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MODIFIED MODELS OF DYNAMICS AND KINETICS OF ADSORPTION: POSSIBLE APPLICATION TO THE DESIGN AND CONTROL OF ADSORPTION AS A UNIT PROCESS IN SYSTEMS FOR WATER TREATMENT AND REUSE

Models describing the dynamics and kinetics of adsorption are given in modified forms and the application of the modified models in engineering practice for water treatment and reuse is considered. However, engineering applications of the models in question require determination of adsorbate particle size in order to determine such parameters that might set some limitations to the course of adsorption process. These are the coefficients of external diffusion, pore diffusion and hydraulic diffusion, and the coefficients of external and internal mass transfer. Taking these all into account, a non-conventional approach to the problem is suggested. In this approach, it is postulated to determine the average equivalent molecular weight of sorbable organics (expressed in terms of TOC). The method of estimating the equivalent molecular weight for dissolved sorbable organics commonly found in surface water and in effluents from treatment processes was verified by similarity analysis. There were compared the plots of kinetic curves obtained in experiments with those achieved by mathematical simulation which made use of the modified adsorption model. The agreement between simulated and experimental kinetic curves is satisfactory.

1. INTRODUCTION

Adsorption on activated carbon has attained considerable popularity for many years, but in the past few years it has become an important part in most technological systems for water treatment and renovation. A successful design and control of the process requires knowledge of some fundamental phenomena involved in mass transfer.

The transfer of adsorbate mass runs in three major stages. During the first stage diffusion and convection occur. Convection should be attributed either to the

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conditions of flow through the carbon medium (when the process is run on activated carbon beds) or to the conditions of mixing (when contact systems are used). The second stage, i.e. that of internal diffusion which is also known as Knudsen diffusion, begins when the free path of moving particles becomes smaller than the internal pore size of the adsorbent. The third stage involves surface diffusion, which accounts for the mixing of adsorbate particles on the internal surface of the adsorbent.

In extreme cases, one of the three diffusion processes acts as an inhibiting mechanism. In actual adsorption systems, which are generally used in water treatment and renovation, the process runs in an intermediate region and is usually governed by the diffusion mechanisms involved in stage one and stage two [1]–[3]. Thus, the course of the adsorption process depends primarily on the following parameters: external diffusion coefficient D_e, internal diffusion coefficient D_i, external mass transfer k_e, and internal mass transfer coefficient k_i. It should be added that in the case of non-stationary isotherm adsorption the course of the process is governed by one more factor, i.e., the coefficient of longitudinal diffusion D_h. Longitudinal diffusion is to be attributed to the mixing of the stream and to a non-uniform distribution of the adsorbate in the bed cross-section, the course of the process being influenced by two other factors — the wall effect (convectional mix near the wall) and external diffusion of adsorbate particles. Hence, we can write

$$D_h = f(V, \varepsilon, M, d_a, D_e) \tag{1}$$

where V denotes velocity of flow, ε indicates bed porosity, M refers to molecular mass of adsorbate, and d_a stands for particle diameter of adsorbent.

The mathematical model of the dynamics of adsorption (which describes the time-space distribution of adsorbate in the adsorbent) includes a set of equations of mass balance, of adsorption isotherm, and of the kinetics of adsorption. Under optimum sorption conditions, i.e., when the process satisfies the model described by the convex isotherm of adsorption $(dx/dc_1) > (dx/dc_2)$, the points of higher concentration move faster than the points of lower concentration (and this is in agreement with the Wickian law). The result is a narrowing of the adsorption front. It should be noted that the longitudinal diffusion effect brings about a broadening of the front of adsorption.

