Adsorption dynamics of chlorinated hydrocarbons from multi-component aqueous solution onto activated carbon

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Abstract

The results and a numerical simulation of studies on dynamics of the adsorption from seven-component aqueous solution of light chlorinated hydrocarbons on activated carbon have been presented. Aqueous solution of 1,2-dichloroethane (12DCE), 1,1,2,2-tetrachloroethane (S-TET), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), 1,1-dichloroethene (VDC), perchloroethene (PER) and 1,1,2-trichloroethene (TRI) was used. Concentrations of chlorohydrocarbons were similar as in wastewater from vinyl chloride plant. A cell model that incorporates the diffusion through a laminar layer of liquid around a particle was used to describe the experimental results. The applied calculation methods, which take kinetics into account, allows to well describe a phenomenon of dynamic adsorption. Mean relative deviations between the experimental and calculated values amounted 17%. The breakthrough curves become steeper along with an increase of the bed height. A consistency of the experimental results with those calculated indicates for a negligible contribution of the axial diffusion on the dynamic adsorption process of light chlorinated hydrocarbons from aqueous solution under the hydrodynamic conditions corresponding to the Reynolds number equal to 1.3. Determined optimal bed height for waste linear flow rate—15 cm/min is in the range 80–120 cm.
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Keywords: Activated carbon; Adsorption; Chlorohydrocarbons; Diffusion; Wastewater

1. Introduction

Wastewater containing chloro-derivatives compounds presents a serious environmental problem because of their high toxicity and possible accumulation in the environment. For example wastewater from vinyl chloride plant contain among other light chlorohydrocarbons like chloroform, tetrachloromethane, vinylidenene chloride, trichloroethylene, perchloroethylene, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane. After steam stripping the waste stream contains mentioned above chloroderivatives at the 5–10 mg/dm^3 level [1]. Further removing enable adsorption on to activated carbon [2–6]. Adsorption is an effective separation process for treating industrial and domestic effluents. Activated carbon is the most widely used adsorbent [2–10]. The apparatus with fixed-bed belong to the fundamental design solution of the adsorbers. The calculations of the adsorption process on a fixed-bed rely on the determination of the course of the breakthrough curve. In the case of multi-component system a problem of the optimal design despite of apparent simplicity is extremely complicated [8,9,11]. The physical phenomena proceeding in the adsorption column operated by a technique of elution chromatography under the isothermal conditions comprise a typical example of non-stationary process. A general mathematical model of multi-component adsorption process is impossible to solve by know methods. Therefore, several simplifications are incorporated into modelling [11].

Paderewski [8,12,13] has divided the models of multi-component adsorption under dynamic conditions, which had been formulated so far in the following way:

1. Pseudo-one-component models, which comprise rather a form of elaboration of the experimental results of mixture adsorption in a column hence, they are utilized in the design of adsorption installation.
2. Model of multi-component adsorption at the stationary stage representing the quantitative changes, proceeding during the adsorption only at large bed height.

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Nomenclature

a	adsorptivity (mmol/g)
a_d	dynamic adsorptivity (mmol/g)
a^0	equilibrium adsorptivity (mmol/g)
C^{exp}	measured concentration (mmol/cm^3)
C	concentration (mmol/cm^3)
C_z	concentration at interfacial space (mmol/cm^3)
C^0	initial concentration (mmol/cm^3)
C^0	initial concentration (mmol/cm^3)
d_z	adsorbent particle radius (mm)
D	molecular diffusivity of component i (cm^2/s)
F	cross-section of the bed (cm^2)
k_l	external mass transfer coefficient (cm/min)
L	bed height (cm)
n_{end}	number of time steps defined by Eq. (3)
q	flow rate (cm^3/min)
Re	Reynolds number, $Re = \frac{wd_z\rho}{\mu}$
Sc	Schmidt number, $Sc = \frac{\mu}{\rho D}$
Sh	Sherwood number, $Sh = \frac{k_l d_z}{D}$
t	time (min)
t_b	throughput time (min)
t_c	contact time (min)
t_{end}	saturation time of bed (min)
U	velocity of the concentrate wave front (cm/min)
V	volume of liquid phase (dm^3)
w	linear flow rate (cm/min)

Greek letters

α	specific surface area of bed (cm^2/cm^3)
δ	relative deviation (%)
ε	porosity
μ	dynamic viscosity (Pa s)
ρ	liquid density (kg/m^3)
ρ_b	bulk density (g/cm^3)

Subscripts

i	component
k	cell
n	time step

3. Models with collected parameters sufficiently describing the course of process, when the rate of process is determined by one kinetic factor (internal or external diffusion).
4. "Diffusion" models enabling a precise prediction of the distribution of particular components in the adsorption column, however, the mathematical description becomes very complicated for a larger number of components [13,14].

