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MODELLING OF THE ADSORPTION PROCESS ON ACTIVATED CARBON IN WATER AND SEWAGE TREATMENT

Based on the assumption that a diffusion film adheres to the adsorbent surface, mathematical models describing the adsorption process on activated carbon (both under static and dynamic conditions) were developed. The models were verified for the following system: aqueous solution of p-cresol and activated carbon of Carbosorbid type. The models in question may be used in the design of the adsorption process, as they include the most important parameters responsible for the course of the process.

NOTATIONS

C — adsorbate concentration, gm^{-3},

C_c — adsorbate concentration on the external carbon surface, gm^{-3},

C_e — equilibrium concentration, gm^{-3},

C_f — final concentration, gm^{-3},

C_i — initial concentration, gm^{-3},

d — adsorbate particle diameter, cm,

D — carbon dose, gm^{-3},

D_m — molecular diffusion coefficient, $cm^2 s^{-1}$,

F — stream diffusion cross-section, cm^2,

F_b — bed cross-section, m^2,

H — bed depth, m,

H_z — adsorption zone depth, m,

k — mass-transfer rate coefficient, s^{-1},

K — Boltzman constant $= 1.38 \times 10^{-16}$ erg K^{-1},

m — adsorbate mass, g,

M — molecular mass of adsorbate, g/mol,

N — Avogadro number $= 6.024 \times 10^{23}$ particle/mol,

Q — flow rate, $cm^3 s^{-1}$,

r_c — carbon particle radius, cm,

r_{cap} — capillary radius, cm,

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t — contact time, s,
t_{opt} — optimal contact time, s,
T — temperature, K,
T_b — time of bed run to break point, h,
T_e — time of bed run to exhaustion, h,
T_r — time of bed run, h,
V_f — filtration rate, cm s^{-1},
V_s — solution volume per one carbon particle, cm^3,
x — carbon adsorption capacity, gg^{-1},
δ — diffusion film thickness, cm,
ε — bed porosity,
η — dynamic viscosity, P,
ϱ_a — adsorbate density, gm^{-3},
ϱ_c — carbon density, gm^{-3}.

1. INTRODUCTION

Adsorption is one of the most effective processes for soluble substance removal in water treatment and renovation. Activated carbon is practically the only available adsorbent. In the adsorption process on activated carbon first of all the following substances are removed: phenols, pesticides, detergents, and other soluble substances which are classified as micropollutants. The rate and effectiveness of adsorption from water solution mostly depend on the size and kind of the activated carbon.

The purpose of the paper was to establish a mathematical model of the adsorption process on activated carbon marketed under the brand name of "Carbosorbid". The considerations presented here are concerned with physical adsorption alone because of the applicability of this process to all dissolved organic pollutants.

2. DISCUSSION

When modelling the process of static adsorption it has been assumed that the adsorption driving force $C_f - C_c$ acts in a film of a thickness adhering to the carbon particle surface. Adsorbate concentration varied from $C_f = C_i$ to $C_f = C_e$ ($C_i, C_e \gg C_c$) [1]. The adsorption process was described in terms of Fick's law:

$$\frac{dm}{dt} = -D_m F \operatorname{grad} C. \tag{1}$$

After suitable transformations, substitutions, and integration from r_c to $r_c + \delta$ and from C_c to C_f, the equation can be written as

$$\frac{dC_f}{dt} = -\frac{4\pi r_c}{V_s}\left(\frac{r_c}{\delta} + 1\right)D_m(C_f - C_c). \tag{2}$$

Assuming that $C_c \ll C_e$ and integrating both sides of the equation, the final form of the model is derived and verified experimentally:

$$-\ln\frac{C_f}{C_i} = kt. \tag{3}$$

The value of k is a product of the molecular diffusion coefficient D_m and of the expression

