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MODELS OF ACTIVATED CARBON ADSORPTION PHENOMENA IN ADVANCED SEWAGE TREATMENT

In the study models identifying elementary phenomena of adsorption process in a dynamic system were given and verified. It was shown that in order to determine explicitly the mechanism of adsorption account should be taken of the parameters characterizing the adsorbate, adsorbent, and the kinetics and dynamics of the process. The effects of adsorption and the diffusivity of adsorbate molecules in the bed have been examined as a function of concentration gradient and flow hydraulics.

NOTATIONS

- m — adsorbate mass, g,
 t — contact time, s,
 r — $\varepsilon \cdot d_w / 6(1-\varepsilon)$ — radius of the capillary, cm,
 ε — bed porosity,
 d_w — carbon grain diameter, cm,
 d — adsorbate molecule diameter, cm,
 $\delta = r - r_0$ — thickness of diffusive boundary layer, cm,
 r_0 — range of hydraulic diffusion in a capillary, cm,
 C — concentration, g/m³,
 C_0 — adsorbate concentration in the inflow, g/m³,
 C_b — adsorbate concentration in the outflow, g/m³,
 C_0^x — number of particles in 1 m³ of the inflow, m⁻³,
 C_b^x — number of particles in 1 m³ of the outflow, m⁻³,
 C_i — concentration on the external carbon surface, g/m³,
 D — diffusion coefficient, cm²·s⁻¹,
 D_e — effective diffusion coefficient, cm²·s⁻¹,
 D_{hi} — hydraulic diffusion coefficient, cm²·s⁻¹,
 $j_d = \frac{k}{V} N_{Sc}^{2/3}$ — mass transfer factor,

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- k — mass transfer coefficient, $\text{cm}\cdot\text{s}^{-1}$,
 V — filtration rate, $\text{cm}\cdot\text{s}^{-1}$,
 $N_{\text{Sc}} = \eta(\rho D)^{-1}$ — Schmidt number,
 η — viscosity of solution, poise = $\text{dyne}\cdot\text{s}\cdot\text{cm}^{-2}$,
 ρ — solution density, $\text{g}\cdot\text{cm}^{-3}$,
 ρ_{mol} — density of adsorbate particle, $\text{g}\cdot\text{cm}^{-3}$,
 $N_{\text{Re}} = V\cdot d_w\cdot[\eta(1-\varepsilon)]^{-1}$ — Reynolds number,
 $K = 1.38 \times 10^{-16}$ erg/K — Boltzman constant,
 T — temperature, K,
 F — bed cross-section surface, cm^2 ,
 $S = 2\varepsilon/r$ — washed surface of carbon per bed unit volume, cm^{-1} ,
 M — molecular mass, g/mol,
 $N = 6.024 \times 10^{23}$ — Avogadro number, part./mol,
 T_0 — process duration until the moment of the bed breakthrough (column operation time), h,
 η_w — number of adsorbate molecules in a monolayer,
 S_{d_w} — active internal carbon surface per carbon unit volume, $\text{m}^2\cdot\text{m}^{-3}$,
 w — number of layers,
 X^2 — mean diffusion-induced dislocation of adsorbate molecule in a unit time, cm^2 ,
 $K_a = 100\sqrt{D_e/D_h}$ — criterion of sorption activity of carbon surface,
 H — height of activated carbon bed layer, cm,
 H_f — height of adsorption front, cm.

1. INTRODUCTION

As a highly effective process, low energy-consuming and simple in operation, adsorption finds wider and wider application in the technology of water purification and renovation. The constantly increasing interest in adsorption is connected both with the increase of natural water pollution and with the deficit of disposable water resources in many regions of our country.

The multiple utilization of water, as well as the tendency towards its renovation as a result of the increase of water consumption, considerably widen the range of application of this process. This situation has inspired a number of experimental studies on the application of adsorption process to the treatment of secondary effluents from municipal sewage treatment plants.

The authors' intention was to define the technological criteria adequate for the conditions of the general system of water renovation, enabling the identification and modelling phenomena of the adsorption process.

2. AIM AND SCOPE OF THE STUDY

The analysis concerns a dynamic system, i.e. sorption columns filled with activated carbon Carbolpol Z-4, and the organic compounds typical of secondary effluent as adsorbate.

When identifying the process it was assumed that summary effects of adsorption in the system under consideration depend upon three elementary processes such as external diffusion, internal diffusion, and the binding of adsorbate molecules on the carbon surface.

The mathematical models have been applied to determine total adsorption effects, intensity of mass exchange in the bed, and the impact of internal diffusion on the course of the process. The formulation of a simple, e.g. one-parameter empirical model, enabling a univocal estimation of the effects of the process would have both a cognitive significance and a practical application in design and operation of water renovation plants.

The exchange of mass between water solution and carbon surface can be a factor determining the general rate of the process; hence the possibility of assessing whether diffusion is a control factor of the process and is very important for taking the maximum advantage of the adsorbing capacity of carbon.

Improving of the effectiveness of the process can also be achieved through trying to utilize to a higher degree the internal pores of the activated carbon grains. Determination of the extent of internal diffusion in the actually applied carbons, which is adequate for water renovation, will enable to evaluate the validity of such an assumption.

Verification of the adsorption models is based on the authors' own investigations as well as on literature data.

