

# Analysis of Reversible Adsorption in Cylindrical Micro/Nanofluidic Channels for Analyte Sensing and Sample Dilution Applications

Ivana Jokić, Katarina Radulović, Miloš Frantlović, Zoran Djurić, *Member, IEEE*,  
Katarina Cvetanović, and Milena Rašljić

**Abstract**—The principle of operation of one class of chemical/biological sensors is based on adsorption of particles of a target substance from a fluid on a surface which can be a wall of a micro/nanochannel. When a channel is used for transport of fluids between different parts of microsystems, adsorption may cause dilution of the transported fluid, which is useful e.g. for sample purification, but detrimental when the fluid has to be delivered with unaltered chemical properties. In both groups of applications the analysis of adsorption phenomena is necessary in order to estimate and then optimize the micro/nanofluidic system performance. In this paper reversible adsorption in cylindrical micro/nanochannels is analyzed by using both the theoretical expressions and computer simulations. Applicability of the two-compartment model for approximation of the particles concentration distribution in a channel is also considered, as it can significantly facilitate the analysis of the adsorption process on the channel walls.

**Index Terms**—Adsorption; microfluidics; nanofluidics; cylindrical channel; sensing; sample dilution.

## I. INTRODUCTION

A microfluidic/nanofluidic device has one or more channels with at least one dimension less than 1 mm/1  $\mu\text{m}$ . Such devices can be fabricated from a variety of materials,

Ivana Jokić is with the Institute of Chemistry, Technology and Metallurgy – Center of Microelectronic Technologies, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: [ijokic@nanosys.ihtm.bg.ac.rs](mailto:ijokic@nanosys.ihtm.bg.ac.rs)).

Katarina Radulović is with the Institute of Chemistry, Technology and Metallurgy – Center of Microelectronic Technologies, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: [kacar@nanosys.ihtm.bg.ac.rs](mailto:kacar@nanosys.ihtm.bg.ac.rs)).

Miloš Frantlović is with the Institute of Chemistry, Technology and Metallurgy – Center of Microelectronic Technologies, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: [frant@nanosys.ihtm.bg.ac.rs](mailto:frant@nanosys.ihtm.bg.ac.rs)).

Zoran Djurić is with the Institute of Technical Sciences of SASA, Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia (e-mail: [zoran.djuric@itn.sanu.ac.rs](mailto:zoran.djuric@itn.sanu.ac.rs)).

Katarina Cvetanović is with the Institute of Chemistry, Technology and Metallurgy – Center of Microelectronic Technologies, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: [katarina@nanosys.ihtm.bg.ac.rs](mailto:katarina@nanosys.ihtm.bg.ac.rs)).

Milena Rašljić is with the Institute of Chemistry, Technology and Metallurgy – Center of Microelectronic Technologies, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: [milena@nanosys.ihtm.bg.ac.rs](mailto:milena@nanosys.ihtm.bg.ac.rs)).

including silicon, glass, metals, ceramics, hard plastics, and elastomers, by using common two- or three-dimensional processes belonging to MEMS (MicroElectro-Mechanical Systems) technologies, such as photolithography, thin film metallization and chemical etching, but also by prototyping techniques (injection molding, hot embossing, soft lithography, etc.) or direct fabrication techniques (laser photoablation or laser micromachining, x-ray lithography, etc.) [1-3].

Micro/nanochannels can be used for transport of fluids between different parts of microsystems. However, they can also be the place where the main function of the microsystem is performed (a chemical reaction, analyte detection, nanoparticles synthesis etc.). Among the most promising applications of micro/nanofluidic devices are those in the field of medicine (e.g. bio/chemical sensors for personalized health monitoring or as a part of medical diagnostic or therapeutic instrumentation) and those in the field of environmental protection (e.g. chemical sensors and biosensors of water and air pollutants) [4-6].

On the walls of a micro/nanochannel adsorption of particles that exist in the fluid occurs, which may or may not be desirable. For example, in sensing applications adsorption enables detection of a target substance or elimination of a competitor substance. Adsorption may also cause dilution of the transported fluid, which is useful e.g. for sample purification, but detrimental when the fluid has to be delivered with unaltered chemical properties. Obviously, the analysis of adsorption phenomena is necessary in order to estimate and then optimize the micro/nanofluidic system performance.

In this paper reversible adsorption in cylindrical micro/nanochannels is analyzed by using both theoretical expressions and computer simulations. Applicability of the two-compartment model for approximation of the particles concentration distribution in a channel is also considered, as it can significantly facilitate the analysis of the adsorption process on the channel walls.

