

# Adsorption equilibrium modelling for different temperature conditions and its influence on adsorption mass transfer

## *Modeliranje adsorpcijskega ravnotežja v različnih temperaturnih pogojih in njegov vpliv na prenos snovi pri adsorpciji*

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**Abstract:** The paper deals with numerical modelling of adsorption kinetics in a narrow channel of a honeycomb type adsorber. The mass transfer model consists of solving the diffusion-convection transport equation for adsorbate species in the fluid phase. The adsorbate flux to the wall is computed implicitly by using the Boundary Element Method for the solution of the transport equation. Scalable boundary condition for the adsorbate concentration on the adsorbent walls is used, defined on basis of the ratio of the accumulated adsorbate mass and the equilibrium adsorbate mass for a given system temperature. As the state of equilibrium is dependent also on the system temperature, a sensitivity study of the adsorption process under different system temperatures is performed. Among the studied adsorption equilibria models, including the Freundlich model, Simplified local density (SLD) model and the Dubinin-Radushkevich model, the latter is proved as the best compromise between accuracy and computational cost and applied in mass transfer kinetics computations. The results of computations show, that the increase in system temperature results in a decrease of breakthrough times, as the equilibrium amounts of adsorbate at the adsorbent walls decrease with increasing temperature, therefore making the derived numerical model suitable for further use in detailed mass transfer kinetics computations.

**Key words:** subdomain boundary element method, laminar viscous fluid flow, mass transfer, adsorption, honeycomb adsorber.

**Povzetek:** V prispevku je predstavljen numerični model za simulacijo adsorpcijskega procesa v kanalu, ki ima na svojih stenah nameščeno plast adsorbenta. V kanalu teče tok nosilnega plina z zelo nizko koncentracijo adsorbata, ki adsorbira v plast adsorbenta. Prenos snovi je simuliran z reševanjem difuzivno-konvektivne prenosne enačbe ohranitve mase adsorbata, diskretizirane z metodo robnih elementov. Adsorpcijski proces je modeliran s prilaganjem vrednosti robne koncentracije, ki je odvisna od razmerja med akumulirano ter ravnotežno množino adsorbata v plasti adsorbenta. Ker se ravnotežno stanje spreminja s temperaturo sistema je v prispevku prikazan vpliv le-te na ravnotežno stanje. Ravnotežna množina adsorbata v plasti adsorbenta je določena s Freundlich. SLD in Dubinin-Radushkevich ravnotežnim modelom, kjer se slednji izkaže za najboljšo izbiro glede na natančnost rezultatov in računski čas. Rezultati izvedenih preračunov kažejo, da se s povečevanjem temperature v sistemu zniža čas pri katerem pride do preboja adsorbata, ker se ravnotežna količina adsorbata na stenah adsorbenta zmanjšuje s povečevanjem temperature sistema. Izdelana numerična rutina omogoča natančno modeliranje adsorpcijskih procesov v kanalu ter napovedovanje prebojne koncentracijske krivulje adsorbata.

**Ključne besede:** podobmočna metoda robnih elementov, laminarni viskozni tok tekočine, prenos snovi, adsorpcija, adsorber s satovjem.