3. MODELLING OF THE ADSORPTION PROCESS IN ACTIVATED CARBON COLUMNS

3.1. THE EFFECTS OF THE PROCESS

Modelling of the summary effects of the adsorption is based on the assumption that the process is controlled primarily by external diffusion as defined by the Fick's equation:

$$\frac{dm}{dt} = -D \cdot F \cdot \text{grad } C. \quad (1)$$

By modelling the porosity of the carbon bed by means of the coherent rectilinear capillaries of radius r and assuming unidimensionality of the stream and occurrence of the concentration gradient, resulting from the activity of the carbon surface, in the layer of the thickness $\delta = r - r_0$ directly adjacent to the active carbon wall, the following equation was obtained:

$$\frac{dC}{C_0 - C_i(t)} = \frac{2Ddt}{r(r - r_0)}. \quad (2)$$

After integration within the intervals from 0 to C_a and from 0 to t , the equation achieved the following form:

$$\ln(C_0 - C_a) - \ln C_0 = - \frac{2Dt}{r(r - r_0)}. \quad (3)$$

The ultimate form of the model is described by the eq. (4):

$$-\ln \frac{C_b}{C_0} = \frac{2Dt}{r^2 \left(1 - \frac{r_0}{r}\right)} \tag{4}$$

Negative sign of the left-hand part of the equation is the consequence of the sign of diffusion coefficient ($D > 0$) and of the fact that concentration decreases along the positive direction of the radius r . Due to this we get $dm/dt > 0$ for $dC/dr < 0$.

The model was verified graphically, the experimental results being represented by the eq. (5) in which t is substituted by H_f/V :

$$-\ln \frac{C_b}{C_0} = f \left(\frac{2H_f}{Vr^2 \left(1 - \frac{r_0}{r}\right)} \right) \tag{5}$$

The linearity of the relationships $y = ax$, $a = D_e$ (fig. 1) indicates that estimation of the adsorption effects in activated carbon beds may be based on the values of the diffusion coefficient being the empirical parameter ($D \rightarrow D_e$).

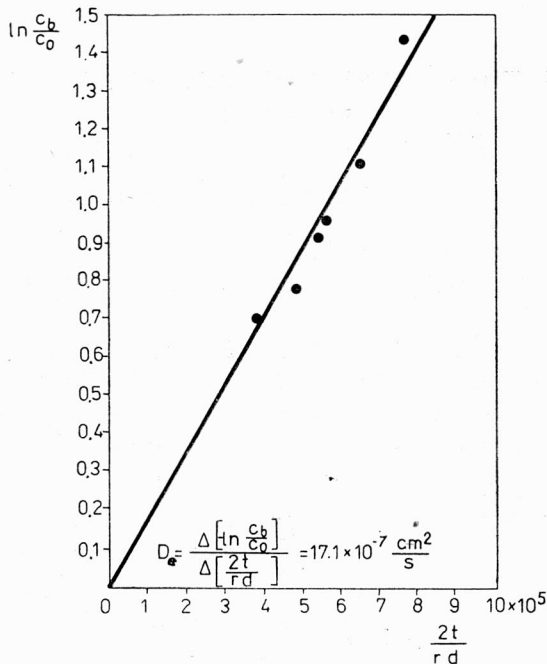


Fig. 1. Relationship $-\ln \frac{C_b}{C_0} = f \left(\frac{2t}{r^2(1-r_0/r)} \right)$

Rys. 1. Zależność $-\ln \frac{C_b}{C_0} = f \left(\frac{2t}{r^2(1-r_0/r)} \right)$

Thickness of the boundary layer in which diffusion occurs was determined on the basis of the following relation:

$$\delta = a \sqrt{\frac{\eta \cdot d_w}{\rho \cdot V}} N_{Sc}^{-1/3} \quad (6)$$

where a coefficient equals 3.0 for a flat surface. After defining the number N_{Sc} and substituting the respective values for $\eta = 10^{-2}P$, $\rho = 1.0 \text{ g} \cdot \text{cm}^{-2}$, and $K = 1.38 \times 10^{-16} \text{ erg} \cdot \text{K}^{-1}$ eq. (6) was transformed into:

$$\delta = \alpha \cdot 3.5 \times 10^{-5} \cdot \sqrt{\frac{d_w}{V}} \cdot d^{-2/3}. \quad (7)$$

Substitution of eq. (7) into (5) yields:

$$-\ln \frac{C_b}{C_0} = f(7.0 \times 10^5 \cdot \alpha^{-1} \frac{H_f \cdot d^{1/3}}{V \cdot r \left(\frac{d_w}{V}\right)^{1/2}}). \quad (8)$$

The above equation was applied directly in approximation of the results of the experiments as shown in fig. 1. The mean values of α obtained from the experimental data are equal to 5.0 for secondary effluent and to 2.0 for coagulated secondary effluent.

3.2. CHARACTERISTICS OF EXTERNAL DIFFUSION IN THE ACTIVATED CARBON BEDS

Estimation of the external diffusion coefficient in the beds D_h was based on the following relations [6]:

$$j_d = \frac{k}{V} N_{Sc}^{2/3}, \quad (9)$$

$$k = \frac{4D_h}{r^2 S}. \quad (10)$$

For carbon beds in which porosity was modelled by means of rectilinear capillaries ($S = 2\epsilon/r$) the D_h coefficient equals:

$$D_h = \frac{j_d \cdot r \cdot \epsilon \cdot V}{2} \sqrt[3]{\left(\frac{\rho D}{\eta}\right)^2}. \quad (11)$$

The value of j_d was determined by the following empirical formula [6]:

$$\lg j_d = 0.7683 - 0.9175 \lg N_{Re} + 0.0817 (\lg N_{Re})^2, \quad (12)$$

whereas that of the molecular diffusion coefficient D , by Stokes-Einstein equation:

$$D = \frac{K \cdot T}{3\pi\eta \cdot d}. \quad (13)$$

It may be shown that the size of adsorbate molecules d (assuming their shape is spherical) equals:

$$d = \sqrt[3]{\frac{6M}{\pi \cdot N \varrho_{\text{mol}}}} \quad (14)$$

or

$$d = 1.469 \times 10^{-8} \sqrt[3]{\frac{M}{\varrho_{\text{mol}}}}. \quad (15)$$