## II. THEORETICAL CONSIDERATIONS

A schematic representation of a cylindrical micro/nanochannel is shown in Fig. 1.

In a group of micro/nanofluidic chemical and biological

sensors [7] using surface-based methods for analyte detection, a binding reaction occurs between the target analyte (present in the sample flowing through the micro/nanochannel) and capturing probes immobilized on the channel wall(s). The sensor response is determined by the number of analyte particles adsorbed on the channel wall(s). The number of adsorbed particles can also be a measure of elimination (useful or detrimental, stimulated or spontaneous) of a certain substance from the fluid transported through the channel. For example, the affinity of surfaces toward proteins may remove pharmacological proteins from the transported media, which can be quantified by the number of protein molecules adsorbed.

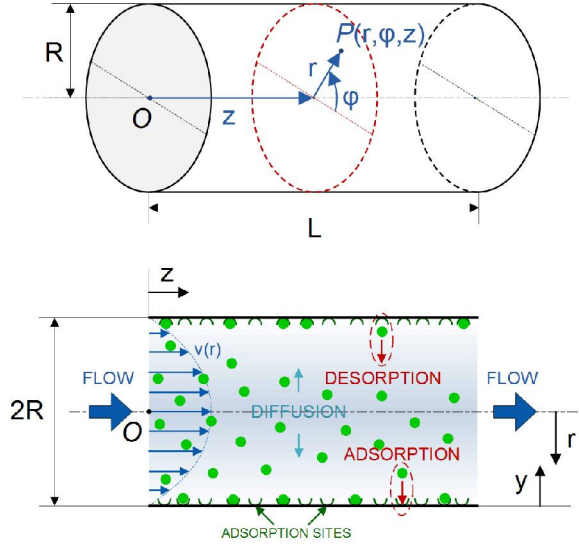


Fig. 1. Schematic representation of a cylindrical micro/nanochannel: basic structure with denoted geometrical parameters and coordinates of the cylindrical coordinate system (top), illustration of adsorption-desorption and transport processes (flow and diffusion) in longitudinal section of the channel, with coordinates relevant for theoretic analysis (bottom).

The number of adsorbed particles on the channel wall,  $N(t)$ , is determined by the affinity of the surface for their binding (specific/nonspecific) and the intrinsic adsorption-desorption (AD) scheme, but also by the transport processes of the particles toward the wall (i.e. the adsorption sites) and in the opposite direction (Fig. 1). In continuous-flow micro/nanochannels a fluid flow is laminar due to the low Reynolds number ( $Re=2\rho v_m R/\mu$ ,  $\rho$  is the fluid density,  $\mu$  is the dynamic viscosity of the fluid, and for aqueous solutions  $\rho=10^3$  kg/m<sup>3</sup> and  $\mu=10^{-3}$  kg/(ms)), thus the parabolic velocity profile within the channel is observed

$$v = V_m(1 - r^2/R^2) = 2v_m(1 - r^2/R^2) \quad (1)$$

( $V_m$  is the maximal velocity,  $v_m$  is the mean velocity,  $R$  is the channel radius, and  $r$  is the radial coordinate of the cylindrical coordinate system; here  $0 \leq r \leq R$  defines the channel cross-section;  $v$  has a component only in the axial ( $z$ ) direction; the

flow rate is  $Q=v_m A_{cs}$ ,  $A_{cs}=R^2\pi$  is the cross-section area). Also, the particles in the fluid move due to diffusion characterized by the coefficient  $D$

$$D = k_B T / (6\pi\mu R_H) \quad (2)$$

( $T$  is the absolute temperature,  $\mu$  is the dynamic viscosity of the fluid,  $R_H$  is the hydrodynamic radius of the adsorbate particle,  $k_B$  is the Boltzmann constant). Thus the spatio-temporal dependent analyte concentration in the channel is given by the convection-diffusion equation (here  $C=C(r,z,t)$ ; the system is rotationally symmetric, so the parameters do not depend on the angular coordinate  $\phi$ )

$$\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial z} = D \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) + \frac{\partial^2 C}{\partial z^2} \right] \quad (3)$$

and the following boundary and initial conditions:

1. at the inlet of the channel ( $z=0$ ) the concentration is equal to the injection concentration, i.e.  $C(r,0,t)=C_i$ ,
2. at the outlet of the channel ( $z=L$ ) a continuation condition assumes free convection (the exit of adsorbate particles is entirely due to flow), i.e.  $\partial C(r,L,t)/\partial z=0$ ,
3. at the channel surface where the adsorption occur (defined by  $r=R$ ,  $0 \leq z \leq L$ ,  $L$  is the adsorption zone length; radial symmetry of the adsorbing surface is assumed) a balance exists between the diffusive flux perpendicular to the surface and the net adsorption rate (expressed as the number of particles adsorbed in unit time per unit area,  $\eta$ )

$$D \frac{\partial C}{\partial r} \Big|_{(R,z,t)} = \frac{\partial \eta}{\partial t} = k_a C_s (\eta_m - \eta) - k_d \eta \quad (4)$$

where  $C_s=C(R,z,t)$  is the adsorbate particles concentration adjacent to the adsorbing surface,  $\eta=\eta(z,t)$ ,  $\eta_m$  is the spatially uniform surface density of adsorption sites,  $k_a$  is the adsorption rate constant, and  $k_d$  is the desorption rate constant. Langmuir scheme of reversible adsorption is assumed since it is general enough to explain the majority of AD processes in molecular biology. If an area without adsorption exists on the channel wall, the no-flux condition, i.e.  $(\partial C/\partial r)|_{(R,z,t)}=0$ , would be valid for it.

4. for the fluid rapidly injected in the channel the uniform initial distribution of adsorbate particles is assumed, i.e.  $C(r,z,0)=C_i$ ,
5. adsorption starts at the moment  $t=0$ , i.e.  $\eta(z,0)=0$ .

Eq. (3) together with the boundary and initial conditions is generally solved for  $C(r,z,t)$  and  $\eta(z,t)$  by using numerical finite element methods.  $N(t)$  can be obtained by integrating  $\eta(z,t)$  across the whole adsorbing surface.

For some transport-reaction regimes in the channel certain approximations can be introduced, enabling simplification of Eq. (3). Different transport-reaction regimes are discerned based on the relation of timescales for convection, diffusion and adsorption in a micro/nanofluidic system of given

parameters (geometry and dimensions of the channel, fluid flow velocity, adsorbate diffusivity and concentration, affinity of the surface toward the adsorbate, density of the adsorption sites).

A significant decrease in mathematical complexity of the problem is possible in cases where it is justified to assume that the adsorbate concentration is uniform in the channel, constant in time, and equal to the injection concentration, i.e.  $C(r,z,t)=C_i$ . In such conditions  $\eta$  is also spatially uniform, thus the number of adsorbed particles  $N(t)=A\eta(t)$  is given by the equation

$$\frac{dN}{dt} = k_a C_i (N_m - N) - k_d N \quad (5)$$

( $A=2\pi RL$  is the area of the adsorption zone;  $N_m=A\eta_m$  is the total number of surface adsorption sites), whose solution is

$$N(t) = \frac{k_a C_i}{k_d + k_a C_i} N_m \left(1 - e^{-(k_d + k_a C_i)t}\right) + N_e e^{-t/\tau} \quad (6)$$

( $N_e$  is the equilibrium number of adsorbed particles, and  $\tau$  is the intrinsic AD process time constant). This regime is formed when a convective and diffusive transport supplies adsorbate particles more quickly than the intrinsic binding reaction on the wall can bind them (the reaction-limited binding kinetics).

If the intrinsic adsorption is faster than the transport of particles to the surface, the ratio of the diffusion and convection time scales in the channel should be considered. The time needed for the particle entering the channel at the point  $O$  (in Fig. 1) to reach the channel wall by diffusion in radial direction is  $t_D=R^2/D$ , while the time for that particle to flow over the entire adsorbing surface of length  $L$  in axial direction is approximated as  $t_C=L/v_m$ . If  $t_D < t_C$  the particles entering the channel at an arbitrary  $r$ ,  $0 \leq r \leq R$ , are able to reach the channel wall by diffusion. In that case the whole channel volume becomes depleted due to the fast adsorption. However, if  $t_D > t_C$  (i.e.  $R^2 v_m / (DL) > 1$ ), only the particles from the layer thinner than  $R$ , which is adjacent to the adsorbing wall, can reach the channel wall and participate in the adsorption process, while other particles exit the adsorbing region carried by the flow before reaching the channel wall. In that case, due to the adsorption, a thin layer depleted of adsorbed particles is formed adjacent to the adsorbing surface. A transport-reaction regime, in which the depletion layer is thin compared to both the channel radius and the channel length, should be considered because it enables the two-compartment model (TCM) approximation for the analyte concentration in the channel to be used [7-9], enabling simplification of Eq. (3) and its boundary conditions. This transport-reaction regime is analyzed in the following part of this section.

