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MATHEMATICAL MODEL OF PAC-ADSORPTION AND ITS APPLICATION IN WATER TECHNOLOGY

A mathematical model is presented, which describes the efficiency of organic matter removal by adsorption onto powdered activated carbon conducted both separately and simultaneously with the coagulation process. The model proposed describes the variations in the efficiency of organic fraction removal (measured in terms of dissolved organic carbon concentration) as a function of time, adsorbent dose and coagulant dose. Empirical formulae are derived to determine the value of the coefficient of adsorbate mass transfer rate. The formulae preserve their accuracy within the ranges used in the technological investigations performed for the purpose of the study.

1. INTRODUCTION

Natural organic matter that occurs in surface water is a mixture of organic compounds differing notably in the size and shape of their particles, whose composition and structures have not yet been entirely established. Although these substances do not pose the direct hazard to human health, there is still a potential danger of their interaction with other water pollutants (e.g., heavy metals), and also a risk that disinfection by-products will form due to their presence. In this context, the removal of natural organic matter from the water to be treated is absolutely indispensable. If the water treatment train includes sorption, organic compounds can block the pores of the activated carbon (thus reducing its volume) and compete for the active sites of the adsorbent with other pollutants, particularly those occurring in trace amounts [1]–[4].

A high extent of organic matter removal from the water to be treated can be achieved when the sorption process involves powdered activated carbon (PAC) and is combined with the conventional coagulation process. The effects of using this type of adsorbent, as well as the factors that limit the process, have been reported by other investigators [5]–[8]. They have found that the efficiency of organic matter removal is

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determined, inter alia, by the properties of the adsorbent used, specifically by the porous structure and by the chemical character of the surface. Other major contributing factors, i.e., solubility, structure, particle size, hydrophobicity and hydrophilicity, are linked with the character of the natural organic compounds. It is essential to note that, apart from the type of the adsorbent used and the adsorbate removed, the efficiency of the simultaneous process of coagulation and PAC adsorption was found to be influenced by the process conditions, i.e., by pH, contact time, stirring parameters, reagent doses and sequence of its dosage [9].

Owing to the complex nature of the treatment train where adsorption and coagulation are performed simultaneously, the problem of an optimal design of new water treatment systems and the question of optimizing the existing ones have taken on a sense of significance. The availability of advanced modelling techniques offers a good chance of formulating the criteria for the applicability of the process and determining such parameters that are of significance to the course of the process.

In this paper, a mathematical model is presented, which enables the efficiency of the coagulation–PAC adsorption process to be established when the time of contact (t) as well as the coagulant dose (D_C) and adsorbent dose (D_{PAC}) are known.

2. THE MODEL ASSUMPTIONS

Considering the complex nature of the phenomenon, the polydispersion of the organic substances that are present in natural water, and the diversity of the adsorbent's grain size, it has been assumed that a single PAC grain and the water volume enclosing this grain are spherical in shape. The radius of the water volume and the radius of the adsorbent's grain being marked with r_{H_2O} and r_{PAC}, respectively. It has further been assumed that the particle of the adsorbent has a central position in the water volume (figure 1).
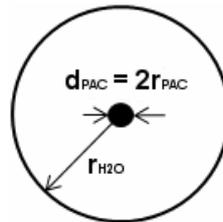

Fig. 1. The PAC position in the water volume enclosing a single grain

Based on the measured values of the adsorbent's particle size, $d_{50} = 15.8 \cdot 10^{-6}$ m has been adopted as an effective diameter of the carbon grain (d_{PAC}). The volume of a single carbon grain for the assumed spherical shape of the adsorbent particle can be expressed by:

$$V_{\text{PAC}} = \frac{4}{3} \cdot \pi \cdot \left(\frac{d_{\text{PAC}}}{2} \right)^3 = 2.065 \cdot 10^{-15} \text{ m}^3 , \tag{1}$$

and the mass of a single adsorbent particle in air-dry state takes the form:

$$m_{\text{PAC\_ad}} = V_{\text{PAC}} \cdot \rho_{\text{PAC}} = 5.16 \cdot 10^{-10} \text{ g} , \tag{2}$$

where V_{PAC} denotes the volume of a single grain (m^3), and ρ_{PAC} stands for the bulk density of the carbon in air-dry state (250 kg/m^3) [10].