$$\frac{4\pi r_c}{V_s}\left(\frac{r_c}{\delta}+1\right)$$
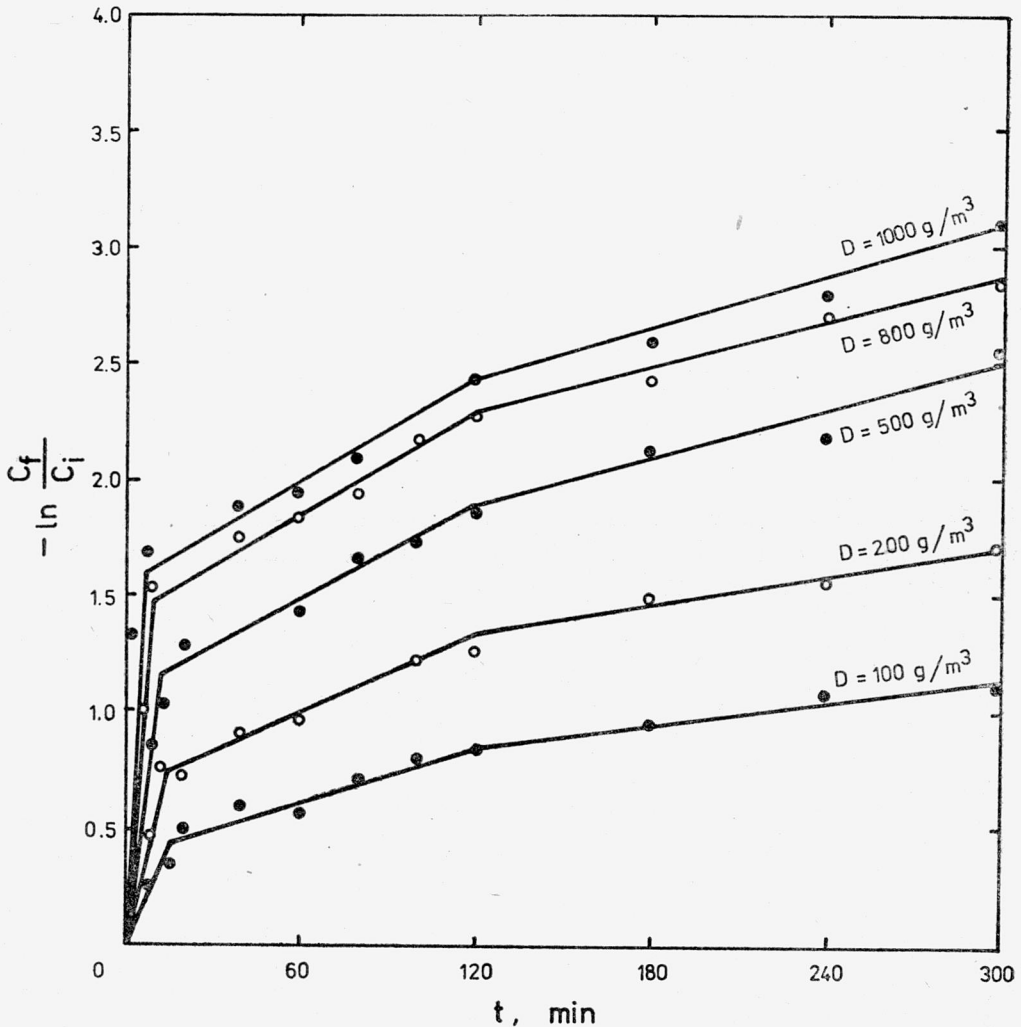
which describes the geometry of the system applied.

Fig. 1. $-\ln C_f/C_i = f(t)$ curves

Rys. 1. Zależność ujemnej wartości logarytmu ze stosunku stężeń adsorbatu od czasu kontaktu

This model has been verified experimentally for the system: water solution of p-cresol and powdered activated carbon. The increased doses of activated carbon were added to the aqueous solution of p-cresol the concentration of which was 18 gm^{-3}. The solution was mixed with an intensity which permitted the prevention of carbon particles sedimentation. The carbon parameters were as follows: density — 0.5 g cm^{-3}; particle diameter — 8×10^{-3} cm; and particle volume — 2.14×10^{-6} cm. After having applied various contact times, residual adsorbate concentration was analysed. The experimental results are shown in fig. 1. From this figure it is evident that there exist three mass transfer rate coefficients for each dose of activated carbon.

The molecular diffusion coefficient for identified particles of the adsorbate (which occurs at low concentrations and does not affect the viscosity of the solution) has a constant value. This results from the Stokes-Einstein law

$$D_m = \frac{KT}{3\pi\eta d}. \tag{4}$$

Adsorption driving force decreases, as the concentration of the adsorbate decreases and the film thickness δ increases. Consequently, the mass transfer rate coefficient decreases. Film diffusion size δ is calculated from the expression:

$$\frac{3r_c(r_c+\delta)}{\delta[(r_c+\delta)^3 - r_c^3]} D_m = k. \tag{5}$$

The diameter of the adsorbate particle is calculated as follows

$$d = \sqrt[3]{\frac{6M}{\pi N \varrho_a}}. \tag{6}$$

The p-cresol molecular diffusion coefficient value which was calculated from the eq. (4) was $D_m = 6.19 \times 10^{-6}$ $cm^2 s^{-1}$. Diffusion film thickness and the parameters for its calculation are listed in tab.