Let us assume that a depletion zone is formed adjacent to the channel wall, and its thickness  $\delta=\delta(z)$  is much smaller than the channel radius,  $\delta=\delta(z) \ll R$ , so

$$\frac{t_D}{t_C} = \frac{R^2 v_m}{DL} \gg 1 \quad (7)$$

Then, instead of the full parabolic flow, only the linearized velocity (the linear shear flow) can be considered in the vicinity of the wall surface, i.e. near  $r=R$ . If the coordinate  $y=R-r$  is introduced, representing the distance from the channel's wall, the linearized velocity is

$$\begin{aligned} u_{sh}(y) &= y \cdot \left. \frac{\partial v}{\partial y} \right|_{y=0} = -(R-r) \cdot \left. \frac{\partial v}{\partial r} \right|_{r=R} \\ &= 2 \frac{V_m}{R} (R-r) = 2 \frac{V_m}{R} y = \gamma \cdot y \end{aligned} \quad (8)$$

and it is valid for  $y \ll R$ . Then the adsorbate particles that enter the channel at the distance  $y=y_0$  from the channel's wall require the time  $t_{Cs}=L/u_{sh}=L/(\gamma y_0)$  to convect to the end of the channel, while the time needed to reach the wall by diffusion is  $t_{Ds}=y_0^2/D$ . By equating these two time intervals the maximum distance can be obtained between the particles able to reach the wall and the wall at the channel inlet

$$y_0 = \sqrt[3]{\frac{DL}{\gamma}} = \sqrt[3]{\frac{DLR}{2V_m}} \quad (9)$$

This value can be used for estimation of the depletion zone thickness. Thus, the depletion zone will be much narrower than the adsorbing surface length when the following is valid

$$y_0 \ll L, \text{ i.e. } \frac{L^2 \gamma}{D} = \frac{2V_m L^2}{DR} = \frac{4v_m L^2}{DR} \gg 1 \quad (10)$$

Expressions (7) and (10) define the conditions under which the depletion zone is thin compared to both the channel radius and the channel length. As mentioned before, when such conditions exist, the channel volume can be approximated with two co-axial cylindrical compartments. The inner compartment, which has the shape of a hollow cylinder, is in the immediate contact with the channel wall. The adsorbate concentration in the inner compartment is  $C_{s,in}$ . In the outer compartment, which occupies the remaining part of the channel volume, the adsorbate concentration can be considered equal to the injection concentration  $C_i$ . Eq. (3) for the inner compartment then becomes

$$\gamma(R-r) \frac{\partial C_{s,in}}{\partial z} = D \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{s,in}}{\partial r} \right) \quad (11)$$

since  $v \approx u_{sh} = \gamma(R-r)$ . Eq. (11) assumes that the diffusion in the  $z$ -direction is negligible compared to convection, which is given by the condition  $L^2/D \gg L/v_m$ , i.e.  $Lv_m/D \gg 1$ . Fulfillment of this condition is implied by the following analysis. A parameter  $P_{eL}=Lv_m/D$  can be introduced as some sort of Péclet

number, defined relative to the length  $L$ . Eq. (7) then becomes  $P_{el}(R/L)^2 \gg 1$ , and (10) becomes  $4P_{el}(L/R) \gg 1$ . If both these conditions are fulfilled,  $P_{el} \gg 1$  will be true, thus confirming the assumption  $Lv_m/D \gg 1$ .

The two-compartment model simplifies the analysis further. Its accuracy when used for approximation of the mass transfer influenced binding kinetics is experimentally confirmed in various microfluidic sensors [7, 10, 11]. In TCM all quantities are spatially constant, i.e. they are averaged over the adsorbing surface. The thickness of the inner compartment corresponds to the thickness of the depletion zone, averaged along the channel length,  $\delta_m$ ,  $\delta_m \ll R$ . According to TCM, the adsorbate concentration in the inner compartment,  $C_{s,TCM}(t)$ , which is constant along the channel, changes in the quasi-steadily manner due to both the transport of the adsorbate particles between the compartments and the AD process taking place on the wall. Thus, for the inner compartment of the volume  $V_{in} = \delta_m A$ , the following relation is valid

$$V_{in} \frac{\partial C_{s,TCM}}{\partial t} = A(-k_a C_{s,TCM}(\eta_m - \eta) + k_d \eta + k_m(C_i - C_{s,TCM}))$$

Due to the quasi-steadily changing concentration  $C_{s,TCM}(t)$ , the previous equation yields ( $N = \eta A$ ,  $N_m = \eta_m A$ , as all the parameters in the TCM are averaged over the adsorbing surface)

$$C_{s,TCM}(t) = \frac{C_i + k_d N / (k_m A)}{1 + k_d (N_m - N) / (k_m A)} \quad (12)$$

In the TCM the mass transfer coefficient  $k_m$  is introduced, which characterizes the transport between the compartments. The TCM equation valid for the adsorbing wall is

$$\partial N / \partial t = k_a C_{s,TCM} (N_m - N) - k_d N \quad (13)$$

where  $C_{s,TCM}$  is given by (12).