Considering the relationships (12)-(15) and assuming (tab. 1) that:

$$\sqrt[9]{\varrho_{\text{mol}}^2} \cong 1 \quad (16)$$

eq. (11) was transformed into (17):

$$D_h = 4.74 \frac{r \cdot \varepsilon \cdot V}{M^{0.222}} f(N_{\text{Re}}) \quad (17)$$

in which

$$f(N_{\text{Re}}) = 10^{[0.7683 - 0.9176 \lg N_{\text{Re}} + 0.0817 (\lg N_{\text{Re}})^2]}. \quad (18)$$

Table 1

Estimation of approximation error $(\varrho_{\text{mol}})^{2/9} = 1$
Ocena błędu przybliżenia $(\varrho_{\text{cz}})^{2/9} = 1$

Organic compound	Compound density ρ	$\sqrt[9]{\varrho_{\text{mol}}^2}$	Approximation error %
Saccharose	1.588	1.108	9.7
Fructose	1.670	1.120	12
Maltose	1.540	1.10	10
Benzene	0.879	0.97	3
Asparaginic acid	1.661	1.11	11
Glucose acid	1.544	1.10	10
Starch	1.50	1.09	9
Stearinic acid	0.838	0.96	4

In the model presented value of the diffusion coefficient is determined by the hydraulic conditions in the bed, its geometry, and molecular weight of the adsorbate.

3.3. SATURATION OF THE ADSORBENT SURFACE AND THE INFLUENCE OF INTERNAL DIFFUSION

The estimation of the saturation degree of the specific surface of activated carbon has been based on mass balance of adsorbate taking into account the internal grain structure. The removed mass of the adsorbate till breakthrough point is represented by the following equation:

$$V \cdot F \cdot T_0 \cdot (C_0^* - C_b^*) = n_w \cdot W \quad (19)$$

or after the adequate substitutions:

$$\frac{V \cdot T_0 \cdot C_0^* \left(-1 \frac{C_b^*}{C_0^*} \right) \pi d^2}{4H} = Sd_w \cdot W. \quad (20)$$

The transformed version of the eq. (20) makes it possible to determine the number of adsorption layers of the carbon/ adsorbate complex:

$$W = \frac{V \cdot T_0 \cdot C_0^* \left(1 - \frac{C_b^*}{C_0^*} \right) \pi d^2}{4H \cdot Sd_w}. \quad (21)$$

4. DATA APPLIED IN THE VERIFICATION OF THE MODELS

Adsorption was investigated applying secondary effluent in a raw state and after its coagulation.

For a precise analysis of the course of the process, as well as for the verification of the models proposed, a detailed identification of adsorbate particles is of fundamental importance.

On the basis of the authors' own analyses, which defined the level of total organic carbon (TOC), as well as on the basis of the data provided by the literature on the subject [1], [4], [5], the hypothetical average composition of the secondary effluent was determined. Fulvic acids (25%) and proteins (25%) constitute secondary effluent TOC by weight, whereas the remainder falls to the carbons of carbohydrates (5%), detergents (mainly ABS, 17%), fatty acids (17%), humic acids (6%), and hylatomelanic acids (5%). Fulvic acids contain elementary units similar to those of humic acids. Hylatomelanic acids, on the other hand, are a spirit-soluble fraction of humic acids. In view of the above and considering the fact the maximum molecular weight of the molecules occurring in this type of sewage is up to 2000 g/mol, the humic, fulvic, and hylatomelanic acids were determined jointly. The structure of the humic acid molecule according to DRAGUNOV was accepted for analysis [3].

Proteins are a combination of twenty amino acids. In sewage they hydrolyze to particles of a mass of up to 2000 g/mol. Five types of protein molecules resulting from the hydrolysis and differing in qualitative and quantitative composition were considered.

As the basic fatty acids do not differ much in molecular mass or in quantity of carbons in a molecule, a mean molecular mass and a mean carbon mass were accepted.

The specification of the molecular composition of proteins, detergents, and carbohydrates is given in tab. 2, and that of molecular masses, the masses of carbon in molecules, and of the quantity of molecules in 1 m³ of sewage is included in tab. 3.

Table 2

Qualitative composition of secondary effluent
Skład jakościowy ścieków biologicznie oczyszczonych

Type of compound present in sewage	The assumed components of the compounds
Proteins	Particle 1 — composed of amino acids possessing maximum number of carbon atoms arginine — phenylalanine — glutamine — histidine — isoleucine — leucine — lysine — methionine — proline — tryptophane — tyrosine — valine
	Particle 2 — composed of a double number of particles possessing maximum number of carbon atoms tyrosine — tryptophane — lysine — leucine — arginine — histidine — phenylalanine — tyrosine — tryptophane — lysine — leucine — arginine — histidine — phenylalanine
	Particle 3 — composed of a triple quantity of particles possessing maximum number of carbon atoms and a triple quantity of particles possessing minimum number of carbons tryptophane — tyrosine — alanine — cysteine — glycine — serine — tryptophane — tyrosine — alanine — cysteine — glycine — serine — tryptophane — tyrosine — alanine — cysteine — glycine — serine
	Particle 4 — composed of all amino acids except for tryptophane and tyrosine (maximum c) and glycine (minimum c) alanine — arginine — asparagine — asparaginic acid — cysteine — phenylalanine — glutamine — glutaminic acid — histidine — isoleucine — leucine — lysine — methionine — proline — serine — threonine — valine
	Particle 5 — composed of particles possessing minimum quantity of carbon alanine — asparagine — asparaginic acid — cysteine — glycine — glutamine — glutaminic acid — methionine — proline — serine — threonine — valine
Detergents	Particle 1 — bimethylbenzenesulphonic acid Particle 2 — bipentylbenzenesulphonic acid Particle 3 — bidecylbenzenesulphonic acid
Carbohydrates	Particle 1 — saccharose, cellobiose, maltose Particle 2 — glucose, fructose