In extremes, the superposition of the broadening front effect (generated by longitudinal diffusion) and the narrowing front effect (induced by the difference in the rate of concentration front migration) can make the sorption front move downwards at a constant rate by virtue of the Wilson equation [4], [5]. When these conditions occur (they are practically optimal and, therefore, desirable), the time of operation for a column of a given height H and a given flow velocity V, up to the moment at which the desired adsorbate concentration c is achieved, can be defined as

$$t = \left[H - \frac{V + \sqrt{V^2 + 4D_h k_g}}{2k_g} \ln \frac{cb(c_0 - c) - c}{c_0 b(c_0 - c) - c} \left(\frac{U}{V} - 1 \right) \right] U^{-1} \tag{2}$$

where b is a parameter included in the Langmuir equation of isotherm, U stands for velocity of adsorption front migration which takes the form

$$U = \frac{V(c_0-c)}{\varrho_a X_m},$$ (3)

c_0 denotes influent concentration of adsorbate, k_g represents the general coefficient of mass transfer which can be written as

$$k_g = f(k_e, k_i, V, D_h),$$ (4)

X_m denotes the quantity adsorbed in a monomolecular layer per unit weight of adsorbent, and ϱ_a is adsorbent density. Equation (2) is derived from the approximate solution to the set of equations for the dynamics of adsorption [4], and from the Zeldovich equation of the operational line of the process.

A static adsorption system, where mixing is carried out to keep the adsorbent in the entire volume of the solution, may be described by a modified form of the fundamental equation of the kinetics of adsorption until the desired concentration c in the effluent is achieved. Thus,

$$t = \frac{c_0}{k_e \cdot n} \ln \left\{ \left| \frac{c_0}{c} [(c-c_0)b-1]^{-1} \right|^{0.5} \left| \frac{c}{c_0} [(c-c_0)b+1]^{-1} \right|^{\left(1-\frac{2c_0 b}{c_0 b-1}\right)} \right\}$$ (5)

where n denotes adsorbent dose $[\mathrm{g\,m^{-3}}]$.

2. DETERMINING THE HYPOTHETICAL AVERAGE MOLECULAR WEIGHT OF ADSORBATE

The application of the models in engineering practice requires determination of the adsorbate particle size. That is why any model describing the dynamics and kinetics of adsorption will be applicable only if model solutions of a determined adsorbate particle are involved. Natural waters are mixtures of a dozen (and in some instances even several dozen) compounds. It is extremely difficult to achieve their full identification. Complex analytical methods, e.g., passage of the solution through molecular sieves, may be of utility, but they lead to an estimation of the particle sizes only. Taking these all into account, investigations were initiated in order to find a simple method of assessing the average molecular weight and, indirect, the average particle size of dissolved organics which not only occur in natural waters or effluents from various treatment processes, but are also prone to adsorption.

A warrant to make such an approach was one of the major principles dealt with in the adsorption process. This reads: adsorbates of higher molecular weight display a higher adsorbing ability. Thus, investigations were carried out for the equilibrium of adsorption in selected model solutions of varying initial concentration and

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Table 1

GAC characteristics

Parameters			
	Values		
Superior and inferior range of fraction d 10^{-3} m	Percentage of fraction	$\alpha = \dfrac{d_{max}}{d_{min}}$	Diameter of particle 10^{-3} m
0.8–1.19	0.187	1.15	1.07
1.2–1.79	0.257	1.56	1.97
1.8–2.19	0.20	1.42	2.51
2.2–2.49	0.067	1.51	3.26
2.5–2.79	0.107	1.34	3.21
2.8–3.19	0.120	1.2	3.37
3.2–3.69	0.050	1.52	4.54
3.7	0.012	1.08	3.89

Pore structure	Volume cm^3/g	Surface area m^2/g
ultramicropores (CO_2 adsorption)	0.055	144
micropores (benzene adsorption)	0.230	460
mezopores (benzene desorption)	0.249	158
macropores (porosimetre measurement)	0.802	2.2
Total	1.336	764.2
External surface		1.043 m^2 kg^{-1}
Density in water		1.92 g cm^{-3}

different molecular weight of the adsorbate. Adsorbate concentration was measured in terms of the TOC level. The adsorbent used in this study was a GAC NORIT type. Its parameters are listed in tab. 1. The Langmuir equation of monomolecular adsorption was used to describe the states of dynamic equilibrium. Hence,

$$X = \frac{X_m bc}{1+bc}. \qquad (6)$$

The relationship of the initial adsorbate concentration and the amount adsorbed in the monolayer X_m follows a linear pattern. It may also be assumed that parameter b is independent on the initial concentration level, and takes a constant value for a given adsorbate. The parameters of the equation of adsorption for the investigated compounds are given in tab. 2. It has also been found that X_m has a linear plot only within a certain range of initial concentration, which falls between 3 and 5 mol/m^3 depending on the kind of the adsorbate, but then X_m becomes constant. As shown by these relations, the proportionality factor $m = X_m/c_0$ may be defined as function of the molecular weight of the adsorbate, m $= f(M)$.