A prediction of adsorption from a six-component chlorohydrocarbons solution with good results was achieved in works of Crittenden et al. and Hand et al. [15–17] by the application of the heterogeneous surface diffusion model. In works of Crittenden et al. and Hand et al. [15–17] was applied a model of the heterogeneous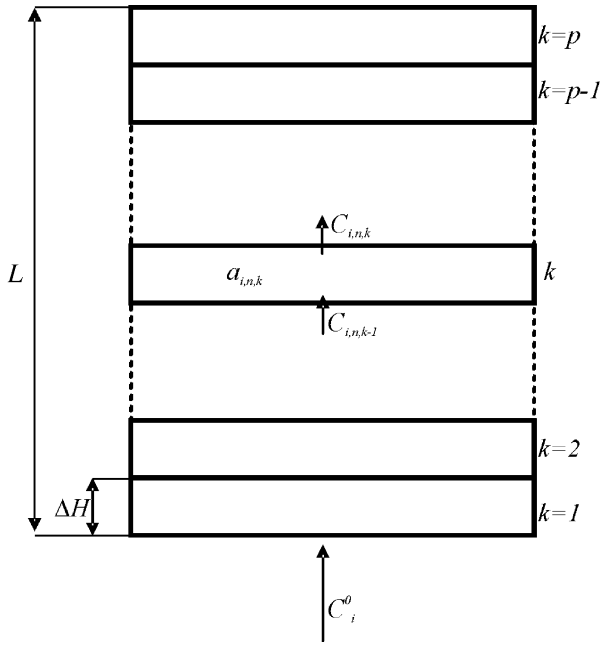 surface diffusion for prediction of the adsorption from a six-component solution with good results. This model assumes that the surface diffusion determines the adsorption rate. To determine the adsorption equilibrium they have used the ideal adsorbed solution (IAS) model based on the Freundlich equation. Moreover the equilibrium model was used for comparative purposes in the Hand work [17]. In the case of large bed height this model can be utilized for estimation of column working time.

In order to facilitate the complicated numerical calculations associated with the description of fixed-bed adsorption, the approximate kinetic equations are commonly used [18,19]. A model with a linear driving force (LDF) developed by Glueckauf [20] for the systems with a constant coefficient of the surface diffusion is frequently used. However, in many adsorption systems it is more appropriate to express the diffusion stream in the pores or the surface diffusion in terms of the gradient of the adsorbate chemical potential.

Several authors have claimed that such expression of the diffusion streams leads to a concentration dependence of the diffusion coefficients with the exception of the case where the isotherm is linear [21–23]. A further consequence of this effect is a fact that in the multi-component system the adsorbate streams combine with each other [24–26]. The diffusion stream of each of the adsorbates depends on the concentration gradient of all the adsorbates. This can be generally formulated by the isotherm equations in the multi-component solutions [27], which confirms a fact, that the adsorption kinetics is also affected by the shape of isotherms of the particular components.

In this work the experimental results and a description of model of a multi-component adsorption under the dynamic conditions are presented.

2. Theory

The following assumptions were made in calculations to predict the breakthrough curves:

1. The total rate adsorption is controlled by the penetration through a laminar layer of liquid surrounding the adsorbent particles [28–30].
2. The adsorbent particles have a spherical shape.
3. The driving force comprises a linear gradient of concentration between the concentration in the bulk of liquid phase surrounding the adsorbent particles and the average concentration in the adsorbent particle.
4. The particular substances diffuse through a laminar layer independently on each other.
5. Equilibrium is instantly established on the activated carbon pores.
6. Concentration in the particle is equivalent to the amount of adsorbed mass.
7. Concentration in the adsorbed phase is incommensurable large in comparison to the concentration in the pores volume.
8. Process proceeds isothermally.

Fig. 1. A model of scheme representing a division of bed on p elementary cells.

The model was based on the division of adsorption bed with a height L on p elementary cells and is schematically presented in Fig. 1.

A one-way flow of liquid, a change of adsorption in any elementary cell k with a height of ΔL amounts:

$$\Delta a_{i,n} = k_{l,i} \frac{\alpha}{\rho_b}(C_{i,n} - C_{z,i,n})\frac{\Delta L}{w} \tag{1}$$

for any time step n the adsorption will be equal to:

$$a_{i,k,n} = \sum_0^{n\Delta t} k_{l,i}\frac{\alpha}{\rho_n}(C_{i,k-1,n} - C_{z,i,k,n})\frac{\Delta L}{w},$$
$$k = 1, 2, \ldots, p; \quad n = 1, 2, \ldots, n_{end} \tag{2}$$

where

$$n_{end} = \frac{t_{end}}{\Delta t} \tag{3}$$

t_{end}, time of reaching the concentration of $0.99C_i^0$ at the column outlet for a component which is the best adsorbed (PER).