Therefore, the introduction of the TCM enables the calculation of the number of particles adsorbed on the channel wall by solving (13) with the initial condition  $N(0) = 0$ , which is much simpler than solving (3) with its initial and boundary conditions. Eq. (13) yields

$$\frac{t}{\tau_{TCM}} = a_{TCM} \frac{N}{N_e} - \ln \left( 1 - \frac{N}{N_e} \right) \quad (14)$$

where  $\tau_{TCM} = \tau [1 + \tau k_a k_d \eta_m / k_m]$ ,  $N_e$  and  $\tau$  are defined in (6), and  $a_{TCM} = (\tau^2 k_a^2 C_i \eta_m / k_m) / \tau_{TCM}$ . The adsorbed particles number  $N(t)$  is given by (14), in the implicit form. From (14) and the expressions for the parameters  $\tau_{TCM}$  and  $a_{TCM}$ , it can be concluded that  $k_m \gg k_a \eta_m$  is the condition under which the transport of particles to the surface is faster than intrinsic adsorption, which is the regime of the reaction limited binding

kinetics, when Eqs. (5) and (6) are valid.  $\tau_{TCM} \approx \tau$  and  $a_{TCM} \approx 0$  both hold true when  $k_m \gg k_a \eta_m$ , so Eqs. (14) and (6) become equivalent.

The mass transfer coefficient  $k_m$ , is determined as

$$k_m = \frac{1}{L} \int_0^L k_{m,l}(z) dz \quad (15)$$

where  $k_{m,l}(z)$  is the local mass transfer coefficient.  $k_{m,l}(z)$  can be estimated as the ratio of the diffusivity and the depletion layer thickness,  $D/\delta(z)$ . Starting from (11) in which  $R-r(z) = \delta(z)$ , and by differentiating with respect to  $y$  instead of  $r$ , we obtain

$$\gamma \delta \frac{\partial C_{s,in}}{\partial y} \frac{dy}{dz} = D \left( \frac{\partial}{\partial y} \left( \frac{\partial C_{s,in}}{\partial y} \right) - \frac{1}{R - \delta} \frac{\partial C_{s,in}}{\partial y} \right) \quad (16)$$

By applying approximations (gradient linearization)  $\partial C_{s,in} / \partial y \approx \Delta C_{s,in} / \Delta y \approx \Delta C_{s,in} / \delta$ ,  $(\partial / \partial y)(\partial C_{s,in} / \partial y) \approx \Delta C_{s,in} / \delta^2$  and  $dy/dz \approx d\delta/dz$  for small  $\delta$  (thin depletion zone,  $\delta \ll R$ ) Eq. (16) is transformed into the equation  $\gamma d\delta/dz = D/\delta^2$ , whose solution is  $\delta(z) = (3Dz/\gamma)^{1/3}$ . Now  $k_{m,l}(z) \approx D/\delta(z) = (D^2 \gamma / 3z)^{1/3}$ , and based on (15) an approximate value (i.e. an estimated order of magnitude) of  $k_m$  is obtained

$$k_m \approx \frac{3}{2} \sqrt[3]{\frac{D^2 \gamma}{3L}} = \frac{3}{2} \sqrt[3]{\frac{4D^2 v_m}{3LR}} \quad (17)$$

Similarly, by averaging the expression for  $\delta(z)$  along the length, an approximate expression is obtained which can be used for the estimation of the depletion zone mean thickness

$$\delta_m \approx \frac{3}{4} \sqrt[3]{\frac{3DL}{\gamma}} = \frac{3}{4} \sqrt[3]{\frac{3DLR}{4v_m}} \quad (18)$$

