adsorbent particle.

The objective here is to find  $q(r, t)$ ,  $D_s$  and  $k_f$  simultaneously by using additional information from experiments.

$$\bar{q}_i = \bar{q}(t_i), \quad i = 1, 2, \dots, N \quad (8)$$

Let  $Q(t)$  be a polynomial interpolation of  $q(t)$  based on Equation (8). Then, we can define from Equation (6):

$$c(t) = c_0 - \frac{MQ(t)}{V} \quad (9)$$

Thus, we can eliminate Equation (6), substituting expression (9) in formula (3). From equality (4) we can also write:

$$c_s = \left( \frac{q}{A} \right)^n \quad (10)$$

Substituting in Equation (3) we can rewrite this condition as:

$$D_s \rho_p \frac{\partial q}{\partial r} = k_f \left( c_0 - \frac{MQ(t)}{V} - \left( \frac{q}{A} \right)^n \right) \quad (11)$$

If we assume that  $D_s$  and  $k_f$  are known, then we obtain boundary value problem Equations (1), (2), (10) and (5) for the diffusion equation.

In this paper a computer program based on the diffusion model was developed using FORTRAN Language. In this investigation the partial differential equation was transformed into a set of algebraic equations using the finite differences method.

Let  $\tau = \Delta t > 0$ ,  $h = \Delta r > 0$  be a step length on time and space coordinate,  $\{0 = t_0 < t_1 < \dots < t_L = T\}$ ,  $\{0 = r_0 < r_1 < \dots < r_J = T\}$ , where  $t_m = m\tau$ ,  $r_j = jh$  denotes a partitions of the  $[0, T]$  and  $[0, R]$ , respectively.

Following the Crank-Nicholson method, the discrimination of Equation (1), (2), (10) and (5) would be:

$$\frac{q_{j,m} - q_{j,m-1}}{t} = \frac{1}{2} \left[ r_{j+1} \frac{q_{j+1,m} - q_{j,m}}{h^2} - r_j \frac{q_{j,m} - q_{j-1,m}}{h^2} + r_j \frac{q_{j+1,m-1} - q_{j,m-1}}{h^2} - r_{j-1} \frac{q_{j,m-1} - q_{j-1,m-1}}{h^2} \right] \quad (12)$$

$$1 \leq j \leq J-1, 1 \leq m \leq L$$

$$\frac{q_{1,m} - q_{0,m}}{h} = 0, \quad 1 \leq m \leq L \quad (13)$$

$$D_s \rho_p \frac{q_{J,m} - q_{J-1,m}}{h} = k_f \left[ c(t_m) - \left( \frac{q_{J,m}}{A} \right)^n \right] \quad (14)$$

$$1 \leq m \leq L$$

and

$$q_{j,0} = 0, \quad 0 \leq j \leq J \quad (15)$$

The following algorithm is employed to find  $D_s$  and  $k_f$ :

At the first step we fix the value  $k_f = k_f^{(0)}$  and change the value  $D_s$  to obtain the best fit of the results of numerical solution of Equations (1), (2), (10) and (5) to the experimental curves for batch adsorption and find  $D_s^{(1)}$ . After that, we fix  $D_s = D_s^{(1)}$  and change the value  $k_f$  to obtain the best fit again to the experimental curves and obtain  $k_f^{(1)}$ . At the second step, we fix  $k_f = k_f^{(1)}$  in the same way to define  $D_s^{(2)}$  and fix  $D_s = D_s^{(2)}$ , to define  $k_f^{(2)}$ . Repeating this step until attaining some accuracy, we define the optimal  $D_s$  and  $k_f$ . In addition, we have compared the theoretical and experimental results for  $\bar{q}(t)$  curves.

## Experimental

### Materials

#### Adsorbates

The reactive azo dye (CIBACRON NAVY P-2R-01), supplied by Ciba Specialty Chemicals was used as adsorbate. This reactive dye was used without further purification. The used azo dye contains a sulfonated mixture with two azo groups at ratios of 10-20% and a sulfonated dye with mono azo groups at ratios of 1-5%. The chemical structure of the used dye is given in Figure 1.

#### Adsorbents

Pumice was used as an adsorbent. Pumice has a density of 0.6 g cm<sup>-3</sup>, particle size of 75 μm and surface area of 85 m<sup>2</sup>g<sup>-1</sup>.

#### Analysis

The dye concentration was assessed by spectrophotometer (HACH DR 2000) at a wavelength corresponding to maximum adsorbent (622 nm). Other devices used in the experiment were a pH-meter (TESTO), a centrifuge (NÜVE NF 615) and a mixer (NÜVE ST 402) with water bath.