Because the amount of mass diffusing to the adsorbent particles during $\Delta t = \Delta L/w$ cannot be larger than the amount of mass adsorbed during $t \to \infty$ (the right side of relation below), thus:

$$k_{l,i}\alpha F \Delta L C_i^0 \frac{\Delta L}{w} < (C_i^0 - C_{z,i})wF\frac{\Delta L}{w} \tag{4}$$

Assuming, that $C_i^0 \gg C_{z,i}$ then the ΔL value amounts:

$$\Delta L < \frac{w}{\alpha k_{l,i}} \tag{5}$$

expression (5) allows the determination of minimum number of the elementary cells into which the bed with a height L should be divided

$$p > \frac{L}{\Delta L} \tag{6}$$

By performing the mass balance in k cell, the concentration at the outlet of cell is:

$$C_{i,k,n} = C_{i,k-1,n} - \frac{\sum_0^{n\,\Delta t}k_{li}\alpha(C_{i,k-1,n} - C_{z,i,k,n})\Delta L/w - \sum_0^{n\,\Delta t}k_{li}\alpha(C_{i,k,n-1} - C_{z,i,k,n})\Delta L/w}{\varepsilon} \tag{7}$$

where $C_{z,i,k,n}$ is the average equilibrium concentration in the particle corresponding to the $a_{i,n,k}$ adsorption:

$$C_{z,i,k,n} = f(a_{1,k,n}, a_{2,k,n}, \ldots, a_{i,k,n}) \tag{8}$$

the value of which is calculated from equations presented in works [4,31].

The initial conditions of process are the following:

$$\begin{aligned} k = 0 && C_{i,0,n} = C_i^0, \\ t = 0, k > 0 \text{ and } n = 0, && C_{i,k}^0 = 0, \\ t = 0 \text{ and } k > 0, && a_{i,k,0} = a_i, \end{aligned} \tag{9}$$

If the adsorbent was not previously loaded, then: $a_{i,k,0} = 0$.

The mass transfer coefficients of the particular components were calculated from dimensionless equation given by Pełech et al. in the form [28–30]:

$$Sh = 2 + 1.54Re^{0.66}Sc^{0.33} \tag{10}$$

3. Experimental

3.1. Sorbent

The adsorbent used in these studies was the activated carbon of the DTO type supplied by GRYFSKAND SA (Poland). According to the manufacturer's specification and our studies [3–6] this adsorbent is generally suitable for water treatment and chlorohydrocarbons removing. Adsorbent was sieved into several discrete particle size ranges. The 0.4–0.63 mm size range of activated carbon was used in these studies. The sieved activated carbon was washed by distilled water to remove fines and then dried at 110 °C in an oven for 24 h. The carbon particles were assumed to be spheres having a diameter given by arithmetic mean value between respective mesh sizes (average particle diameter d_z was 0.53 mm). Their properties are presented in Table 1. The surface area and pore volume were measured

Table 1
Physical properties of DTO activated carbon

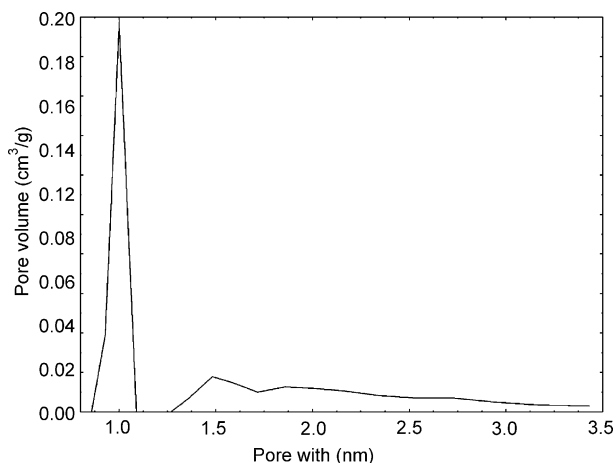|	
Bulk density (g/cm³)	0.40
Apparent density (g/cm³)	0.86
Total surface (N₂ BET method) (m²/g)	943
Pore volume (cm³/g)	0.53
Pore volume < 1.5 nm (cm³/g)	0.25
Porosity	0.45
Average particle diameter (mm)	0.53

Fig. 2. Pore size distribution for DTO activated carbon.

with N_2 (g) adsorption (ASAP 2010 Pore Structure Analyser, Micromeritrics, USA) at 77 K with liquid N_2; the remaining values were taken on the basis of data given by the manufacturer. The pore distribution size of the DTO activated carbon is shown in Fig. 2.

3.2. Sorbates

Seven chlorinated hydrocarbons, namely 1,2-dichloroethane (12DCE), 1,1,2,2-tetrachloroethane (S-TET), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), 1,1-dichloroethene (VDC), perchloroethylene (PER) and 1,1,2-trichloroethene (TRI) were used in these studies. Reagents were obtained from Fluka (purum >99.0%). Methanol was obtained from POCh, Poland (puriss p.a.) and distilled water were used in adsorption experiments.