The mass of a single grain in hydrated state has been calculated as follows:

$$m_{\text{PAC\_h}} = m_{\text{PAC\_ad}} + m_{\text{H}_2\text{O}} = 5.16 \cdot 10^{-10} + 3.71 \cdot 10^{-10} = 8.87 \cdot 10^{-10} \text{ g} , \tag{3}$$

where $m_{\text{H}_2\text{O}}$ is the water mass in the pores of a single PAC particle determined on the basis of the total carbon pore volume ($V_{\text{total}} = 0.719$ cm^3/g) for water density at 20 °C [11].

The radius of the water volume enclosing a single PAC grain ($r_{\text{H}_2\text{O}}$) has been determined for the water volume ($V_{\text{H}_2\text{O}}$) being treated with a single adsorbent particle in hydrated state. The value of $V_{\text{H}_2\text{O}}$ varied, depending on the adsorbent dose applied. Calculations were performed for water samples of a 2 dm^3 volume. The results are summarized in table 1.

Table 1

Determination of radius of the water volume enclosing a single PAC grain

D_{PAC} (g/m^3)	Quantity of PAC grains in 2 dm^3 of sample (n_{PAC}) (number)	Water volume enclosing a single PAC grain ($V_{\text{H}_2\text{O}}$) (m^3)	Radius of water volume enclosing a single PAC grain ($r_{\text{H}_2\text{O}}$) (m)
5	19370635	$1.032 \cdot 10^{-10}$	$2.911 \cdot 10^{-4}$
10	38741270	$5.162 \cdot 10^{-11}$	$2.310 \cdot 10^{-4}$
30	116223809	$1.721 \cdot 10^{-11}$	$1.602 \cdot 10^{-4}$
75	290559522	$6.883 \cdot 10^{-12}$	$1.180 \cdot 10^{-4}$

3. THE MODEL FORMULATION

In the adsorption efficiency model proposed for the description of the PAC-aided coagulation process, use was made of the equation of Fick's first law of steady-state diffusion [12]:

$$\frac{dm}{dt} = -D_m \cdot F \cdot \frac{dC}{dr} , \tag{4}$$

where: m – the adsorbate mass, g; t – the time of diffusion, s; C – the adsorbate concentration, g/m^3; r – the path of diffusion, m; F – the surface of the field of diffusion flux, m^2, D_m – the molecular diffusion coefficient, m^2/h.

Assuming that the adsorbate mass equals:

$$m = (C_e - C_i) \cdot V \, , \tag{5}$$

where: m – the adsorbate mass, g; C_e – the effluent concentration of adsorbate, g/m^3; C_i – the adsorbate concentration in the boundary film, g/m^3; V – the volume, m^3, Fick's equation takes the following form:

$$\frac{4}{3} r \frac{d}{dt} (C_e - C_i) \, dr = -D_m dC \, . \tag{6}$$

Upon separating the variables and integrating the left-hand side of equation (6) over $r_{\mathrm{H_2O}}$ to r_{PAC}, and the right-hand side over C_e to C_i, we have:

$$\frac{d}{dt} (C_e - C_i) = -\frac{2D_m}{2(r_{\mathrm{H_2O}}^2 - r_{\mathrm{PAC}}^2)} (C_e - C_i) \, . \tag{7}$$

Assuming that the adsorbate concentration (C_i) in the boundary film is constant, we obtain:

$$\frac{dC_e}{dt} = -\frac{3D_m}{2(r_{\mathrm{H_2O}}^2 - r_{\mathrm{PAC}}^2)} (C_e - C_i) \, , \tag{8}$$

where the term on the right-hand side defines the coefficient of the adsorbate mass transfer rate (K), describing the diffusivity and geometry of the system:

$$K = \frac{3D_m}{2(r_{\mathrm{H_2O}}^2 - r_{\mathrm{PAC}}^2)} \, . \tag{9}$$

Hence, equation (8) can be written as:

$$\frac{dC_e}{dt} = -K(C_e - C_i) \, . \tag{10}$$

Upon appropriate substitutions:

$$C_e = C_0 - C_a \, , \tag{11}$$

$$\delta = \frac{C_a}{C_R} \, , \tag{12}$$

where: C_0 – the initial adsorbate concentration, g/m^3; C_a – the concentration of C_0 adsorbed, g/m^3; C_R – the equilibrium concentration, g/m^3, equation (10) can be transformed as follows:

$$\frac{d}{dt}(C_0 - \delta C_R) = -K(C_0 - \delta C_R - C_i), \tag{13}$$

$$\frac{d\delta}{dt} = K\left(\frac{C_0}{C_R} - \delta - \frac{C_i}{C_R}\right). \tag{14}$$