Table

Diffusion film thickness calculation
Wyznaczenie grubości dyfuzyjnej warstwy przyściennej

Carbon dose	Carbon particles quantity per m^3 of solution	Solution volume per one carbon particle	Mass transfer rate coefficient			Diffusion film thickness δ		
			k_1	k_2	k_3			
gm^{-3}	—	cm^3	s^{-1}	s^{-1}	s^{-1}	cm	cm	cm
100	93.4×10^6	0.01070	4.66×10^{-4}	7.33×10^{-5}	1.83×10^{-5}	0.0632	0.1210	0.195
200	186.9×10^6	0.00535	8.33×10^{-4}	9.50×10^{-5}	3.00×10^{-5}	0.0511	0.1110	0.162
500	467.3×10^6	0.00214	1.66×10^{-3}	1.16×10^{-4}	4.83×10^{-5}	0.0395	0.0103	0.140
800	747.3×10^6	0.00134	2.16×10^{-3}	1.23×10^{-4}	5.50×10^{-5}	0.0359	0.1011	0.134
1000	934.5×10^6	0.00107	2.33×10^{-3}	1.25×10^{-4}	6.00×10^{-5}	0.0349	0.1005	0.130

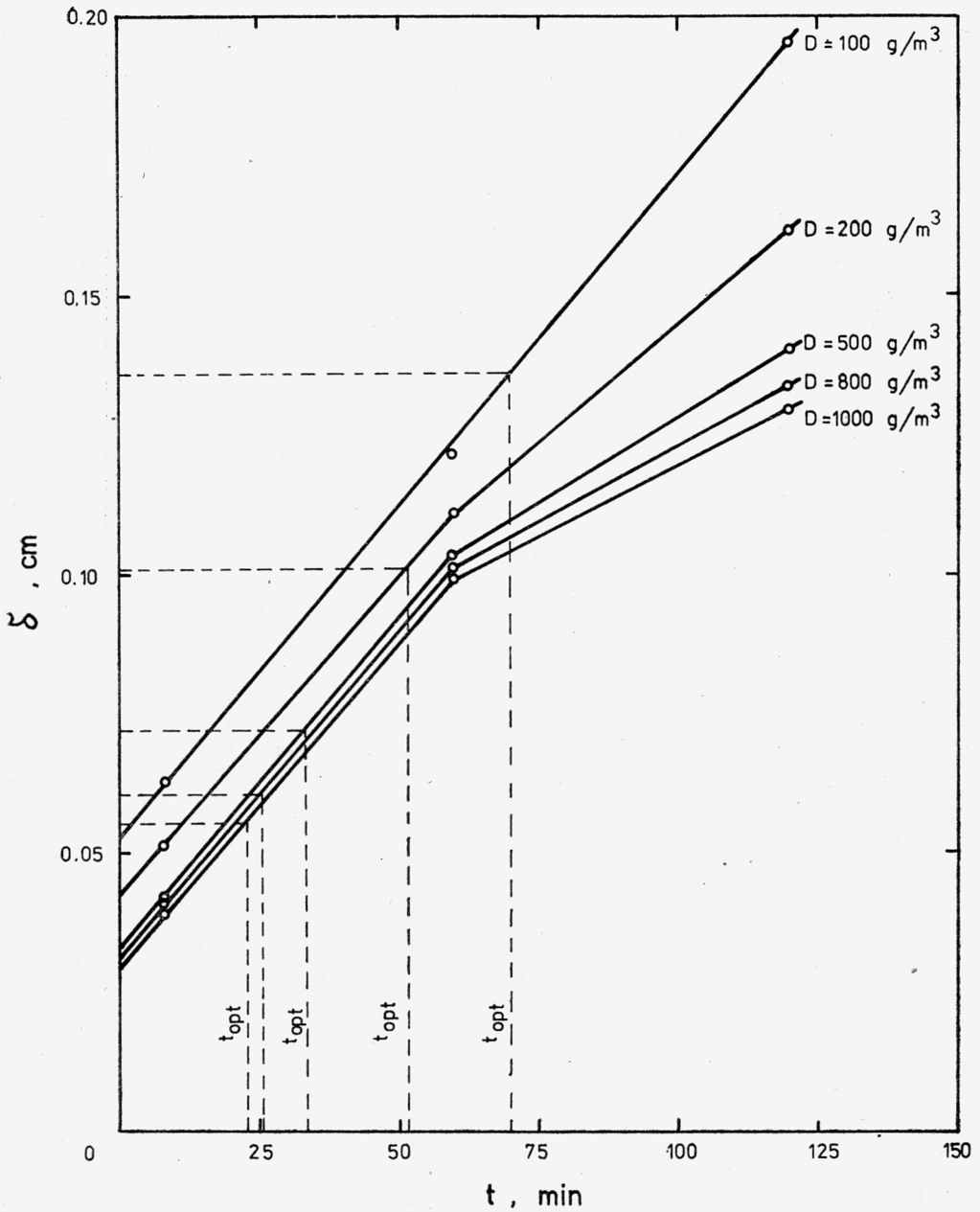Fig. 2. Diffusion film thickness versus contact time
Rys. 2. Grubość dyfuzyjnej warstwy przyściennej w funkcji czasu kontaktu
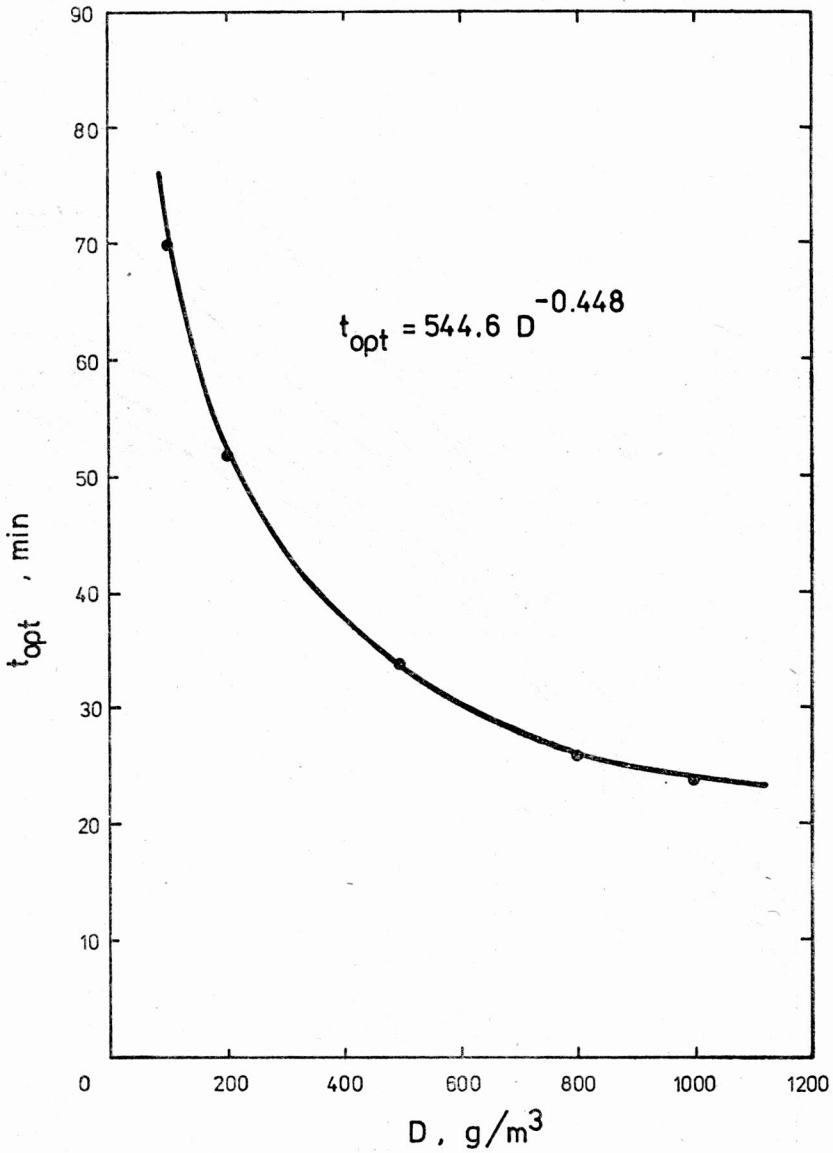
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Fig. 3. Relationship between optimal contact time and activated carbon dose for the same initial adsorbate
concentration
Rys. 3. Zależność optymalnego czasu kontaktu od dawki węgla aktywnego przy tych samych stężeniach
początkowych adsorbatu