3.3. Experimental method

The studies were carried out under the isothermal conditions 30 ± 0.5 °C. The experimental set-up is shown in Fig. 3. The column was thermal isolated of a glass wool. An aqueous solution of chlorinated hydrocarbons was passed through a glass column with the diameter of 2.4 cm and height 15 cm, which was packed with DTO activated carbon. The composition of feeding solution was as follows: CCl_4, 12DCE, S-TET, VDC, TRI and PER with a concentration 0.5 mg/dm^3 and $CHCl_3$ 1.5 mg/dm^3. This composition corresponds to the average concentration of these compounds in wastewater from a plant manufacturing the vinyl chloride by dichloroethane method with the chlorine balance [1]. A seven-component solution was supplied to the bottom of column by peristaltic pump at the flow rate of 67 cm^3/min. A linear velocity recalculated on an empty adsorber amounted to 15 cm/min. For such established hydrodynamic conditions the Reynolds number was $Re = 1.3$. Samples of solution were collected at three heights of 4, 8 and 12 cm and were analysed for the content of chlorinated hydrocarbons. During the process operation the inlet concentration was also controlled. In order to maintain the constant concentration it was necessary to
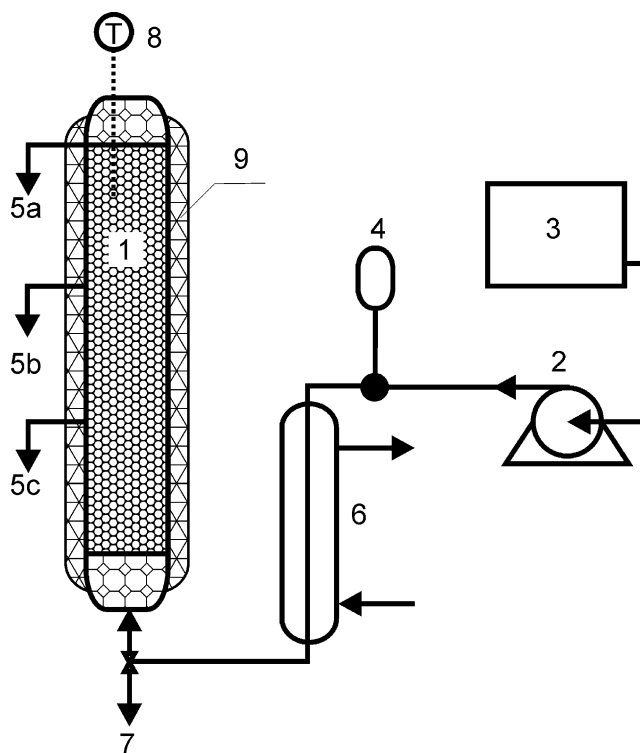

Fig. 3. Schematic diagram of the experimental system: 1, glass adsorption column; 2, peristaltic pump; 3, solution reservoir; 4, damper; 5, sampling of eluate; 6, thermostat; 7, inlet concentration control; 8, temperature control; 9, glass wool.

supplement a loss of a given chlorinated hydrocarbons due to its evaporation. For this purpose the methanol solutions of the respective components with the concentration of 50 mmol/dm^3 were used which were added progressively as the concentration was decreasing so that a required initial concentration C_i^0 of a given component was maintained. According to the literatures [4,5,32,33], methanol has no influence on the adsorption of the chloro-derivatives studied from aqueous solution onto activated carbon.

3.4. Analytical method

The concentration of studied compounds was determined chromatographically on a Thermoquest GC 8000^{Top} instrument with an electron-captured detector (ECD) by a head-space method. The sample of solution (2.0 cm^3) was placed in the vial (15 cm^3) sealed PTFE/silicone septum. The vials were thermostatic (30 ± 0.1 °C) for 1 h. After this time the 500 μl head space gas was take by syringe and injected to GC. The determination were conducted with an external standard method and following analytical conditions: capillary column—(J&W DB1) 30 m, 0.53 mm i.d., 1.5 μm film thickness (100% dimethyl polisiloxane), carrier gas—He 6 cm^3/min, detector temperature—300 °C, injector temperature—150 °C (split 1:6), oven—temperature program—40 °C (7 min) to 180 °C at 15 °C/min. The average error of this method for all the compounds is equal to 3.2%.

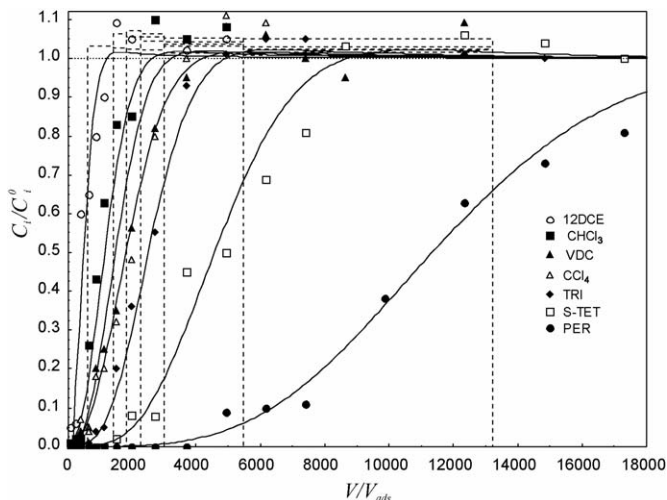Fig. 4. Breakthrough curves of studied chlorohydrocarbons, bed depth 12 cm.

Fig. 6. Breakthrough curves of $CHCl_3$.