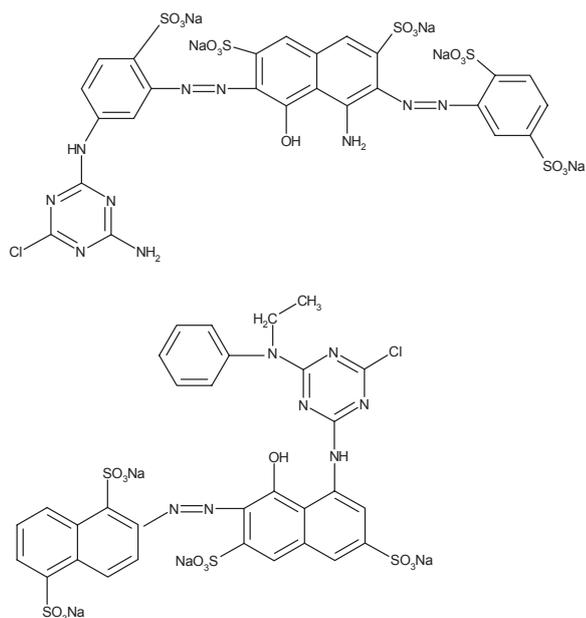


Fig. 1. The chemical structures of the reactive azo dyes.

### Equilibrium Isotherms

To determine adsorption isotherm, stock solution of  $200 \text{ mg L}^{-1}$  was prepared. Different concentrations ranging between  $30\text{--}100 \text{ mg L}^{-1}$  was supplied from stock solution by dilution. Chosen solution volume used in experiments was  $50 \text{ mL}$ .  $1\text{--}5 \text{ g}$  of pumice was added to samples. The resulting mixture was mechanically shaken. Experimental studies were carried on at  $23^\circ\text{C}$ .  $\text{pH}=4$  is chosen in all experimental studies.

### Batch Contact-time Experiments

The effect of initial dye concentration and adsorbent mass on dye removal was assessed by using a batch mixer reactor. Variation in stirring speed was held in the range  $50\text{--}250 \text{ rpm}$  whereas initial dye concentration varied in the interval  $30\text{--}100 \text{ mg L}^{-1}$ .

## Results and Discussion

### Adsorption Isotherm

The empirical Freundlich equation based on a heterogeneous surface is given by the following expression:

$$q_s = A c_s^{1/n} \quad (16)$$

where  $A$  is the Freundlich constant and  $n$  the Freundlich exponent. A linear form of the Freundlich expression will yield the constants  $A$  and  $n$ . Hence,

$$\log q_s = \log A + \frac{1}{n} \log c_s \quad (17)$$

Therefore, a plot of  $\log q_s$  versus  $\log c_s$  enables the constant  $A$  and exponent  $n$  to be determined. Figure 2 shows the dependence of  $\log q_s$  from  $\log c_s$ .

Adsorption capacities ( $A$ ) and adsorption intensities ( $n$ ), for pumice, were found to be  $0.024 \text{ mg g}^{-1}$  and  $1.469$ , respectively. The Freundlich isotherm equation for azo dye adsorption on the pumice is then:

$$q_s = 0.024 c_s^{0.6807} \text{ with } R^2 = 0.9862 \quad (18)$$

### Diffusion Model Results

The effect of initial dye concentration on the pumice capacity to remove reactive azo dye was examined within the interval  $30\text{--}100 \text{ mg L}^{-1}$ . First curves in Figure 3a and in Figure 3b show the results and relevant theoretical curve relating to the temporality of the average value of solid phase concentration  $\bar{q}(t)$  at dye concentration given as  $c_0 = 50 \text{ mg L}^{-1}$ . Experimental and theoretical analyses show good agreement. Table 1 gives  $k_f$  and  $D_s$  values obtained from numerical solutions on the diffusion model. The value of  $k_f$  is not associated with  $c_0$  and other parameters, whereas  $D_s$  is associated with initial dye concentration.

The study also examined the effect of stirring speed on dye removal by changing the speed in the interval  $50\text{--}250 \text{ rpm}$ . Second curves in Figure 3a and 3b show experimental data and the theoretical curve expressing the temporality of  $\bar{q}(t)$  at stirring speed of  $200 \text{ rpm}$ . Once more, experimental data conform to theoretical inferences. It was found that external mass-transfer coefficient  $k_f$  and solid diffusion coefficient ( $D_s$ ) are not associated with stirring speed. The summary of the results are provided in Table 1.