### III. RESULTS & DISCUSSION

Fig. 2a shows the 3D distributions of adsorbate concentration in three microchannels of different radii (200  $\mu\text{m}$ , 50  $\mu\text{m}$  and 10  $\mu\text{m}$ ), while the values of other parameters are the same for the three channels ( $L = 500 \mu\text{m}$ ,  $v_m = 0.5 \text{ mm/s}$ ,  $D = 8 \cdot 10^{-11} \text{ m}^2/\text{s}$ ,  $\eta_m = 1 \cdot 10^{-11} \text{ mM}$ ,  $C_i = 1 \cdot 10^{-9} \text{ M}$ ,  $k_a = 8 \cdot 10^7 \text{ 1/(Ms)}$ ,  $k_d = 0.08 \text{ 1/s}$ ,  $1 \text{ M} = 1 \text{ mol/dm}^3$ ). They are obtained by simulations performed using the COMSOL Multiphysics software, based on Eq. (3) and finite element modeling (FEM). In Fig. 2b the corresponding 2D concentration distributions in the longitudinal channel sections are shown. The results show that a layer depleted of the adsorbate particles, which is thin compared to both  $R$  and  $L$ , is formed in the widest channel, while in the narrowest channel almost the entire volume is depleted. Based on (7) and (10) it can be concluded that the increase of  $R$  while  $L$  is kept constant results in the decrease of the depletion zone

thickness compared to  $R$ , and its increase compared to  $L$ . Application of TCM becomes increasingly justified as  $R$  increases for given  $L$ , as long as  $R \leq L$ . Further increase of  $R$  can jeopardize the fulfillment of the condition given by (10), and the critical value of  $R$ , beyond which the use of TCM is no longer justified, depends on the value of  $P_{eL}$ .

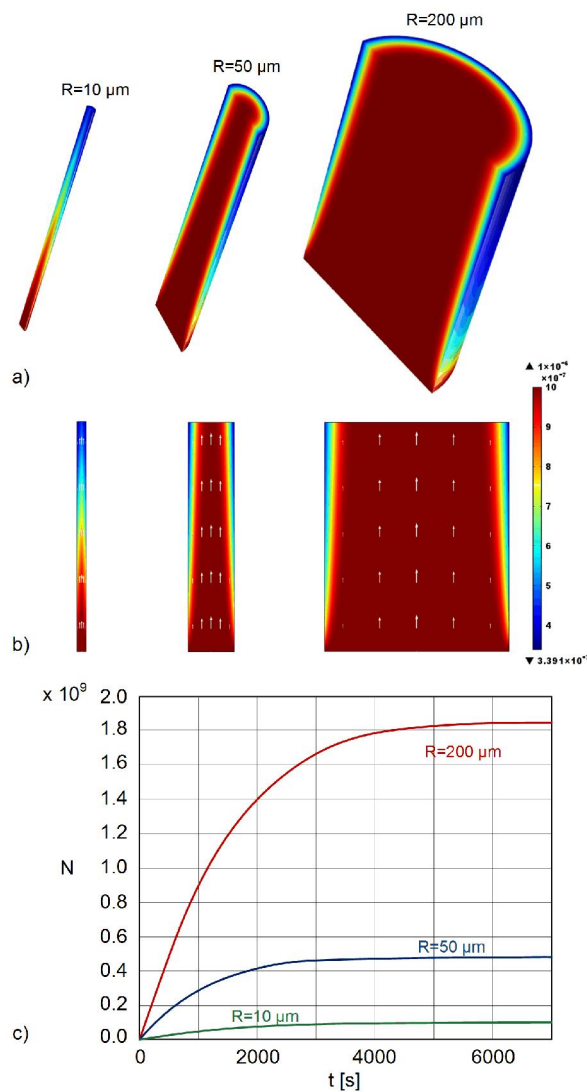


Fig. 2. FEM simulation results (COMSOL Multiphysics software) based on the general equation (3): a) 3D distributions of adsorbate concentration in three microchannels of different radii (200  $\mu\text{m}$ , 50  $\mu\text{m}$  and 10  $\mu\text{m}$ ); due to the axial symmetry only one half of each channel is shown. b) The corresponding 2D concentration distributions in the longitudinal channel sections. The depletion zones are clearly visible. c) The time evolutions of the number of adsorbed particles for the three channels.

The time evolution of the number of adsorbed particles,  $N(t)$ , for the three channels (Fig. 2c) is also obtained by FEM based computer simulation. If the channels are used as sensors, it can be seen that their response rate is somewhat faster if the channels have a smaller cross-section. However, the steady-state signal value is lower. The same computer

simulation enables the analysis of the dependence of the adsorbate concentration distribution and  $N(t)$  on the channel dimensions, flow velocity and surface density of capturing probes, yielding the optimal parameter values for the desired transport-reaction regime, higher sensor signal level, optimum depletion of the sample etc.