## 1. Introduction

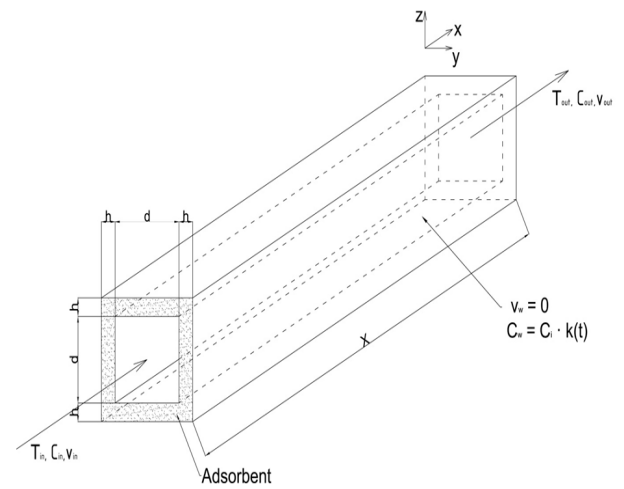
Adsorption based technologies are increasingly used in various fields of engineering. Their use range from the classical applications in gas cleaning (Dreisbach et. al. [1]), where the selective physical or chemical bonding of gas species on solid matrix of adsorbent is the most important effect, to applications in heat exchange applications, for example in domestic appliances. In both cases, adsorption is characterised by heat release and consequent increase in the system temperature, if no cooling is applied. The increase in temperature has a negative effect on the state of equilibrium between adsorbent and adsorbate, effectively reducing the maximum amount of adsorbate, that can be bound on the outer and inner surface of adsorbent. A lot of research the work was already done in the field of adsorption equilibrium modelling (Rangarajan et. al. [2], Soule et. al. [3], Fitzgerald et. al. [4]). In adsorption equilibrium modelling simple analytical models like Henry, Langmuir or Freundlich isotherms are predominantly used, although more accurate models are being developed, like Monte Carlo simulations (MC) and Molecular Dynamics simulations (MD), as noted by Fedorov [5]. For engineering calculations empirical models like Dubinin-Radushkevich model are still the preferred choices over more complex MC and MD simulations (Fedorov [6], Valdés-Solís et al. [7]). Lately, new types of special adsorbers have been developed, among them a honeycomb adsorber where adsorbent material is attached to the honeycomb structure as a thin film on the surfaces of the channels (Valdés-Solís et. al. [8]). The main advantage of such configuration is fast mass exchange rate between the bulk flow and the adsorbent walls, enabling very short time intervals for cycling of adsorption/desorption processes, and a low pressure drop in the device (Wajima et. al. [9]), decreasing cost of operation.

In the present paper, the influence of the increased temperature in a channel of a honeycomb type adsorber on mass transfer characteristics of the device is investigated. A special attention is given as well as to local mass transfer characteristics as to transient behaviour in form of a breakthrough curve. The paper builds on previous research, reported in work Štívec et. al [10] and [11].

The paper is organized as follows. After a short description of the adsorbent geometry and governing equations, Section 2, selected thermodynamic equilibrium models are described and evaluated in Section 3. Details of the applied numerical model for the solution of the mass transfer kinetics in the channel are given in Section 4, where also main computational results and their analysis is presented. The paper closes with conclusions.

## 2. Problem description and governing equations

The configuration of adsorption device under consideration is a honeycomb structure adsorber with narrow channels. Since the channels are decoupled from one another by the solid walls, it is possible to study the adsorption kinetics only inside a single channel, shown in Figure 1. The channel surfaces are covered with adsorbent material, which adsorbs the adsorbate species, entering the channel. Since the mixture mass flow in a single channel is low enough, it is possible to consider flow as incompressible and laminar. Also, since the adsorption mass flux is negligibly small in comparison to the mixture mass flow, it is assumed that adsorption process does not affect the flow field. This allows decoupling the fluid flow from adsorption kinetics, leading to lower computational cost of simulations.



**Figure 1.** Configuration of a narrow channel of a honeycomb adsorber.

In our case, the flow field is considered as fully developed and the analytical solution of Chen [12] is used, as already reported in [10]:

$$v_x(y,z) = \frac{4 \cdot d^2}{\mu \cdot \pi^3} \cdot \frac{12\mu}{d^2} \cdot \frac{v_0}{1 - \frac{192}{\pi^5} \cdot \frac{d}{\sum_n \frac{1}{n^5} \cdot \tanh\left(n \cdot \pi \cdot \frac{d}{2 \cdot d}\right)}} \cdot \sum_n \left[ \frac{1}{n^3} \cdot (-1)^{\left(\frac{n-1}{2}\right)} \cdot \left( 1 - \frac{\cosh\left(n \cdot \pi \cdot \frac{y}{d}\right)}{\cosh\left(n \cdot \pi \cdot \frac{d}{2 \cdot d}\right)} \right) \cdot \cosh\left(n \cdot \pi \cdot \frac{z}{d}\right) \right] \quad (1)$$

where  $\mu$  is dynamic viscosity,  $d$  channel width,  $d$  channel height,  $v_0$  average inflow velocity,  $y$  and  $z$  coordinates in the channel.