Table 2

Parameters of adsorption isotherms for model solutions

Adsorbate	Initial concentration as TOC $g\,C\,m^{-3}$	X_m $g\,kg^{-1}$	b
phenol $M = 94$	3.83	0.609	
	5.36	1.018	
	7.66	1.19	
	9.19	1.73	0.623
	11.49	2.283	
	15.32	2.853	
nitrobenzene $M = 123$	2.925	1.316	
	5.85	2.63	
	11.7	5.556	0.626
	17.55	8.424	
	29.25	14.28	
p–nitroaniline $M = 138$	2.61	1.333	
	5.22	2.35	1.958
	7.83	3.88	
	10.44	5.55	
p–nitrophenol $M = 139$	2.59	1.282	
	5.18	2.63	0.748
	7.77	4.04	
	10.36	5.26	
o–cresol $M = 108$	3.89	1.282	
	7.78	2.56	0.325
	11.67	3.85	
	15.56	5.0	
pyridine $M = 79$	3.795	0.698	
	7.59	1.515	0.37
	11.385	2.174	
	15.18	2.703	
chlorobenzene $M = 112$	3.214	0.961	
	6.43	1.92	0.545
	9.645	3.07	
	12.86	4.167	
fuchsin $M = 338$	3.55	2.66	
	7.10	5.26	0.304
	10.65	7.69	
	14.2	10.52	
fluorescein $M = 332$	1.446	1.0	
	3.615	2.53	
	7.23	5.0	0.638
	10.84	7.59	
	14.46	9.85	

Making use of the parameters of adsorption isotherms reported in the literature for more than 10 organics expressed as TOC [6], [7] (some of them are the same as those tested in this study) and considering the similar plot of the adsorption isotherms for that kind of organic substances, the X_m values for our system involving a GAC NORIT type have been calculated.

Assuming that the straight-line relation is also valid for the adsorption parameters reported [6], [7], the proportionality factors m have been evaluated. The calculated data are listed in tab. 3. The $m = f(M)$ relation in fig. 1 may either be expressed as

$$m = 0.1\,(M - 80)^{0.37} \tag{7}$$

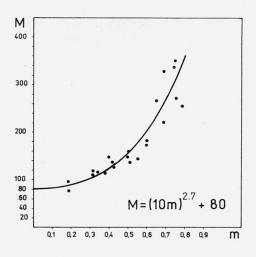or defined in terms of a more convenient formula, which takes the form
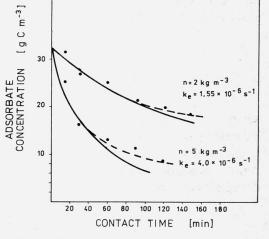
$$M = (10\,m)^{2.7} + 80. \tag{8}$$

Both the relations hold for the investigated range of molecular weights, $M \in (80, 400)$.

Table 3

Values of calculated data

Compound	m	Molecular weight g/mole	Carbon weight in mole g C/mole
phenol	0.185	94	72
pyridine	0.185	79	60
o–cresol	0.325	108	84
nitrobenzene	0.475	123	72
p–nitroaniline	0.51	138	72
p–nitrophenol	0.51	139	72
fuchsin	0.74	338	240
fluorescein	0.685	332	240
chlorobenzene	0.312	112	72
p–cresol	0.40	108	84
α–naphthol	0.55	144	120
hexachlorobutadiene	0.75	265	48
nonylphenol	0.68	220	180
bromoform	0.65	253	12
acridine	0.60	179	156
diphenylamine	0.60	171	144
guanine	0.45	151	60
anethole	0.50	148	120
benzothiozole	0.475	135	84
adenine	0.42	135	60
o–anisidine	0.42	123	84
dimethyl phthalate	0.4	148	120
hydroquinone	0.375	110	72
p–xylene	0.325	106	96
styrene	0.25	104	72
DDT	0.75	354	168