The first stage of the adsorption process was described by the coefficient k_1. This stage lasted from about 16 minutes for a 100 gm^{-3} dose to about 12 minutes for a 1000 gm^{-3} dose. The second stage which was characterized by the coefficient k_2 lasted (together with the first stage) 2 hours for all the doses. The third stage (k_3) began after two hours of the process. The much more smaller value of k_3 as compared to k_1 and k_2 is due to the increase in the diffusion film up to a thickness which is much greater than the thickness of the hydrophylic layer around the carbon particle. The effectiveness of the process tends to minimum values.

The relationships between δ and optimal contact time for different activated carbon doses are given in fig. 2. The optimal contact time is calculated from the equation

$$t_{opt} = 544.6 \, D^{-0.448}. \tag{7}$$

Optimal contact time versus carbon dose for initial p-cresol concentration of 18 gm^{-3} is shown in fig. 3. At the optimum time of the process the diffusion film size is equal to the water solution layer belonging to a single carbon particle. This has been verified experimentally and shown in fig. 4.

To describe the adsorption process under dynamic conditions, a mathematical model based on the adsorbate mass balance was used [2]:

$$QC(H,t)dt - QC(H+dH,t)dt - \varrho_c(1-\varepsilon)F_b dH dx = F_b dH[C(H, t+dt) \\ -C(H,t)]. \tag{8}$$

Transformation of the eq. (8) results in equation

$$-Q\left(\frac{\partial C}{\partial H}\right)_t - \varrho_c(1-\varepsilon)F_b\frac{dx}{dt} = \varepsilon F_b\left(\frac{\partial C}{\partial t}\right)_H. \tag{9}$$

Neglecting the adsorbate solution accumulation in the pores among the particles of the adsorbent, the balance equation is simplified to

$$-\frac{V_f}{\varrho_c(1-\varepsilon)}\frac{dC}{dH} = \frac{dx}{dt}. \tag{10}$$

Application of the external diffusion equation [2] leads to

$$-\frac{V_f}{(1-\varepsilon)}\frac{dC}{dH} = k\varepsilon(C_f-C_c). \tag{11}$$

With the same assumptions as those for the model under static conditions and integrating eq. (11), the final form of the adsorption model is derived