The adsorption is accompanied by the heat release, which causes the change in the temperature in the channel. Since the maximum amount of adsorbate, that can be adsorbed to the solid surface, changes with temperature, it is important to consider this in the

numerical model. It is therefore important to include in the numerical model an equilibrium model for adsorption, that involves also the temperature as a system unknown. The data on thermodynamic equilibrium is used in two ways, first in setting the upper limit of the amount of adsorbed species, computed as a sum of time varying species mass fluxes to the local wall area,

$$Q_{accum}(t) = \sum_0^t \dot{q} \cdot \Delta t. \quad (2)$$

where species mass flux is defined as

$$\dot{q} = \int_A D \vec{\nabla} C \cdot \vec{n} dA \quad (3)$$

where  $D$  is the diffusion coefficient of adsorbate in the carrying fluid and  $A$  is the outer surface area of the adsorbent layer.

Second, the thermodynamic equilibrium data is used in setting up a scalable wall boundary condition, based on the ratio between the accumulated adsorbent mass and the equilibrium amount of adsorbent mass,

$$\frac{q(t)}{q_{eq}} = k(t) \quad (4)$$

which is then used in setting the wall boundary condition

$$C_w = C_i k(t), \quad (5)$$

with  $C_i$  the concentration in the vicinity of the wall. This boundary condition is applied in the numerical solution of the diffusion-convection transport equation for adsorbate species,

$$\frac{\partial C}{\partial t} + (\vec{v} \cdot \vec{\nabla}) C = \frac{1}{ReSc} \nabla^2 C. \quad (6)$$

Due to very low species concentrations in the mixture, less than 1% of total mass in the flow, the mixture properties are assumed constant. In the above model for species transport buoyancy forces, thermal diffusion and inter diffusion effects are neglected.

### 3. Adsorption equilibrium models

Adsorption process in the channel stops when thermodynamic equilibrium is reached, and the numerical model must reflect this fact in order to be able to realistically describe mass transfer conditions inside the channel. Additionally, since the temperature of the system also increases as the adsorption progresses, a thermodynamic model must include also the system temperature as a state parameter. There are several thermodynamic equilibrium models, developed

for the use in modelling of adsorption equilibrium. As stated in introduction, for engineering calculations and also computational mass transfer models empirical thermodynamic equilibrium models are still the preferred choices over more complex Monte Carlo and Molecular Dynamics simulations. As numerical simulations based on solving the mass transport equations in the fluid phase typically require dense computational grids, especially in the vicinity of solid walls, and hence long computational times, equilibrium model used should also offer low computational cost in order to reach feasible computational times in computing time dependent problems, like numerical determination of the breakthrough curve.

In the present work, three adsorption equilibrium models for the case of adsorption of buthane from the air mixture on activated carbon are considered. First, the accuracy study of the models for a predefined and experimentally measured thermodynamic conditions is performed, followed by the application of the most favourable model in computation of mass transfer characteristics for the cases with different system temperature.