The effect of adsorbent mass in the removal of azo dye by using pumice was examined in the interval  $1\text{--}5 \text{ g}$ . Third curves in Figure 3a and 3b show experimental data and curve expressing temporality  $\bar{q}(t)$  at an adsorbent mass value of  $M = 1 \text{ g}$ . External mass-transfer and solid diffusion coefficients are given in Table 1.

Both experimental and theoretical conclusions point out that solid diffusion coefficient ( $D_s$ ) is associated with initial dye concentration. Figure 4 shows this dependency of  $D_s$  for a given adsorbent mass. It is clear in Figure 4 that higher initial dye concentration leads to a linear increase

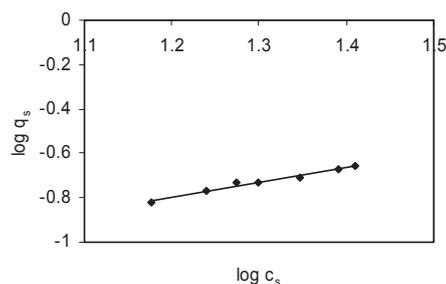


Fig. 2. Freundlich adsorption isotherm for azo dye on pumice.

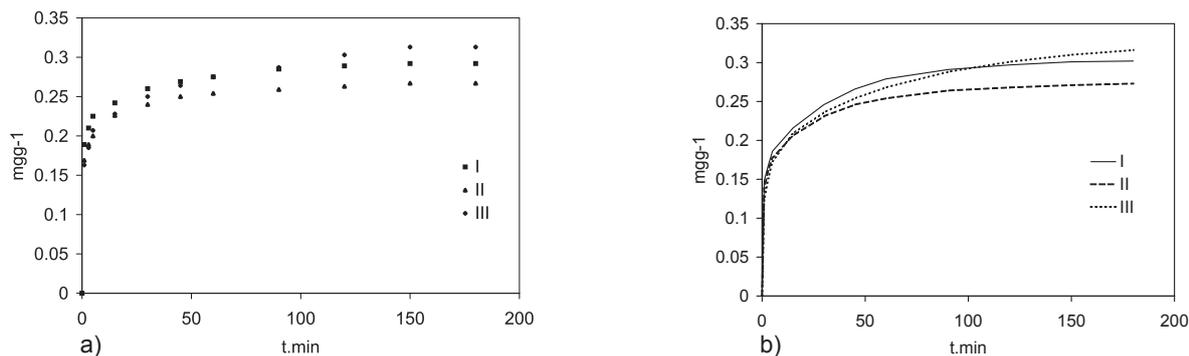


Fig. 3. Time dependence of solid phase concentration average value, a) experimental dates, b) theoretical curve: I:  $T=23^{\circ}\text{C}$ ,  $M=5\text{ g}$ ,  $c_0=50\text{ mg L}^{-1}$ , 100 rpm; II:  $T=23^{\circ}\text{C}$ ,  $M=5\text{ g}$ ,  $c_0=30\text{ mg L}^{-1}$ , 200 rpm; III:  $T=23^{\circ}\text{C}$ ,  $M=1\text{ g}$ ,  $c_0=30\text{ mg L}^{-1}$ , 100 rpm.

in the value of  $D_s$ . Meshko et al. [14] demonstrated the same effect in their own systems of inquiry.

As seen from Table 1 in the case adsorbent mass ( $M$ ) and agitation speed are chosen same, then solid diffusivity ( $D_s$ ) is linear to initial concentration ( $c_0$ ). If adsorbent mass and agitation speed are different, ( $D_s$ ) and ( $c_0$ ) are not linear.

It is shown that changing adsorbent mass does not have any influence on the external mass-transfer coefficient. However, it was found that the solid diffusivity ( $D_s$ ) varied in line with adsorbent mass.

The association between  $D_s$  and adsorbent mass while initial dye concentration is given as fixed is shown in Figure 5. As the figure shows, higher adsorbent mass is associated with lower diffusion coefficient.

## Conclusions

Pumice was used as adsorbent for removing reactive azo dye from watery solutions. The relationship between

the amount of dye removed and such parameters as initial dye concentration, stirring speed and adsorbent mass was analyzed. The diffusion model was used to explain the working of the adsorption mechanism. Experimental and theoretical analysis points to the following conclusions:

- Pumice, which can be found easily in Turkey, is an appropriate adsorbent for removing dye from wastewater.
- The Freundlich adsorption showed that it could describe experimental results. The value for adsorption capacity ( $A$ ) was found as  $0.024\text{ mg g}^{-1}$  and adsorption intensity ( $n$ ) as 1.469.
- The diffusion model was numerically assessed by using the Crank-Nicholson method and it was found that average solid-phase concentration varied by time in different circumstances. There was conformity between theoretical inferences and practical outcomes. Furthermore, theoretical values for  $D_s$  and  $k_f$  were found from the diffusion model.