Table 3

Properties of molecules and percentage of organics in secondary effluent
 Właściwości cząsteczek i udziały związków organicznych ścieków biologicznie oczyszczonych

Types of organics of secondary effluents	Percentage of a component in TOC of the secondary effluents %	Molecular weight of hypothetical components of particular compounds g	Mass of carbon in particles g	Real mass of molecules g	Real mass of TOC in organics g	TOC of sewage compounds g/m ³	Number of molecules per 1 m ³ of sewage	Diameter of molecules <i>d</i> cm	
Proteins	25	1496	912	248.4×10^{-23}	151.4×10^{-23}	4.5	min 226×10^{19}	16.8×10^{-8}	
		2060	1200	342.0×10^{-23}	199.3×10^{-23}			18.7×10^{-8}	
		2001	1116	332.2×10^{-23}	185.3×10^{-23}			18.5×10^{-8}	
		1969	972	326.9×10^{-23}	161.4×10^{-23}			18.4×10^{-8}	
		1232	564	204.6×10^{-23}	93.6×10^{-23}			mean 285×10^{19}	15.75×10^{-8}
Anionic detergents ABS	17	173	84	28.7×10^{-23}	13.9×10^{-23}	3.1	min 972×10^{19}	8.2×10^{-8}	
		229	132	38.0×10^{-23}	21.9×10^{-23}			max 223×10^{20}	9.0×10^{-8}
		299	192	49.6×10^{-23}	31.9×10^{-23}			mean 137×10^{20}	9.8×10^{-8}
Fatty acids	17	272	205	45.2×10^{-23}	34.0×10^{-23}	3.1	912×10^{19}	9.5×10^{-8}	
Fulvic acids	24								
Humic acids	6	1308	768	217.2×10^{-23}	127.5×10^{-23}	6.5	51×10^{20}	16.1×10^{-8}	
Hymetomelanic acids	6								
Carbohydrates	5	342	144	56.8×10^{-23}	23.9×10^{-23}	0.9	376×10^{19}	10.3×10^{-8}	
		180	72	29.9×10^{-23}	11.9×10^{-23}			756×10^{19}	8.3×10^{-8}
Summary values	100	max 2060 min 173	max 1200 min 72	max 342×10^{-23} min 28.7×10^{-23}	max 199.3×10^{-23} min 11.9×10^{-23}	18.1	337.6×10^{20} 299.6×10^{20}	max 18.7×10^{-8} min 8.2×10^{-8}	

The relative concentrations of the adsorbate (C/C_0) in the adsorption column effluent as a function of the column operation time, its height, and filtration rate was determined in the low-scale investigations. The heights of the adsorption fronts, i.e. those of the carbon layers in which the decrease of the adsorbate concentration from the initial to that characteristic of the bed breakthrough takes place, were also determined. The average concentrations of TOC and COD of the secondary effluent amounted to 18 g/m^3 and 45 g/m^3 , respectively. Coagulation of the secondary effluent with $200 \text{ g Al}_2(\text{SO}_4)_3 \cdot 18 \text{ H}_2\text{O/m}^3$ resulted in the decrease of the pollution load by 55% on the average.

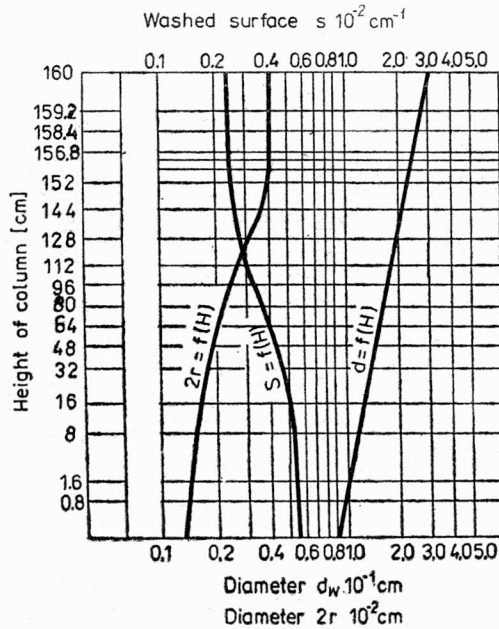


Fig. 2. Carbon bed characteristics
Rys. 2. Geometria złoża węglowego

Table 4

Characteristics of the porous structure of the Polish activated carbon Carbolpol Z-4
Charakterystyka struktury porowatej węgla Carbolpol Z-4

	Specific surface m^2/m^3	Characteristic dimension m
Washed surface	0.033×10^5	0.0273×10^{-2}
Macropores	5.2×10^5	$5.0 \times 10^{-7} - 2.0 \times 10^{-6}$
Transition pores	104.0×10^5	$2.0 \times 10^{-9} - 1.0 \times 10^{-7}$
Micropores	1976.0×10^5	1.0×10^{-9}
Total surface	2085.233×10^5	

Geometry of the carbon bed is presented in fig. 2. Four filtration rates were applied: 2.5, 5.0, 10.0, 15.0 m/h.