The first considered model was the adsorption equilibrium model of Dubinin-Radushkevich [13], giving equilibrium amount of adsorbate per adsorbent volume as

$$q_{eq} = q_{max} \left\{ - \left( \frac{RT}{\beta E_0} \ln \frac{C_{sat}}{C} \right) \right\}. \quad (7)$$

In the case of air-buthane activated carbon system, the  $q_{max} = 509.34 \text{ kg/m}^3$  is the maximum amount of adsorbate adsorbed at the saturation pressure,  $R$  is the gas constant,  $T$  is system temperature,  $C_{sat} = 6.48 \text{ kg/m}^3$  is the vapour pressure of adsorbate at ambient conditions,  $C = C_{in}$  is concentration of adsorbate and affinity coefficient multiplied with energy parameter is  $\beta E_0 = 22767 \text{ J/molK}$ . The second equilibrium model was the three parameter Freundlich model:

$$q_{eq} = \left( \frac{k_1}{T} + k_2 \right) C^n, \quad (8)$$

with the  $k_1$  and  $k_2$  and  $n$  are empirically determined coefficients with values  $k_1 = 1.0$ ,  $k_2 = 628.0$  and  $n = 0.15$ . The third model used was the Simplified local density (SLD) model, which enables determination of surface excess of adsorbate species on the solid active surface of adsorbent

$$\Gamma^{ex} = \int_{z_0}^{\infty} (\rho_{ad}(z) - \rho_{ad/bulk}) dz. \quad (9)$$

where  $\Gamma^{ex}$  is surface excess,  $\rho$  is adsorbate partial density at the distance  $z$  from the active surface of

adsorbent and in the bulk of the fluid mixture The theoretical structure of the model with computational details is presented in [11]. With computed surface excess the equilibrium amount of adsorbate is computed as

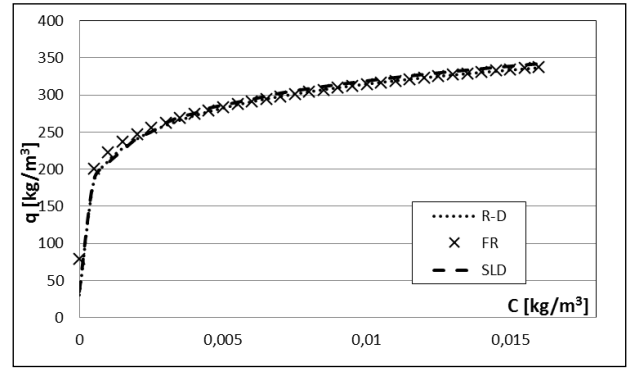
$$q_{eq} = \Gamma^{ex} \rho_{mas} A_{AO} M . \tag{10}$$

with  $\rho_{mas}$  the adsorbent mass density,  $A_{AO}$  the value of active surface relative to the adsorbent mass and  $M$  adsorbate molar mass. In the Table 1, parameters, used in the SLD model with Peng-Robinson equation of state, are listed.

**Table 1.** Parameters used in SLD calculations.

Parameter	Value	Units
$\sigma_{ff}$	$2.725 \cdot 10^{-10}$	m
$\sigma_{ss}$	$2.8 \cdot 10^{-10}$	m
M	0.05812	kg/mol
$T_c$	647.1	K
$p_c$	$2.206 \cdot 10^7$	Pa
w	0.34486	

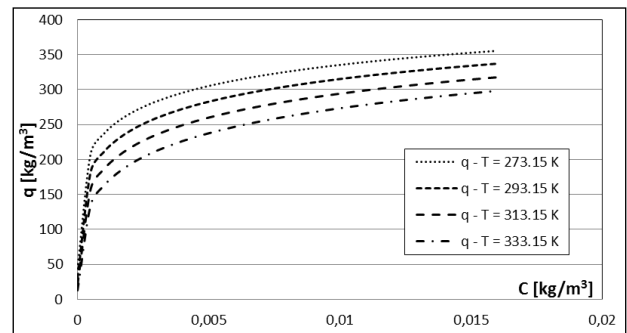
In order to assess the physical correctness of the described equilibrium models the adsorption isotherm, reported in Valdés-Solís et. al. [7], valid for system temperature  $T = 293.15 K$  was evaluated with all three equilibrium models. From the results of equilibrium curves, shown in Fig. 2., it can be concluded that the SLD model and Dubinin-Radushkevitch model give nearly identical results in the whole range of adsorbate concentrations, whereas the Freundlich model overshoots in the low concentration range. Due to the latter fact the Freundlich model was not selected for further investigation. The same conclusion was made for the SLD model, which gives excellent results in terms of accuracy, but at a very high computational cost in comparison to Dubinin-Radushkevitch model. The latter fact originates in numerical integration procedure and numerical solution of a nonlinear equation by the Newton's method in computing the adsorbate density profile in the vicinity of the active surface.