4. Results and discussion

The experimental breakthrough curves (points) and those calculated from the equilibrium column model (ECM) (broken line) [31], as well as the curves calculated from kinetic cell model (KCM) (solid line) for a coordinate of location in a column $k \, \Delta L = 12$ cm are presented in Fig. 4. The curves of the particular components for a coordinate of location in a column $k \, \Delta L = 4$, 8, 12 cm are shown in Figs. 5–11. The concentration profiles of all the components in the eluate for a location in the column $k \, \Delta L = 12$ cm are presented in Fig. 12. The profiles were presented in the range of relative concentrations $0.95C^0 – 1.08C^0$ in order to visualize the overshoot concentration degree of the particular chlorohydrocarbons in the eluate, resulting from their mutual displacement from the bed. The overshoot concentration degrees calculated from ECM and KCM at the bed height of 12 cm are compiled in Table 2. It can be seen from this compilation that this effect is not distinctly marked for given process conditions. Moreover, it should not deteriorate the degree of solution purification.
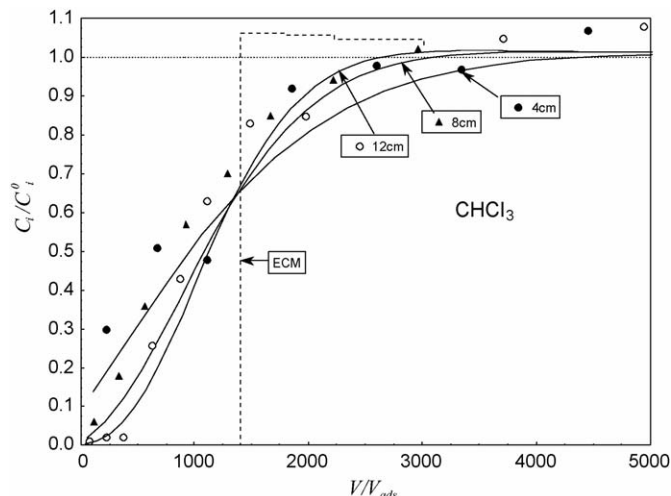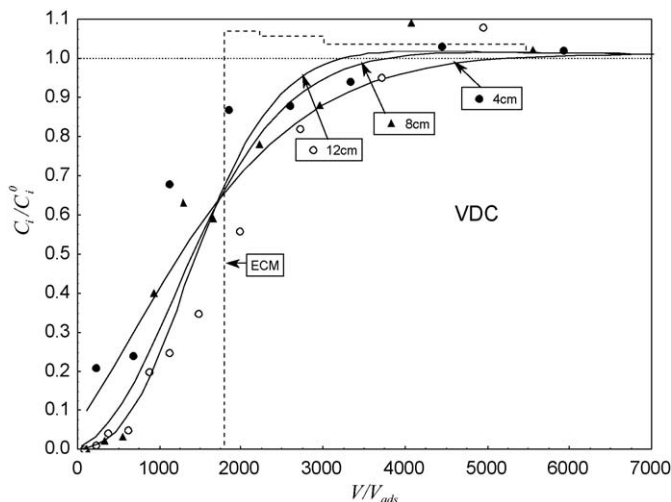

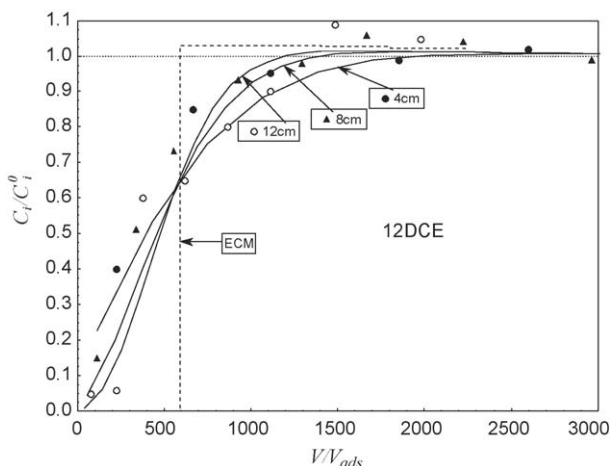Fig. 7. Breakthrough curves of VDC.

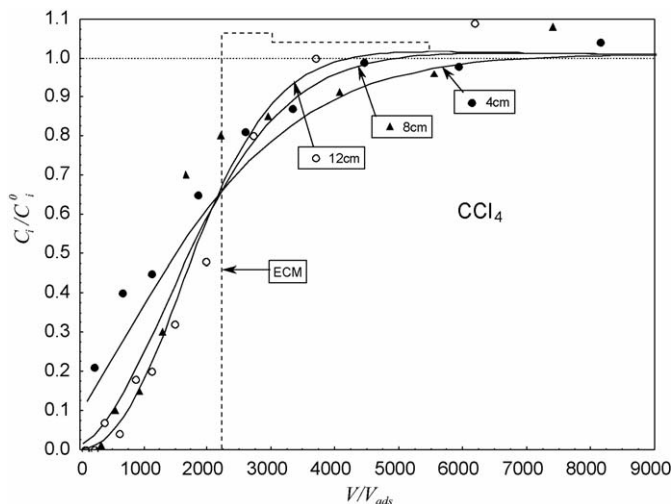Fig. 5. Breakthrough curves of 12DCE.