$$-\ln\frac{C_f}{C_i} = \frac{(1-\varepsilon)\varepsilon H_z}{V_f}k, \tag{12}$$

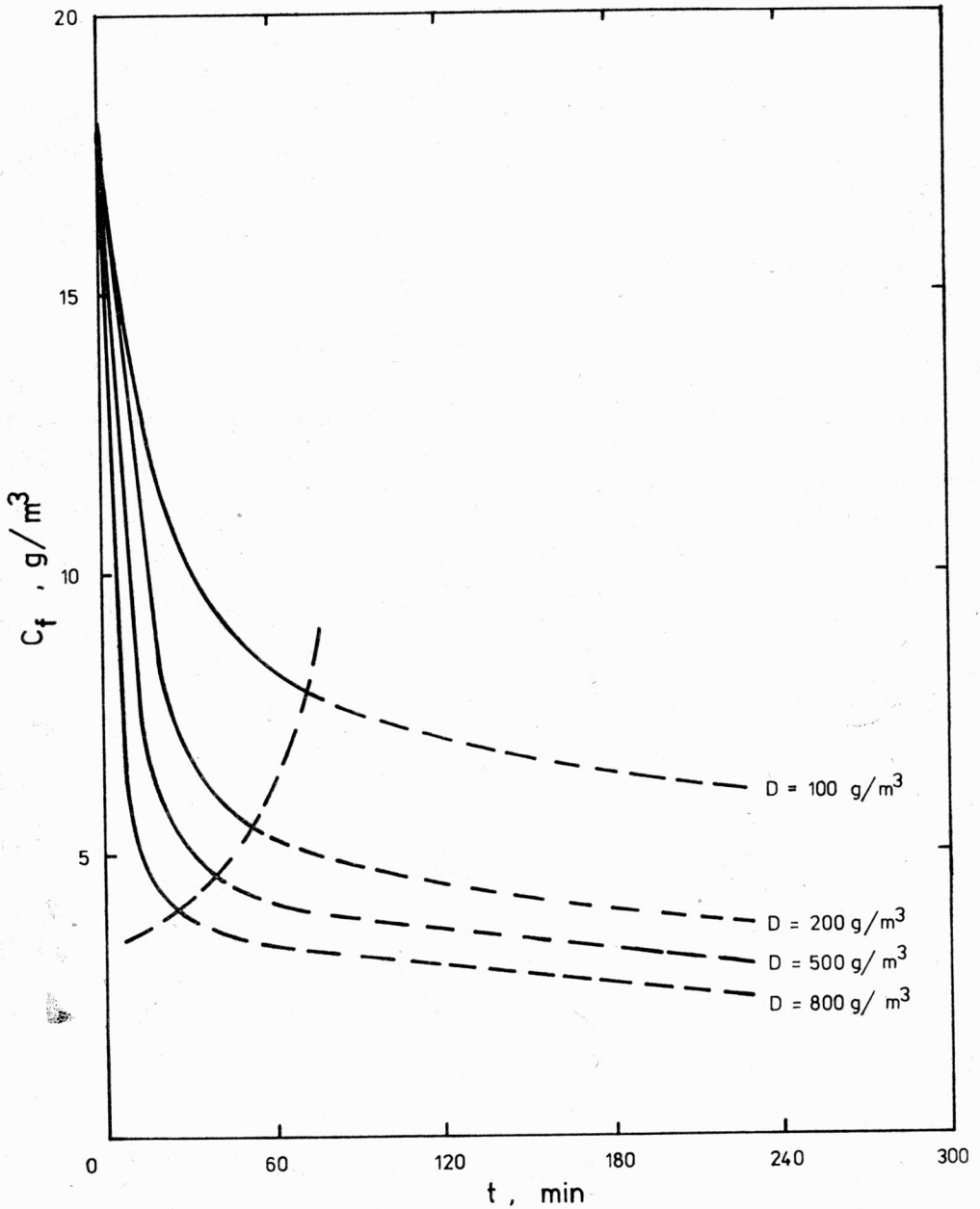where $H_z V_f^{-1}$ is bed contact time t.

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Fig. 4. Adsorbate concentration change versus contact time for each carbon dose applied
Rys. 4. Zmiana stężenia adsorbatu w zależności od czasu kontaktu dla poszczególnych dawek węgla ak-
tywnego

Then the eq. (12) is simplified to

$$-\ln \frac{C_f}{C_i} = (1-\varepsilon)\varepsilon kt \tag{13}$$

which is the adsorption model under dynamic conditions.

The adsorption process under dynamic conditions was performed at different depths of granular activated carbon beds. The process parameters were as follows: filtration rate — 5.0 mh^{-1}; carbon particles diameter — 0.2 cm; bed porosity ε — 0.45; and initial p-cresol concentration C_i — 18 gm^{-3}.

The model presented here is adequate for a bed depth equal to that of the adsorption zone. The value of the adsorption zone was calculated from Michels equation [3]

$$\frac{H_z}{H} = \frac{T_e - T_b}{T_e - \dfrac{C_i}{C_f}(T_e - T_b)} . \tag{14}$$