**Figure 2.** Adsorption isotherms for the case of : FR - Freundlich model , R-D Dubinin-Radushkevitch model and SLD – SLD Peng-Robinson model.

#### 4. Computational results

The adsorption case, studied in Valdés-Solís et. al. [7], was selected as the test case for the study of the influence of temperature on adsorption characteristics. Adsorption equilibrium for different system temperatures was modeled with Dubinin – Radushkevich equation. A range of temperatures from 273.15K to 333.15K was selected. The computed Dubinin – Radushkevich equilibrium isotherms are shown on Figure 3. One of the important facts is that the geometrical shape of the curves is more or less comparable throughout the computed concentration range, a fact that will also help explain the mass transfer conditions in the moving concentration front along the wall.



**Figure 3.** Adsorption equilibrium for different system temperatures, Dubinin-Radushkevich model.

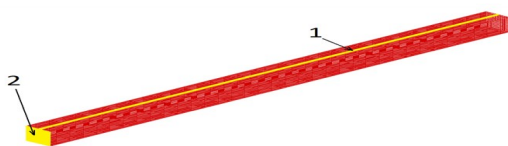
In Table 2, values of equilibrium amounts of adsorbate per volume of adsorbent are given, computed with Dubinin-Radushkevich model for the case of adsorbate concentration  $C = 0,007358 kg/m^3$ . Clearly, with increasing the temperature the equilibrium amount of adsorbate is decreased, leading to the need for shorter operation periods of an adsorber.

**Table 2.** Specific equilibrium amounts of adsorbate  $q_{eq}$  for adsorbate concentration  $C=0,007358 \text{ kg/m}^3$  at different system temperatures.

T	$q_{eq}$
273.15 K	322.34 $\text{kg/m}^3$
293.15 K	300.71 $\text{kg/m}^3$
313.15 K	279.16 $\text{kg/m}^3$
333.15 K	257.89 $\text{kg/m}^3$

Next, mass transfer kinetics inside the narrow channel of the honeycomb adsorber was studied. The air mixture considered had constant physical properties density  $\rho_0 = 1.164 \text{ kg/m}^3$  and kinematic viscosity  $\nu_0 = 1.522 \cdot 10^{-5} \text{ m}^2/\text{s}$ . In the channel, the species of buthane are transported within the air mixture by means of convection and diffusion, and are adsorbed or desorbed on the wall. Due to lack of accurate data the species diffusivity  $D_0 = 1.13 \cdot 10^{-5} \text{ m}^2/\text{s}$  was selected for  $T=293.15\text{K}$  and was considered as constant, leading to the Schmidt number value  $Sc = \nu_0/D_0 = 1.347$  and the Reynolds number value  $Re = v_0 d/\nu_0$ , with  $v_0$  the average inflow velocity, was set to 2.92. At the inflow the constant species concentration  $C_{in} = 0.007358 \text{ kg/m}^3$  was prescribed. On the outflow of the channel the convective boundary condition was set, allowing the unhindered outflow of the concentration fronts. Adsorbate concentration on the channel wall  $C_w$  was set to 0 only in the first time step of the simulations.