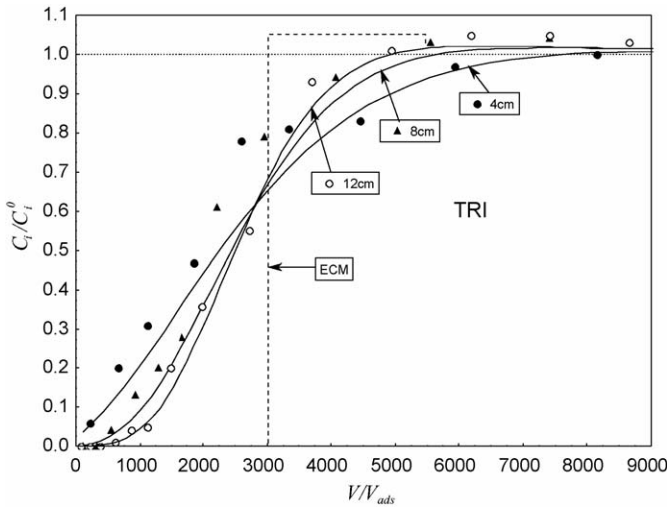Fig. 8. Breakthrough curves of CCl_4.
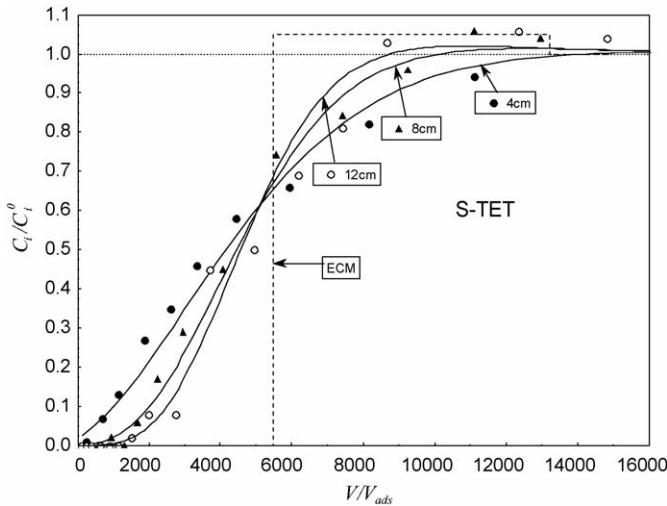
Fig. 9. Breakthrough curves of TRI.

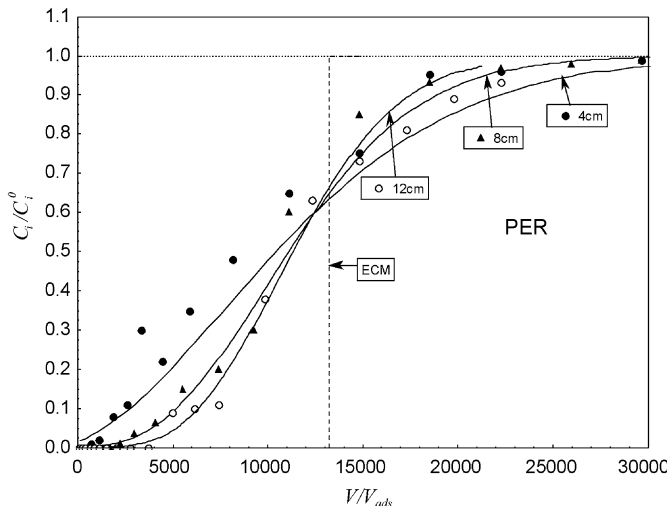Fig. 10. Breakthrough curves of S-TET.

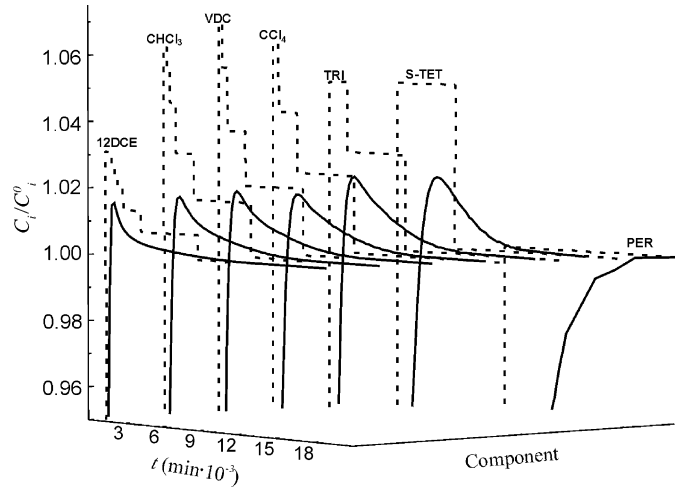Fig. 11. Breakthrough curves of PER.

Fig. 12. Breakthrough curves calculated from ECM and KCM in the relative concentration range of 0.95–1.08.