The relationship $C_f/C_i = f(T_r)$ is presented in fig. 5. The parameters of eq. (14) were calculated from the break-through curve (fig. 5). The depth of the adsorption zone is about 0.3 m.
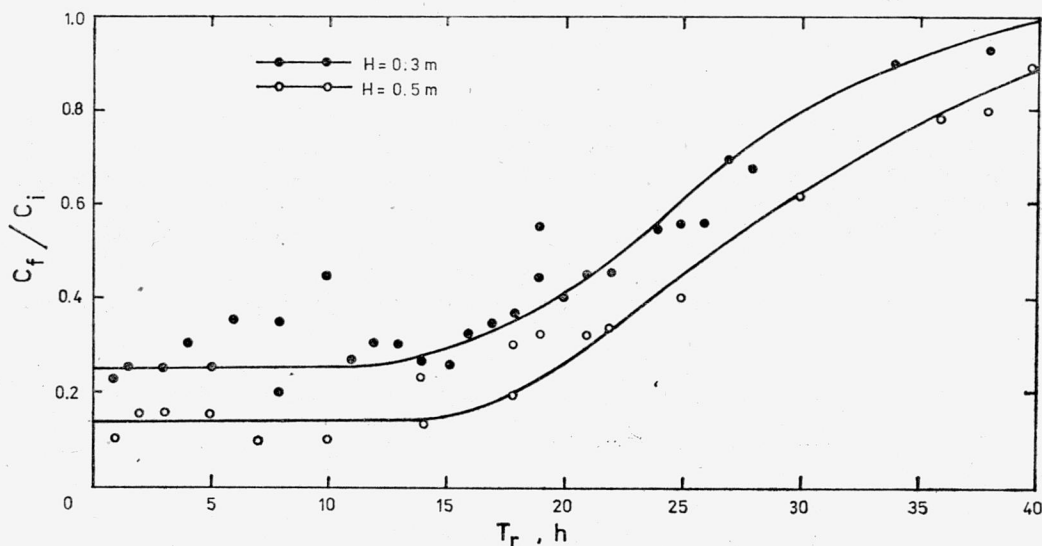

Fig. 5. Inflow and outflow concentration ratio versus time of bed run
Rys. 5. Stosunek stężenia odpływu do stężenia dopływu w funkcji czasu pracy kolumny węgla aktywnego

Carbon bed porosity was modelled by parallel capillaries of a radius $r_{cap} = 0.0273$ cm

$$r_{cap} = \frac{\varepsilon r_c}{3(1-\varepsilon)} . \tag{15}$$

The mass transfer rate coefficient in adsorption on activated carbon is constant. Its value for a filtration rate $V_f = 5$ mh^{-1} and an initial p-cresol concentration $C_i = 18$ gm^{-3} is 0.0259 s^{-1}. Diffusion film thickness is 0.0154 cm which is about half (0.56) of the capillary radius.

The adsorption driving force has a constant value for the adsorption zone, and acts in a film whose thickness is δ. The change in the adsorption driving force results from the influence of the internal diffusion on the external diffusion. It makes the adsorption zone to be displaced to the bottom of the carbon bed. The break point is an indication that the adsorption zone has left the carbon bed. In consequence, the contact time is shortened and the adsorption efficiency deteriorated.

3. CONCLUSIONS

The model has been verified experimentally in a p-cresol solution. The experiments substantiate the good agreement between synthetic and measured parameters of the adsorption process.

The model presented can be used in the design of the adsorption process, as it includes most of the parameters influencing the course of the process.

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MODELOWANIE PROCESU ADSORPCJI NA WĘGLU AKTYWNYM W TECHNOLOGII WODY I ŚCIEKÓW

W oparciu o założenie występowania dyfuzyjnej warstwy przyściennej na omywanej powierzchni węgla aktywnego, wyprowadzono modele matematyczne procesu adsorpcji w warunkach statycznych i dynamicznych. Modele zweryfikowano dla układu: wodny roztwór p-krezolu–węgiel aktywny typu Carbosorbid. Podane modele mające charakter poznawczy i aplikacyjny uwzględniają najistotniejsze parametry decydujące o efektywności procesu adsorpcji.

MODELLIERUNG DER AKTIVKOHLE-ADSORPTION IM WASSER

Unter der Annahme des Vorkommens einer Diffusionsschicht an der Oberfläche der bespülten Aktivkohlepartikeln, wurden mathematische Adsorptionsmodelle für statische und dynamische Bedingungen formuliert. Die Modelle wurden für das System: wässrige p-Kresollösung und Aktivkohle „Carbosorbid" bewahrheitet. Sie erbrachten Erkenntnisse die anwendungsreif sind und alle wesentlichen Parameter der Adsorptionseffektivität beinhalten.

МОДЕЛИРОВАНИЕ ПРОЦЕССА АДСОРБЦИИ НА АКТИВИРОВАННОМ УГЛЕ В ТЕХНОЛОГИИ ВОДЫ И СТОЧНЫХ ВОД

На основе допущения о наличии диффузионного граничного слоя на омываемой поверхности активированного угля были введены математические модели процесса адсорбции в статичных и динамических условиях. Была произведена верификация моделей для системы водный раствор р-крезол — активированный уголь типа карбосорбит. Приведенные модели, имеющие познавательный и аппликационный характер, учитывают наиболее существенные параметры, обусловливающие эффективность процесса адсорбции.