The characteristics of the porous structure of carbon, based on the data supplied by the producer [2] and provided by the literature, is given in tab. 4.

5. VERIFICATION OF THE MODELS AND DISCUSSION OF THE RESULTS

Diffusion coefficient in the activated carbon beds is the function of the properties of the molecules of adsorbate and solvent, the sorption activity of the carbon grains surface as well as of the character of the bed structure and the stream hydrodynamics. Sorption activity of the activated carbon surface, determining the concentration gradient and the mass flow, is defined by model eq. (4). Experimental verification of the model, presented in fig. 1, justifies the possibility of defining the effects of adsorption process in secondary effluent, both after and without coagulation, by means of D_e value. The obtained value of the effective diffusion coefficient $D_e = 17.1 \times 10^{-7} \text{ cm}^2/\text{s}$, identical for both the media, shows that the influence of the increase of concentration C_0 and the effect of the increase

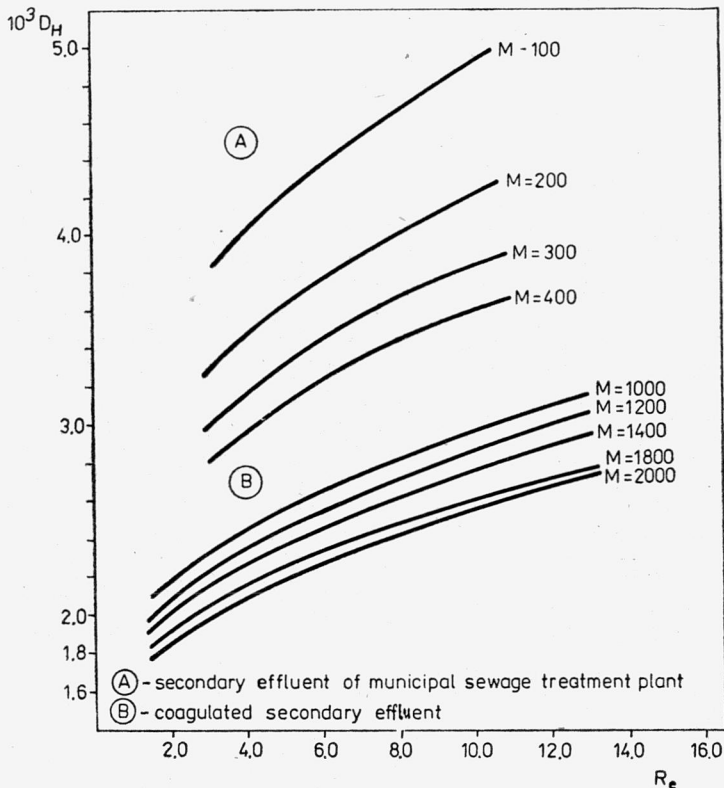


Fig. 3. Relationship $D_h = f(M, Re)$

Rys. 3. Zależność $D_h = f(M, Re)$

of molecular weight of organic compounds on D_e value are neutralized. This conclusion is valid for the concentration range $C_0 \in (7.0, 20.0)$ g C/m³ and for the molecular weight range $M \in (400, 2000)$.

Due to the mixing of water fluxes in carbon beds the concentrations of adsorbate are equilized and the value of hydraulic diffusion coefficient increases substantially ($D_h \gg D_e$).

The values of D_h as a function of molecular masses and Reynolds number have been presented in fig. 3. The impact of the value of N_{Re} on coefficient of D_h increases with the decrease of the molecular weight of the adsorbate. Thus, sewage coagulation leads to the considerable increase in the value of the hydraulic diffusion coefficient D_h of the adsorbate molecules in the beds. The influence of molecular weight on the value of D_h can be represented by a simplified relation (22):

$$D_h = \frac{f(d_w, V)}{M^{0.222}} \quad (22)$$

where the values of the function $f(d_w, V)$ for 293 K and $\varepsilon = 0.45$ are given in tab. 5.

Table 5

Values of the function $f(d_w, V)$
Wartości funkcji $f(d_w, V)$

d_w	2.5	5.0	7.5	10.0	15.0	20.0
	m/h					
cm	0.0694	0.1389	0.2082	0.2718	0.4167	0.5556
	cm/s					
0.05	9.104×10^{-3}	9.587×10^{-3}	10.037×10^{-3}	10.445×10^{-3}	11.156×10^{-3}	11.380×10^{-3}
0.10	9.579×10^{-3}	10.437×10^{-3}	11.147×10^{-3}	11.765×10^{-3}	12.820×10^{-3}	13.723×10^{-3}
0.15	10.032×10^{-3}	11.151×10^{-3}	12.049×10^{-3}	12.823×10^{-3}	14.137×10^{-3}	15.258×10^{-3}
0.20	10.439×10^{-3}	11.769×10^{-3}	12.823×10^{-3}	13.727×10^{-3}	15.260×10^{-3}	16.567×10^{-3}
0.25	10.811×10^{-3}	12.322×10^{-3}	13.511×10^{-3}	14.531×10^{-3}	16.257×10^{-3}	17.729×10^{-3}
0.30	11.152×10^{-3}	12.826×10^{-3}	14.138×10^{-3}	15.262×10^{-3}	17.165×10^{-3}	18.789×10^{-3}