Table 2
Relative maximum values of overshoot concentration

Component	PER	S-TET	TRI	CCl$_4$	VDC	CHCl$_3$	12DCE
ECM	1.000	1.050	1.051	1.063	1.069	1.062	1.031
KCM	1.000	1.015	1.017	1.017	1.017	1.022	1.021

It was found (Figs. 5–11) that the breakthrough curves become steeper along with an increase of the bed height. The shape is approaching to the equilibrium profile. This cause that along with on increase of bed height the time of appearance of a given component at the column outlet approaches to the time calculated from the ECM [31]. The concentration at the column outlet corresponding to $0.11C_i^0$ was taken as the breakthrough point for a given component. However, in the case of adsorption from multi-component solution, the breakthrough of each compound can be considered individually or in relation to the sum of component concentrations as $\sum C_i / \sum C_i^0$. The breakthrough times of the particular components are collected in Table 3.

At the initial stage of process a broadening of the sorption front of the component i take places. Subsequently, in accordance with the Wicke's law [8,11], the concentration points

Table 3
Throughput time of particular component t_{bi} (min)

L (cm)	PER	S-TET	TRI	CCl$_4$	VDC	CHCl$_3$	12DCE
Measurement							
4	700	200	140	0	0	0	0
8	2500	1100	480	300	280	120	50
12	5000	2500	1000	590	550	400	200
KCM							
4	800	270	140	25	30	10	5
8	2900	1100	580	290	263	175	55
12	5200	2000	1000	600	570	380	150
ECM							
4	3566	1477	813	602	487	379	159
8	7133	2955	1627	1205	974	758	319
12	10699	4432	2440	1807	1461	1137	478

Table 4
Dynamic adsorptivity relatively individual component to throughput time a_{di} (mmol/g)

L (cm)	PER	S-TET	TRI	CCl$_4$	VDC	CHCl$_3$	12DCE
Measurement							
4	0.0193	0.0055	0.0049	0.0009	0.0009	0.0025	0.0006
8	0.0345	0.0150	0.0084	0.0045	0.0066	0.0069	0.0012
12	0.0460	0.0227	0.0116	0.0059	0.0087	0.0153	0.0031
KCM							
4	0.0200	0.0080	0.0038	0.0014	0.0013	0.0040	0.0005
8	0.0400	0.0160	0.0077	0.0038	0.0035	0.0070	0.0009
12	0.0470	0.0180	0.0095	0.0053	0.0050	0.0090	0.0013
ECM							
Any	0.1035	0.0399	0.0213	0.0155	0.0124	0.0286	0.0039

Fig. 13. Dependence of relative dynamic adsorptivity as a function of bed height.

for higher concentrations are shifting faster along the adsorption column in the case of convex adsorption isotherm [12]. This effect causes a narrowing of the sorption front. This phenomenon was confirmed experimentally. Hence, it can be said that, in the adsorption process of chlorohydrocarbons on DTO activated carbon from aqueous solution at the Reynolds number of approximately 1.3 the contribution of the longitudinal effects is small and can be neglected. The sorption zone of a given component for a bed height $L \to \infty$ will be approaching to a rectangular shape. Hence, the distribution of concentrations of particular components in the column for $L \to \infty$ will be corresponding to that obtained from ECM.

A parameter determining the adsorptivity of bed is its dynamic activity. The dynamic activities for the particular components for a bed height of 4, 8 and 12 cm calculated from KCM and ECM are presented in Table 4. This magnitude was calculated from equation:

$$a_{di} = \left(C_i^0 t_{bi} - \int_0^{t_{bi}} C_i \mathrm{d}t \right) \frac{q}{m} \tag{11}$$

whereas in the case of ECM from equation:

$$a_{di}^0 = \frac{q t_{bi} C_i^0}{F L \rho_b} = \frac{w C_i^0}{U_i \rho_b} \tag{12}$$

The dynamic activity was found to be independent on a bed height in the case of ECM [31]. The dynamic activity calculated based on measurement data and that calculated from the KCM increases along with increase of a bed height. The adsorption zones of the particular components become narrower with moving along the bed, which causes the above effect. The dynamic activity will be approaching to the equilibrium value at $L \to \infty$. A dependence of the relative dynamic activity a_i/a_i^0 as a function of a bed height is shown in Fig. 13. The extrapolation beyond the experimental points was performed with the assumption that a ratio of $a_i/a_i^0 \to 1$ for $L \to \infty$.