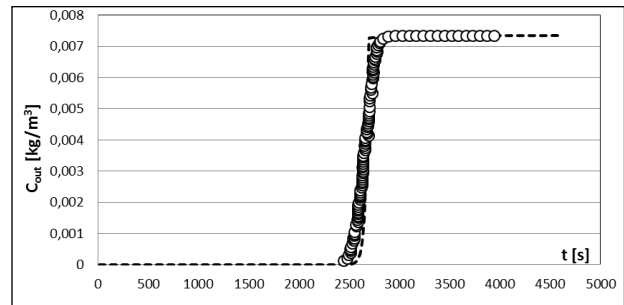
Computational scheme based on the subdomain Boundary Element Method [10] was used for the numerical simulation of the adsorption process in a honeycomb adsorber. A diffusion-convection transport equation (6) for species transport was solved for the mass transfer in the fluid with implementation of dynamic boundary condition for adsorbent concentration at the wall (5). Adsorption equilibrium was calculated with the use of the Dubinin-Radushkevich equilibrium model. Initial validation of the numerical scheme was done with the information provided in the work of Valdés-Solís et. al. [7]. Based on this the computational grid with  $8 \times 8 \times 378$  elements and 546215 nodes and the time step  $\Delta t = 0.25\text{s}$  were selected.



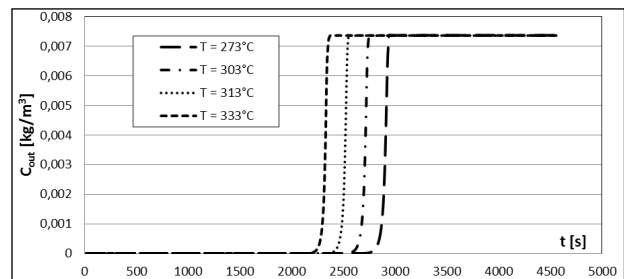
**Figure 4.** Computational domain with highlighted centerline (1) along the channel, which was used for analysis of mass transfer characteristics, and outlet plane (2), where concentration kinetics ( $\bar{C}_{out}$ ) was monitored.

In Fig. 5 the computed breakthrough curve for the case of  $T=293.15\text{K}$  and its comparison with results of Valdés-Solís et. al. [7] is shown. A very good agreement can be observed, although there are some differences in the velocity of the concentration front, which can be attributed to the use of two different diffusion coefficients of adsorbate species for radial and axial direction and also to the art of experimental evaluation of concentration values in the multichannel configuration, both reported in [7].

In Figure 6, the computed breakthrough curves for different values of system temperature are given. The effect of increasing the temperature is shortening the time of the concentration front breakthrough, meaning that the adsorber has a decreased operational time period, which is a consequence of the decrease in the equilibrium amount of adsorbate (see Table 2).



**Figure 5.** Simulation results for  $T = 293,15 \text{ K}$ , the breakthrough curve for  $T=293,15\text{K}$ : o Valdés-Solís, - - - present model.



**Figure 6.** Average concentration  $\bar{C}_{out}$  at the outlet of the channel for different system temperatures.

The adsorbate mass transfer characteristics were studied based on the evaluation of local values of the Sherwood number, defined as

$$Sh = \frac{1}{C - C_0} \frac{\partial C}{\partial n} L \tag{11}$$

with  $C$  the local concentration,  $C_0$  the inlet concentration,  $\frac{\partial C}{\partial n}$  the concentration gradient in direction normal to the wall, computed implicitly by the BEM based computational algorithm [10], and  $L$  the characteristic length, equal to the channel width.

In terms of mass transfer nondimensional variable, the Sherwood number, the same effect as in breakthrough curves can be observed. In Figure 7 local values of the Sherwood number along the line (1) at the time instant of  $t=460s$  are shown.