Table 1. External mass transfer and diffusion coefficients for the adsorption of reactive azo dye on pumice.

Run No.	$c_0$ ( $\text{m L}^{-1}$ )	$M$ (g)	Agitation speed (rpm)	$k_f \cdot 10^5$ ( $\text{m s}^{-1}$ )	$D_s \cdot 10^{14}$ ( $\text{m}^2\text{s}^{-1}$ )
1	30	5	100	3.72	0.86
2	50	5	100	3.72	0.97
3	70	5	100	3.72	1.08
4	100	5	100	3.72	1.24
5	30	5	50	3.72	0.86
6	30	5	150	3.72	0.86
7	30	5	200	3.72	0.86
8	30	5	250	3.72	0.86
9	30	1	100	3.72	2.16
10	30	2	100	3.72	1.42
11	30	3	100	3.72	1.06

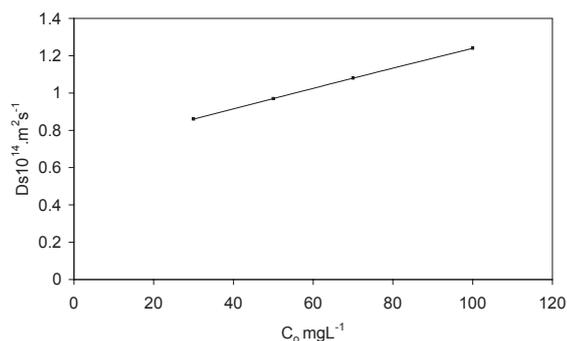


Fig. 4. Concentration dependence of solid diffusivity.

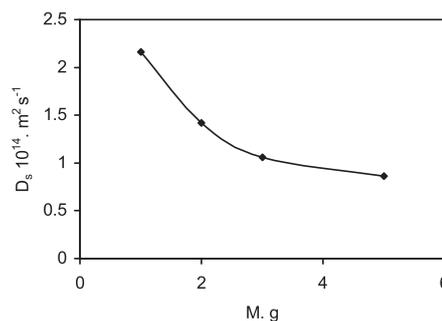


Fig. 5. Adsorbent mass dependence of solid diffusivity.

- It was shown that external mass-transfer coefficient ( $k_f$ ) was not associated with dye concentration ( $c_0$ ) and that  $D_s$  increased linearly as initial  $c_0$  did. Furthermore,  $D_s$  was found to be associated with adsorbent mass.

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### Nomenclature

- A - parameter in the Freundlich equation, mg g<sup>-1</sup>
- c - liquid-phase concentration, mg L<sup>-1</sup>
- $c_0$  - initial value of c, mg L<sup>-1</sup>
- $c_s$  - liquid-phase concentration at liquid-pellet interface, mg L<sup>-1</sup>
- $D_s$  - solid diffusivity, m<sup>2</sup> s<sup>-1</sup>
- $k_f$  - external mass-transfer coefficient, m s<sup>-1</sup>
- M - adsorbent mass, g
- n - parameter in the Freundlich equation
- $\bar{q}$  - solid-phase concentration, mg g<sup>-1</sup>
- $q_s$  - value of q at liquid pellet interface, mg g<sup>-1</sup>
- q - average value of q, mg g<sup>-1</sup>
- r - radial distance measured from the center of a pellet, m
- R - pellet radius, m
- t - time, s
- V - volume of solution, m<sup>3</sup>
- q(t) - average value of q at moment t, mg g<sup>-1</sup>
- $\bar{q}(r,t)$  - solid-phase concentration at moment t in the point r, mg g<sup>-1</sup>
- q(t<sub>i</sub>) - average value of q at moment t<sub>i</sub>, mg g<sup>-1</sup>
- i, j, m - natural numbers
- Q(t) - polynomial interpolation of q(t)
- h - step length on space coordinate, m

- $t_0$  - initial value of time, s
- J - number of coordinate steps
- L - number of time steps
- $q_{j,m}$  - solid-phase concentration at moment  $t_m$  in the point  $r_j$ , mg g<sup>-1</sup>
- $k_f^{(1)}$  - initial value of  $k_f$ , m s<sup>-1</sup>
- $D_s^{(1)}$  - value of  $D_s$  in the first approximation
- $k_f^{(0)}$  - value of  $k_f$  in the first approximation
- $\tau$  - step length on time, s
- $\rho_p$  - particle density, kg m<sup>-3</sup>

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