For a bed height of about 70–80 cm, the a_i/a_i^0 ratio distinctly increases. Above this height the growth is already small. An increase of bed height above 100 cm does not cause a substantial improvement of the effective utilization of adsorbent. It only allows to prolong the time of adsorption cycle. However, such operation may adversely affect the process due to an increase
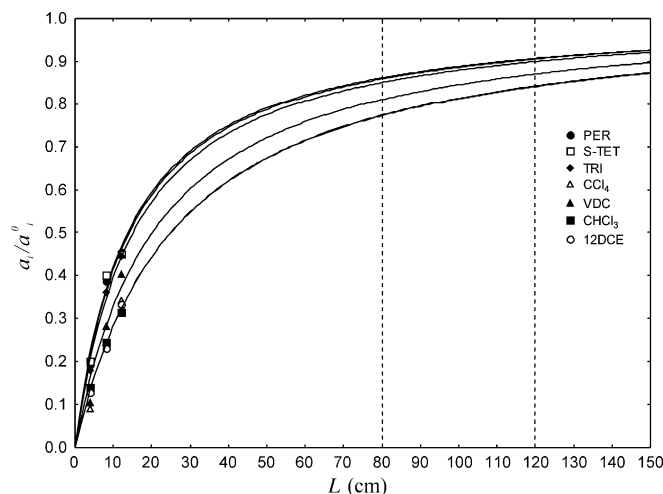
of the flow resistance. Moreover, during the operation with too high adsorption bed its large part does not participate in the mass transfer process. This part forms an inactive layer of the adsorbent, which only causes the flow resistances.

The ECM allows to determine the neighbourhood of the middle point ($C_i/C_i^0 \cong 0.5$) of the breakthrough curve [31]. A narrowing of the sorption fronts takes place around these points. This model should allow the estimation of distribution of concentrations in the adsorption column for the bed with a height exceeding 100 cm. This in turn, allows to determine in a simple way the times of appearance of the particular components at the column outlet for engineering purposes based on Eq. (13) [31].

$$t_{bi} = \frac{L}{U_i} \tag{13}$$

The dependence of the total concentration of chlorohydrocarbons at the column outlet as a function of time $\sum C_i / \sum C_i^0 = f(t)$ at a bed height equal to 12 cm is presented in Fig. 14.

A very good agreement of the modelling calculations with the experiment indicates that for given process conditions a contribution of longitudinal diffusion is negligible and can be omitted.
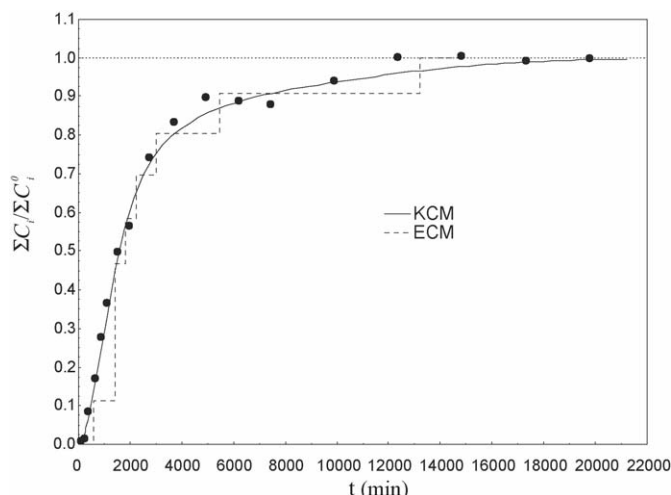

Fig. 14. Summary breakthrough curves.

Table 5
Mean relative deviations between the experimental and calculated values

L (cm)	δ (%)						
	PER	S-TET	TRI	CCl$_4$	VDC	CHCl$_3$	12DCE
4	25.5	16.9	15.9	13.5	19.8	14.5	7.7
8	9.4	12.8	15.5	17.0	22.4	29.9	15.4
12	10.4	12.0	9.4	24.2	18.5	31.7	28.9

With a lack of longitudinal effects for examined flow rate $Re = 1.3$ one can expect that the system will be behaviour similarly at larger linear flow velocities. For the flow velocity corresponding to the Reynolds number $Re < 7$, the course of the curves can be most probably determined using the presented method. In the case of larger flow velocities, the internal resistance should be taken into account in the calculations at least for CCl$_4$, VDC, CHCl$_3$ and 12DCE [28–30].

The average relative deviation between the experimental points and those calculated from the KCM are compiled in Table 5.

$$\bar{\delta}_i = \frac{\sum \delta_i}{N} 100\% \qquad (14)$$

where

$$\delta_i = \frac{|C^{\mathrm{exp}}_{i,k,n} - C_{i,k,n}|}{C_{i,k,n}} \qquad (15)$$

These results demonstrate that the applied calculation method that takes into account the external mass transfer coefficient well describes the course of the breakthrough curves in the presented adsorption process.

5. Conclusion

An analysis of the experimental results demonstrates that the formulated calculation model allows to precisely determine the course of the breakthrough curves during the adsorption of light chlorohydrocarbons on the fixed-bed DTO activated carbon.

A satisfactory consistency of the model with the experimental results confirms the correctness of made assumption about a decisive influence of the diffusion through the laminar layer of liquid surrounding the adsorbent particle on the rate of adsorption.

A comparison of the calculated values with those obtained experimentally also reveals that under the measurement conditions the longitudinal dispersion has no an essential significance. For the flow rate 15 cm/min an increase of bed height above 100 cm does not cause a substantial improvement of the effective utilization of adsorbent. Under the conditions of this study, the overshoot concentration does not exceed 10% of influent concentration.

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