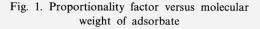Fig. 1. Proportionality factor versus molecular weight of adsorbate

Fig. 2. Kinetic curves simulated by using the modified model (solid line) and kinetic curves obtained by direct measurement (dashed line)

3. VERIFICATION

The method of estimating the average molecular weight of the adsorbate was verified for a system which involved a GAC and municipal sewage treated by alum coagulation at its optimum dose. Consideration was given to the similarity of kinetic

Table 4

Parameters of adsorption isotherms for municipal sewage

Initial concentration as TOC $g\,C\,m^{-3}$	X_m $g\,kg^{-1}$	b	m
32.0	22.23		
21.3	14.28	0.0143	0.685
13.8	9.53		

curves obtained by experiments and those simulated by using eq. (5) after the k_e coefficient had been determined. Influent TOC and COD amounted to 125.1 g C m^{-3} and 284.2 g O$_2$ m^{-3}, respectively. Application of alum (200 g Al$_2$(SO$_4$)$_3$·18H$_2$O m^{-3}) yielded TOC and COD of 32 g C m^{-3} and 101.7 g O$_2$ m^{-3}, respectively. Initial concentration of adsorbate was changed by its dilution with distilled water. The parameters of the adsorption isotherm are given in tab. 4.

The value of M calculated in terms of eq. (8) is 260.5 g mol^{-1}. The coefficient of external mass transfer k_e depends on two factors, external diffusion D_e and external

surface of carbon particles through which diffusion of adsorbate proceeds. The Stokes–Einstein equation is sufficient to calculate the D_e value:

$$D_e = \frac{KT}{3\Pi\eta d}\, [\text{cm}^2\,\text{s}^{-1}] \qquad (9)$$

where K is Boltzman constant $(1.38 \times 10^{16}\ \text{erg}\,\text{K}^{-1})$, T denotes temperature (K), η indicates viscosity of solution $(0.01\ \text{dyne}\,\text{s}\,\text{cm}^{-2})$, and d represents adsorbate particle diameter (cm). Assuming that the error of approximation $\varrho_{\text{mol}}^{-1/3} = 1$, where ϱ_{mol} denotes adsorbate particle density is negligible [8], the diameter of the adsorbate particle becomes

$$d = 1.469 \cdot 10^{-8}\ \sqrt[3]{M}\, [\text{cm}]. \qquad (10)$$

The diameter of adsorbate particles d and the diffusion coefficient D_e for the municipal sewage under study amounts to $9.38 \times 10^{-8}\,\text{cm}$ and $4.5 \times 10^{-6}\ \text{cm}^2\text{s}^{-1}$, respectively. The value of parameter k_e in a non-through-flow system depends on the geometry of the adsorption system by virtue of [8], [9]

$$k_e = \frac{2\Pi d_a}{V_s}\left(\frac{d_a}{2\delta}+1\right)D_e \qquad (11)$$

where d_a denotes equivalent diameter of activated carbon particle, V_s indicates volume of solution per unit particle of adsorbent and may be defined as

$$V_s = \frac{1000\Pi d_a^3 \varrho}{6n}\, [\text{cm}^3], \qquad (12)$$

and δ represents thickness of near-wall diffusion layer which is identical to the radius of solution volume per unit particle of adsorbate (finite batch experiment). Hence, we can write

$$k_e = 0.012\frac{n}{d_a^2\varrho}\left(0.1\ \sqrt[3]{\frac{n}{\varrho}}+1\right)D_e. \qquad (13)$$

The value of coefficient k_e amounts to $1.55 \times 10^{-6}\,\text{s}^{-1}$ and $4.0 \times 10^{-6}\,\text{s}^{-1}$ for the 2 g cm^{-3} dose and 5 g cm^{-3} dose, respectively. Figure 2 gives the plots of experimental kinetic curves and the kinetic curves simulated by making use of eq. (5).