The effects of adsorption estimated as the function of the value of hydraulic diffusion coefficient and the height of the bed layer are presented in fig. 4. The figure shows that with the increasing value of the D_h adsorption effects decrease in the secondary effluent both after and without coagulation. This indicates the increasing role of desorption in the investigated process. The decrease of the effects was greater in the case of the secondary effluent. A comparison of values of the diffusion coefficients D_e and D_h is shown in fig. 5. The D_e/D_h ratio determines the part of the diffusing mass flux expressed in TOC which is adsorbed by a unit carbon bed surface in a time unit. This ratio in general ranges within:

$$0 \leq D_e/D_h \leq 1, \quad (23)$$

where $D_e/D_h = 0$ represents a bed completely devoid of sorption properties, while $D_e/D_h = 1$ represents that of ideal sorption properties no occurring in reality. The increase of

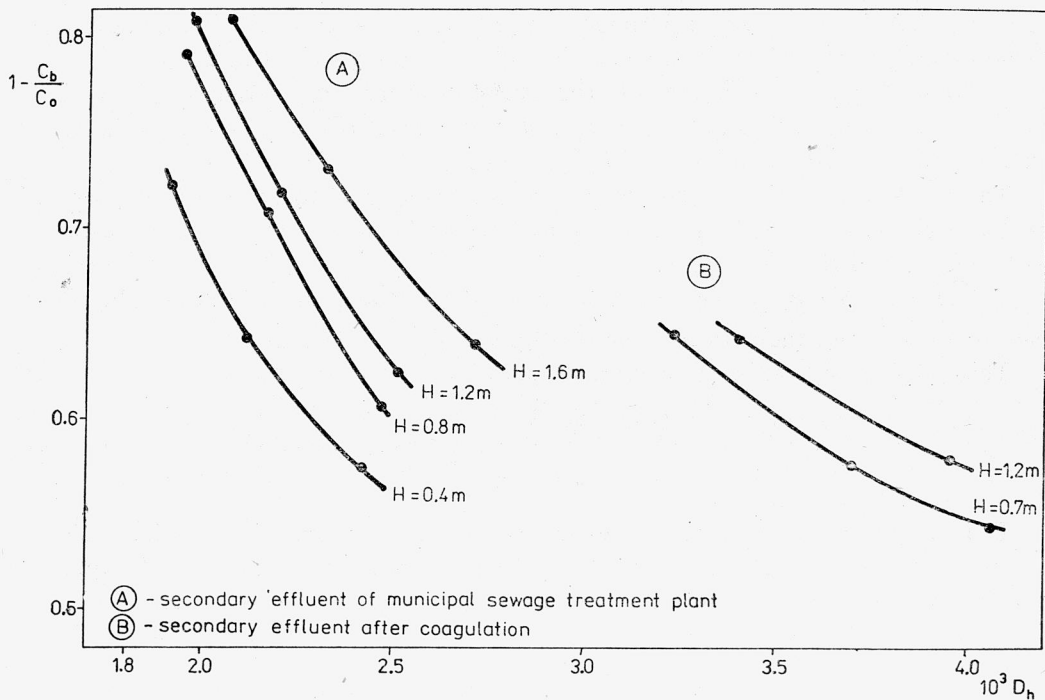


Fig. 4. Relationship $1 - \frac{C_b}{C_0} = f(D_{h,H})$

Rys. 4. Zależność $1 - \frac{C_b}{C_0} = f(D_{h,H})$

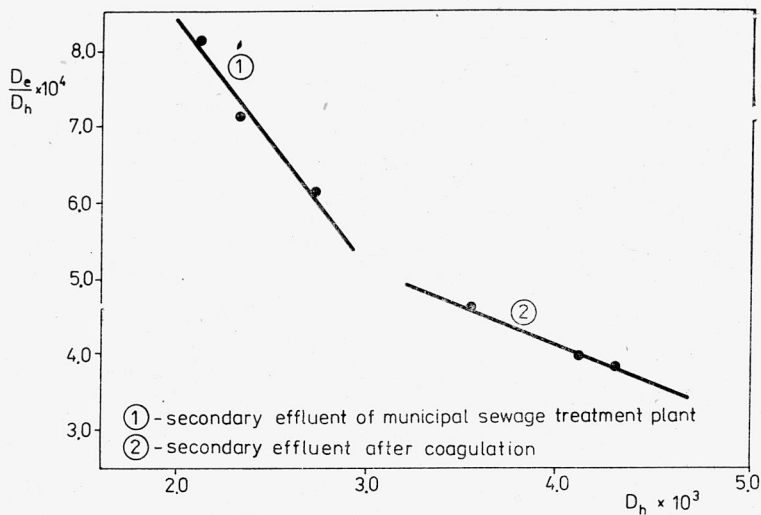


Fig. 5. Relationship $D_e \cdot D_h^{-1} = f(D_h)$

Rys. 5. Zależność $D_e \cdot D_h^{-1} = f(D_h)$

this ratio with the increasing of filtration rate gives the evidence to the fact that diffusion is the limiting factor, while its decrease — to the increasing role of desorption.

In the investigated carbon bed of Carbopol Z-4 the value of D_e/D_h ranged from 3×10^{-4} to 8×10^{-4} . Among several different carbon beds the most effective one is that characterized by the highest value of the D_e/D_h ratio.

The comparison of the sorption properties of different beds by means of the proposed ratio can be made on the basis of adsorption effects obtained in these beds for different hydraulic and grain-size ranges.

The expression $\sqrt{D_e/D_h}$ can be interpreted as the efficiency of collisions of the adsorbate molecules with the surface of carbon grains.