The channel with the radius  $R=200 \mu\text{m}$ , shown in Fig. 2, is a good candidate for application of TCM. This can be verified based on the given theoretical expressions, and then by using computer simulations. For the parameter values given at the beginning of this section, we obtain  $R^2 v_m / (DL) = 500 \gg 1$  (Eq. (7)),  $4v_m L^2 / (DR) = 31250 \gg 1$  (Eq. (10)), and  $P_{eL} = 3125 \gg 1$ , which means that theoretically determined conditions for TCM application are met. Based on (17) the approximate value (the order of magnitude) can be determined of the mass transfer coefficient  $k_m = 5.24 \cdot 10^{-6}$  m/s. The condition  $k_m < k_a \eta_m = 8 \cdot 10^{-4}$  m/s is fulfilled, which implies the existence of the depletion zone. The depletion layer's mean thickness of  $\delta_m = 17 \mu\text{m}$  is determined based on (18) (Fig. 2 confirms that this value is a good estimate). It is much thinner than both  $R$  and  $L$ . The results of the theoretical analysis show that (14) can be used for determination of the number of adsorbed particles on the wall of this channel. This will now be verified by using the computer simulation.

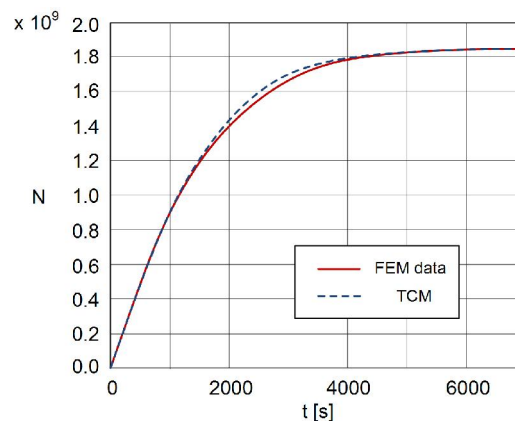


Fig. 3. The time evolution of the number of adsorbed particles on the microchannel wall ( $R=200 \mu\text{m}$ ) obtained by the FEM computer simulation (solid line) based on (3), and obtained by TCM based numerical computation using (14) (dashed line).

Fig. 3 shows the time evolution of the number of adsorbed particles on the microchannel wall ( $R=200 \mu\text{m}$ , other parameter values are given at the beginning of Section III), obtained by the FEM computer simulation (solid line) based on (3), and obtained by numerical computation using (14) (dashed line). Excellent matching of the two curves means that the TCM curve is a good approximation of the FEM curve. Therefore, the computer simulation confirmed the results of the theoretical analysis, and also the applicability of (14) for the analysis and interpretation of the time response of a sensor using the analyzed channel as the sensing element. The simulation also confirmed that the theoretically defined

conditions for TCM applicability are correct.

The dashed line in Fig. 3 is obtained for  $k_{mc}=2.9\cdot 10^{-6}$  m/s and it is the corrected value of the mass transfer coefficient. It is obtained by adjustment, starting from the theoretically determined approximate value, and proceeding until the difference between the TCM model and the simulation data was minimized. The correction factor is  $c=k_{mc}/k_m=0.56$ . For several different examples of cylindrical micro/nanochannels, adsorbates and flow velocities, approximately the same value of  $c$  was obtained (not shown in this paper due to the limited space). Now it is possible for an arbitrary cylindrical channel, for which the TCM is applicable, to determine the exact value of the mass transfer coefficient as  $k_{mo}=k_m c$ , where  $k_m$  is given by (17).

The time required for the sample to be diluted to a certain extent through adsorption can be determined based on the dependence  $N(t)$  obtained by simulation (Fig. 3), and from (14) in cases where TCM is applicable. Also, dependences of this time on different parameters can be analyzed, thus enabling determination of the conditions (convection rate, type and density of functionalization, channel dimensions, sample passing duration) at which a desired depletion level is achieved. Furthermore, it is possible to determine the conditions at which the sample depletion is negligible or maximal, depending on the objective of the given application.

#### IV. CONCLUSION

In this paper the theoretical model which enables the analysis of reversible adsorption in cylindrical micro/nanochannels is given. A complete theory based on the application of the two-compartment model (TCM) for approximation of the adsorbate concentration distribution in a channel is presented in detail. The TCM-based analytical expression significantly simplifies the analysis of the adsorption process on the channel wall, and also enables its optimization.

Since the simulation software provides the results of numerical tests before fabrication, it yields more economical and rapid development of micro/nanofluidic systems with optimal performance. The performed computer simulations based on the finite element modeling (FEM) enable the analysis of the dependence of adsorbate concentration spatial distribution and the time evolution of the number of adsorbed particles on the channel dimensions, flow velocity and surface density of capturing probes, yielding the optimal parameter values for the given application (sensing, transport of the sample with unaltered chemical properties, sample dilution etc.).