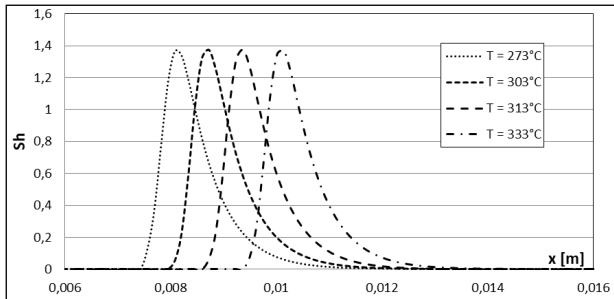


Figure 7. Local values of the Sherwood number along line (1) at the  $t = 460s$ .

Each curve with non-zero point values denotes the area along the line (1), where mass transfer (adsorption) is taking place. Along each  $Sh$  curve, the area to the left of the non-zero values corresponds to the saturated conditions, where adsorption had already reached equilibrium, and the area to the right corresponds to the unsaturated conditions along the wall, where no contact with incoming mixture flow has yet been established, see also Figure 8 for the distribution of concentration values and Figure 9 for distribution coefficient  $k(t)$  values.

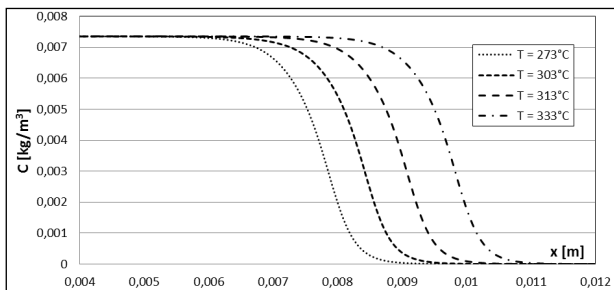


Figure 8. Local values of concentration  $C_w$  along the line (1) at  $t = 460s$ .

The position of the  $Sh$  curve (Figure 7) for the highest temperature, the  $k(t)=1$  values (Figure 9) as well as  $C = C_{in}$  values have advanced furthest along the direction of the flow (to the right), proving, that the process of adsorption is decreasing in strength as the temperature of the system increases. The similar magnitude of the curve peaks and strong similarity in the shapes (Figure 7) is the result of the adsorption isotherm data at different temperature levels, which also show a very high degree of similarity, as depicted in Figure 3.

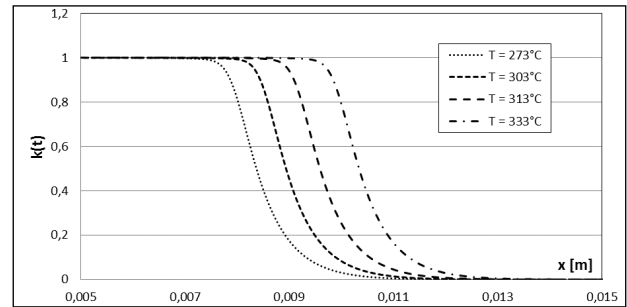


Figure 9. Local values of distribution coefficient  $k(t)$  along the line (1) at  $t = 460s$ .

### 5. Conclusions

In the presented work the effect of different system temperatures on the adsorption characteristics in a narrow channel of a honeycomb type adsorber has been studied. The applied numerical method, based on the Boundary Element Method computational algorithm. Three different adsorption equilibrium models for the use in the numerical model were tested, including the Freundlich model, Dubinin-Radushkevich model and Simplified Local Density model. As the Dubinin-Radushkevich model proved to offer accurate results with low computational cost, it was selected as the model for study of mass transfer kinetics at different system temperatures. The computed results indicate that the effect of increasing the temperature is shortening the time of the concentration front breakthrough, meaning that the adsorber has a decreased operational time period, which is a consequence of the decrease in the equilibrium amount of adsorbate, that can be adsorbed at the walls of the channel. This is an expected result, which proves, that the developed physical and numerical model is capable of solving complex time-dependent analysis of mass transfer kinetics at varying system temperatures. This also indicates, that the model can be extended to simulation of non-isothermal cases, where release of heat during adsorption locally increases temperature, which negatively affects the thermodynamic equilibrium at the wall. The latter consideration will be considered in the scope of the future work.

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