This is explained by the following relation:

$$\frac{\sqrt{\bar{X}_e^2}}{2r} \left(\frac{\sqrt{\bar{X}_K^2}}{2r} \right)^{-1} = \sqrt{\frac{D_e}{D_h}} \quad (24)$$

Its left hand side defines the ratio of the path travelled by the adsorbate molecules in a time unit to the diameter of the capillary. For $D_e/D_h \cong 10^{-4}$ (fig. 5), it may be approximately assumed that 1% of collisions of adsorbate particles with carbon surface is effective.

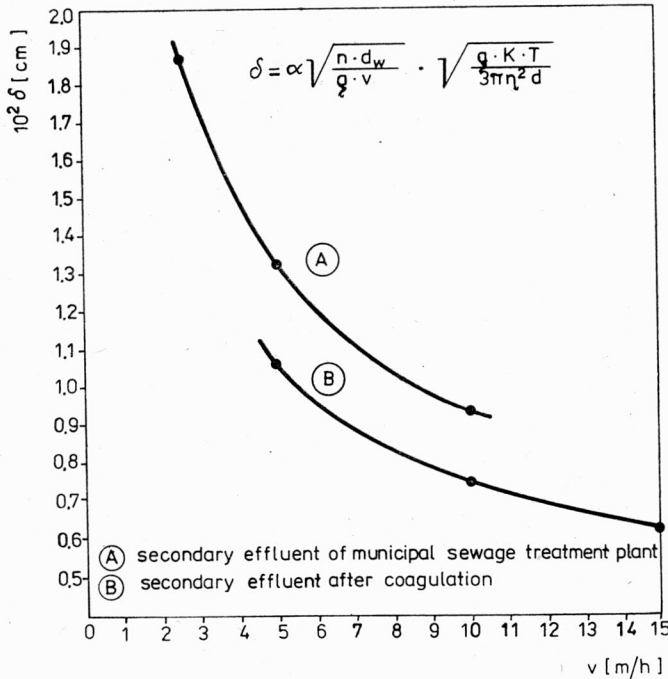


Fig. 6. Relationship $\delta = f(V)$

Rys. 6. Zależność $\delta = f(V)$

Table 6

Analysis of utilization of the activated carbon surface in the adsorption process from secondary effluents
 Analiza wykorzystania powierzchni węgla Carbopol Z-4 w procesie adsorpcji z biologicznie oczyszczonych ścieków

Constituents of secondary effluent	Number of adsorbed molecules per unit volume of carbon till the breakthrough of the bed. $H = 160 \text{ cm}$ $A = VT_0 C_0^* \left(1 - \frac{C_b^*}{C_0^*}\right) H^{-1}; \text{ cm}^{-3}$			Surface occupied by the adsorbed molecules $Af_{\text{mol}}; \text{ m}^2/\text{m}^3$			Utilization degree of the surface of Carbopol Z-4 %											
							Washed surface			Accessible degree			Internal structure surface					
				V m/h			2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0
Proteins	18138×10^{13}	27533.2×10^{13}	37430.6×10^{13}	442550	671786	913274	19.2	19.2	19.2	4.05	6.15	8.35	0.21	0.32	0.44			
ABS	87189.6×10^{13}	132352.6×10^{13}	179929.6×10^{13}	554395	841564	1144082	23.9	23.9	23.9	5.07	7.7	10.5	0.27	0.40	0.55			
Fatty acids	58041.6×10^{13}	88106.3×10^{13}	119778×10^{13}	411203	624200	848582	17.8	17.8	17.8	3.76	5.7	7.76	0.20	0.30	0.40			
Humic acids	32457.5×10^{13}	49269.9×10^{13}	66981.1×10^{13}	660445	1002544	1362930	28.5	28.5	28.5	6.04	9.17	12.47	0.32	0.50	0.65			
Carbohydra- tes	36021.4×10^{13}	54680×10^{13}	74335.9×10^{13}	244566	371248	504701	10.6	10.6	10.6	2.24	3.4	4.62	0.12	0.18	0.24			
Mixture	231848.1×10^{13}	351942×10^{13}	478455.2×10^{13}	2313159	3511342	4773569	100.0	100.0	100.0	21.15	32.12	43.68	1.12	1.70	2.28			

tive. This value can be taken as the criterion in estimation of carbon surface sorption activity which, expressed in percentage, is defined by the formula:

$$K_a = 100\sqrt{D_e/D_h}. \quad (25)$$

Considering the porous structure characteristic of carbon, the balance eq. (20) of adsorbate mass and the results of the experiments in [1], the degrees of utilization of the washed, accessible and total internal carbon surface were analysed.

From the data given in tab. 6 it follows that in the removal of compounds present in secondary effluent only the washed carbon surface is utilized. This surface constitutes merely 0.0016% of the total carbon surface. The degree of utilization of the total carbon surface varied from ~ 1.12 to 2.28%.

The utilization of adsorption-accessible surface, i.e. those of macropores and transition pores ranged from about 21% at filtration rate $V = 2.5$ m/h up to 44% at $V = 10.0$ m/h.

Due to coagulation of the secondary effluent the degree of utilization of the total surface of carbon internal structure increased from 1.3 to 1.5 times, i.e. from 1.7 to 3.0%. This increase corresponded to an almost double increase of carbon column operation time. The utilization of surface accessible to adsorption for compounds present in the sewage after coagulation (detergents, fatty acids, and carbohydrates) ranged from 31% at filtration rate $V = 5.0$ m/h to 56% at filtration rate $V = 15.0$ m/h.

The data presented in tab. 6 indicate a slight influence of internal diffusion on the efficiency of adsorption process. It may be expected that molecules of carbohydrates, fatty acids, and detergents are most susceptible to internal diffusion.