4. CONCLUDING COMMENTS

Analyzing the mathematical models of the dynamics and kinetics of adsorption, it becomes obvious that their application in engineering practice has a certain limit established by the necessity of knowing the adsorbate particle size. Our investigations on the equilibrium of the adsorption process made use of organic compounds, expressed as TOC, which varied in initial concentration and molecular weight and were adsorbed from model solutions. The sets of data obtained from this study corroborate the correlation between molecular weight, variation of maximum adsorbing capacity, and initial concentration of adsorbate. A formula was derived to determine the average equivalent molecular weight of pollutants generally found in natural waters. The formula is valid for GAC NORIT type systems of fixed parameters. To determine the parameters of the equation for any other activated carbon it is necessary to find the similarity of plots between the adsorption isotherms for GAC NORIT type and the adsorption isotherms for the activated carbon in question.

The method of evaluating the equivalent molecular weight of the adsorbate was verified on a variety of natural water samples. The verification procedure involved similarity analyses of the kinetic curves obtained via simulation in terms of a mathematical model for the kinetics of adsorption, and of the kinetic curves achieved by direct measurement. The agreement between the theoretical and experimental kinetic curves is satisfactory and makes the method applicable to engineering practice.

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MODYFIKACJA MODELI DYNAMIKI I KINETYKI ADSORPCJI: ZASTOSOWANIE W PROJEKTOWANIU I STEROWANIU PRZEBIEGIEM ADSORPCJI W UKŁADACH TECHNOLOGICZNYCH UZDATNIANIA I ODNOWY WODY

Zaprezentowano modele dynamiki i kinetyki adsorpcji w zmodyfikowanej postaci i ich zastosowanie w technologii uzdatniania i odnowy wody. Zastosowanie modeli wymaga określenia rozmiaru cząstek adsorbatu w celu wyznaczenia współczynników dyfuzji zewnętrznej, wewnętrznej i hydraulicznej oraz współczynników zewnętrznego i wewnętrznego przenoszenia masy.

Na podstawie badań adsorpcji z modelowych roztworów o zróżnicowanej masie cząsteczkowej adsorbatu i zróżnicowanym stężeniu początkowym mierzonym poziomem CWO oraz w oparciu o podstawowe prawa adsorpcji wprowadzono pojęcie i empirycznie wyznaczono zastępczą masę cząsteczkową sorbowalnych rozpuszczonych związków organicznych występujących w wodzie i ściekach po różnych procesach technologicznych ich oczyszczania. Sposób szacowania zastępczej masy cząsteczkowej adsorbatu zweryfikowano poprzez analizę podobieństwa krzywych kinetycznych symulowanych zaproponowanymi modelami i krzywych uzyskanych z bezpośredniego pomiaru.

МОДИФИКАЦИЯ МОДЕЛЕЙ ДИНАМИКИ И КИНЕТИКИ АДСОРБЦИИ: ПРИМЕНЕНИЕ В ПРОЕКТИРОВАНИИ И УПРАВЛЕНИИ ХОДОМ АДСОРБЦИИ В ТЕХНОЛОГИЧЕСКИХ СИСТЕМАХ ПОДГОТОВКИ И ВОССТАНОВЛЕНИЯ ВОДЫ

Показаны модели динамики и кинетики адсорбции в модифицированном виде и их применение в технологии подготовки и восстановления воды. Применение моделей требует определения размера частиц адсорбата с целью установления коэффициентов внешней, внутренней и гидравлической диффузии, а также коэффициентов внешней и внутренней массопередачи.

На основе исследований адсорбции из модельных растворов с дифференцированной молекулярной массой адсорбата и дифференцированной начальной концентрацией измеренной уровнем CWO, а также на основе принципов адсорбции введено понятие и эмпирически определено заменяющую молекулярную массу сорбирующих растворенных органических соединений выступающих в воде и в стоках из разных технологических процессов их очистки. Способ определения заменяющей молекулярной массы адсорбата проверено-путем анализа подобия кинетических кривых моделированных предложенными моделями и кривых полученных из непосредственного измерения.