A comparison of the FEM-based simulation results with those obtained by the TCM equations was used for the evaluation of applicability of the TCM for various sets of parameter values. Excellent matching of the results is obtained for the parameters that satisfy the theoretically defined conditions for the applicability of TCM. In this way the applicability of TCM is confirmed for the analysis and interpretation of the adsorption data, and it is also verified that

the theoretically defined conditions for the TCM applicability are correct.

The mathematical expression is derived for the approximate value of the mass transfer coefficient valid in cylindrical channels. The correction factor is determined, enabling the calculation of the exact value of the mass transfer coefficient which is an essential parameter for application of TCM equations.

The presented theory and analysis are useful in the fields of microfluidic sensors and nanosensors (e.g. plasmonic sensors with cylindrical flow-through nanoholes, fiber-optic sensors etc.), microfluidic systems for nanoparticle synthesis, and micro/nanofluidic systems for sample transport or purification.

#### ACKNOWLEDGMENT

This work is funded by the Serbian Ministry of Education, Science and Technological Development (Project 32008) and the Serbian Academy of Sciences and Arts (Project F/150).

#### REFERENCES

- [1] J. Wu, and M. Gu, "Microfluidic sensing: state of the art fabrication and detection techniques," *J. Biomedical Optics*, vol. 16, no. 8, pp. 080901 1-12, Aug, 2011.
- [2] S. J. Harrison, K. Fluri, K. Seiler, Z.-H. Fan, C. S. Effenhäuser, and A. Manz, "Micromachining a miniaturized capillary electrophoresis-based chemical analysis system on a chip," *Science*, vol. 261, pp. 895-897, 1993.
- [3] Ž. Lazić, M. M. Smiljanić, M. Rašljčić, I. Mladenović, K. Radulović, M. Sarajlić, and D. Vasiljević-Radović, "Wet isotropic chemical etching of Pyrex glass with masking layers Cr/Au," Proc. 1<sup>st</sup> Int. Conf. on Electrical, Electronic and Computing Engineering IeETAN 2014, Vrnjačka Banja, Serbia, vol. MOI, pp. 1.1 1-4, June 2-5, 2014.
- [4] E. K. Sackmann, A. L. Fulton, and D. J. Beebe, "The present and future role of microfluidics in biomedical research," *Nature*, vol. 507, no. 7491, pp. 181-189, Mar, 2014.
- [5] C. Rivet, H. Lee, A. Hirsch, S. Hamilton, and H. Lu, "Microfluidics for medical diagnostics and biosensors," *Chem. Eng. Science*, vol. 66, pp. 1490-1507, 2011.
- [6] H.-F. Li, and J.-M. Lin, "Applications of microfluidic systems in environmental analysis," *Anal. Bioanal. Chem.*, vol. 393, no. 2, pp. 555-567, Nov, 2008.
- [7] D. G. Myszk, X. He, M. Dembo, T. A. Morton, and B. Goldstein, "Extending the Range of Rate Constants Available from BIACORE: Interpreting Mass Transport-Influenced Binding Data," *Biophys. J.*, vol. 75, pp. 583-594, Aug, 1998.
- [8] W. Kusnezow, Y. V. Syagailo, S. Ruffer, K. Klenin, W. Sebald, J. D. Hoheisel, C. Gauer, and I. Goychuk, "Kinetics of antigen binding to antibody microspots: Strong limitation by mass transport to the surface," *Proteomics*, vol. 6, pp. 794-803, 2006.
- [9] M. Frantlović, I. Jokić, Z. Djurić, and K. Radulović, "Analysis of the competitive adsorption and mass transfer influence on equilibrium mass fluctuations in affinity-based biosensors," *Sens. Actuators B*, vol. 189, pp. 71-79, 2013.
- [10] K. Sigmundsson, G. Masson, R. Rice, N. Beauchemin, and B. Oebrink, "Determination of active concentrations and association and dissociation rate constants of interacting biomolecules: an analytical solution to the theory for kinetic and mass transport limitations in biosensor technology and its experimental verification," *Biochemistry*, vol. 41, pp. 8263-8276, 2002.
- [11] H. Anderson, G. Wingqvist, T. Weissbach, D. Wallinder, I. Katardjiev, and B. Ingemarsson, "Systematic investigation of biomolecular interactions using combined frequency and motional resistance measurements," *Sens. Actuators B*, vol. 153, pp. 135-144, 2011.