6. CONCLUSIONS

1. In the study, models identifying the elementary phenomena of the adsorption process performed in a dynamic system on an activated carbon column, were presented and verified. The models proposed are based on general physical laws, such as mass balance, Fick's law, as well as on empirical relations determining the mass exchange in beds, and on the hypothesis of diffusion boundary layer. The models were verified to suit the conditions and parameters of adsorption process adequate for the systems of water renovation from secondary effluent treated with carbon Carbopol Z-4.

2. It was been shown that in order to perform an univocal and precise analysis of mechanisms of adsorption process it is necessary to take account of the variable parameters characterizing the adsorbate and adsorbent as well as the kinetics and dynamics of the process.

The adsorbate was determined in terms of TOC considering its molecular weight and the size of the molecules.

The adsorbent was defined by the size of the grains in the bed, its washed surface as well as such parameters of the internal structure as: micropores, transition pores, and

macropores. Among the kinematic and dynamic parameters of the process the following were included: flow rate, contact time, and the process efficiency defined by the ratio of initial to final concentrations of organic compounds.

3. The effects of adsorption and the diffusivity of adsorbate molecules were investigated as being dependent on the concentration gradient and flow hydraulics. The influence of the concentration diffusion was limited to the layer adhering the surface of carbon grains. It has been shown that the flow rate significantly influences the thickness of diffusive boundary layer, determined by means of the transformed relation (7) (fig. 6).

Given below are the models defining the coefficients of concentrational and hydraulic diffusion in a carbon bed:

$$-\ln \frac{C_b}{C_0} = \frac{2D_e t}{r^2 \left(1 - \frac{r_0}{r}\right)},$$

$$D_h = \frac{f(d_w, V)}{M^{0.222}}.$$

They may also be used for interpretation of the effects of water or sewage treatment in adsorption process.

4. The quotient D_e/D_h or $\sqrt{D_e/D_h}$ was suggested as a general criterion in the estimation of sorption activity of carbon beds.

In its first form, this criterion is a measure of the ratio of adsorbate mass transferred due to the concentration gradient to that transferred due to the motion of liquid in the bed. In its second form the criterion represents the ratio of the effective collisions of adsorbate molecules with carbon surface to the total number of collisions. The criterion proposed can also be used to estimate the probability that diffusion is a limiting factor in the adsorption process, as well as of the desorption.

5. It has been shown that a slight influence of internal diffusion upon the efficiency of the process can be only partially accounted for by the inaccessibility of the carbon surface. The fact the macropores and the transition pores accessible to all kinds of adsorbate molecules are not fully utilized indicates the necessity of further research on intensification of internal diffusion in home-made carbons with respect to the molecules of the most typical organics, e.g. proteins in the secondary effluents.

REFERENCES

- [1] ADAMSKI W., *Kinetyka adsorpcji w procesie odnowy wody*, doctor's dissertation, Technical University of Wrocław, Wrocław 1979.
- [2] *Katalog — Informator. Węgla aktywne*, Wydawnictwo Katalogów i Cenników, Warszawa 1968.
- [3] KONOWA M., *Substancje organiczne gleby*, PWRiL, 1968.

- [4] LOCHR R., TOTH I., *Aerobic degradation of low-chain fatty acids salts*, JWPCF, No. 11 (1978), p. 365.
 [5] MANKA I., REKHUM M., *Characterization of organics in secondary effluents*, Envir. Scien. Techn., No. 12 (1974), p. 1017.
 [6] WALLAS S. M., *Kinetyka reakcji dla inżynierów chemików*, WNT, Warszawa 1963.

MODELE ZJAWISK SORBCJI NA WĘGLACH AKTYWNYCH DLA POTRZEB WYSOKOEFEKTYWNYCH SYSTEMÓW OCZYSZCZANIA SCIEKÓW

W pracy podano i zweryfikowano modele identyfikujące elementarne zjawiska procesu adsorpcji w układzie dynamicznym.

Wykazano, że dla jednoznacznego określenia mechanizmów zjawiska niezbędne jest uwzględnienie zmiennych parametrów charakteryzujących adsorbat, adsorbent oraz kinetykę i dynamikę procesu. Efekty adsorpcji oraz dyfuzyjność cząsteczek adsorbentu w złożu uzależniono od gradientu stężeń oraz hydrauliki przepływu.

MODELLE DER AKTIVKOHLESORPTION FÜR DEN BEDARF DER WEITERGEHENDEN ABWASSERREINIGUNG

Bewahrheitet wurden Modelle welche elementare Erscheinungen der Adsorption unter dynamischen Bedingungen beschreiben. Für eine eindeutige Beschreibung der Effektmechanismen ist die Einbeziehung der variablen Parameter die das Adsorbat, das Adsorbens, sowie die Kinetik und Dynamik des Verfahrens charakterisieren unentbehrlich. Die Effekte der Adsorption sowie die Diffusion der Adsorbatpartikeln im Schüttbett hängen grundsätzlich vom Konzentrationsgradient und von der Fließhydraulik ab.

МОДЕЛИ ЯВЛЕНИЙ СОРБЦИИ НА АКТИВИРОВАННОМ УГЛЕ ДЛЯ НУЖД ВЫСОКОЭФФЕКТИВНЫХ СИСТЕМ ОЧИСТКИ СТОЧНЫХ ВОД

В работе приведены верифицированные модели, идентифицирующие элементарные явления процесса адсорбции в динамической системе.

Доказано, что для однозначного определения механизмов явления необходимо учитывать переменные параметры, характеризующие адсорбат, адсорбент, а также кинетику и динамику процесса. Эффекты адсорбции, а также диффузионная способность адсорбата в слое обусловлена градиентом концентраций, а также гидравликой движения жидкости.