On the assumption that the extent of desorption is negligibly small, which means that the adsorbate concentration in the boundary film (C_i) is noticeably lower than the equilibrium concentration (C_R), we can write:

$$\frac{C_R}{C_0} \cdot \frac{d\delta}{dt} = K\left(1 - \frac{C_R}{C_0}\delta\right). \tag{15}$$

Upon separating the variables and integration of both sides of equation (15), we arrive at:

$$-\ln\left(1 - \frac{C_R}{C_0}\delta\right) = K \cdot t. \tag{16}$$

After a suitable transformation, the equation describing the efficiency of adsorption in the combined treatment process takes the form:

$$\frac{C_e}{C_0} = e^{-Kt}. \tag{17}$$

4. DERIVATION OF EMPIRICAL FORMULAE FOR THE COEFFICIENT OF ADSORBATE MASS TRANSFER RATE (K)

Upon transforming equation (17) with respect to K we obtain:

$$K = -\frac{1}{t} \cdot \ln\frac{C_e}{C_0}. \tag{18}$$

With this formula, the values of the coefficient of the adsorbate mass transfer rate were computed for a treatment train where adsorption was conducted as a single process (RW+PAC) or was combined with coagulation (RW+C+PAC). For the purpose of calculations, use was made of the results obtained in experimental studies where the relative values of adsorbate concentration (C_e/C_0) referred to dissolved organic carbon (DOC). The coagulant doses applied amounted to 2.15, 2.46 and 3.07 g Al/m^3, the PAC doses being equal to 5, 10, 30 and 75 g/m^3. The calculated values are given in tables 2 and 3.

Calculated values of the coefficient K for adsorption conducted as a separate process (RW+PAC)

t (h)	$D_{PAC} = 5$ g/m^3	$D_{PAC} = 10$ g/m^3	$D_{PAC} = 30$ g/m^3	$D_{PAC} = 75$ g/m^3
0.25	0.122	0.290	0.843	3.665
0.50	0.082	0.189	0.575	1.989
0.75	0.054	0.155	0.400	1.475
1.00	0.062	0.128	0.342	1.139

Calculated values of the coefficient K for adsorption combined with coagulation (RW+C+PAC)

D_C (g Al/m^3)	$D_{PAC} = 5$ g/m^3	$D_{PAC} = 10$ g/m^3	$D_{PAC} = 30$ g/m^3	$D_{PAC} = 75$ g/m^3
2.15	1.232	1.347	2.043	3.121
2.46	1.308	1.150	2.217	3.544
3.07	1.308	1.427	2.342	3.544

The coefficient K for a set time of the process varies, depending on the removal of organic substances measured in terms of DOC concentration. This function takes the form of the ratio of the DOC concentration persisting in the water upon the termination of the process to the initial DOC concentration (C_e/C_0). The efficiency of the adsorption of pollutants from natural water was found to be influenced primarily by the pH value, the time of the PAC contact with the water being treated, and by the adsorbent dose applied. In the case under analysis, when adsorption was carried out using the parameters of the technological process (pH 6.0 and the contact time of 1 h), the efficiency of adsorbate removal varied, depending on the PAC dose. In the system where adsorption and coagulation were performed simultaneously, the dose of the coagulant was an additional factor that affected the efficiency of the process.

Statistical analysis of the dependence of the coefficient K on D_{PAC} and D_C (figure 2) makes it clear that these parameters can be approximated in terms of an exponential function of the following generalized form: $y = a_0 \exp(a_1 x)$. The adopted condition was the minimization of the sum of squares and the maximization of the coefficient of determination r^2.

As the result of regression analysis, empirical formulae were derived, which describe the coefficient of the adsorbent mass transfer rate for a treatment train, where adsorption was conducted both as a separate process (RW+PAC):

$$K = 0.171 \exp(0.033 \cdot D_{PAC}) \qquad (19)$$

and as the process combined with coagulation (RW+C+PAC):

$$K = a \cdot \exp(0.013 \cdot D_{PAC}), \qquad (20)$$

where the coefficient *a* is described by the equation:
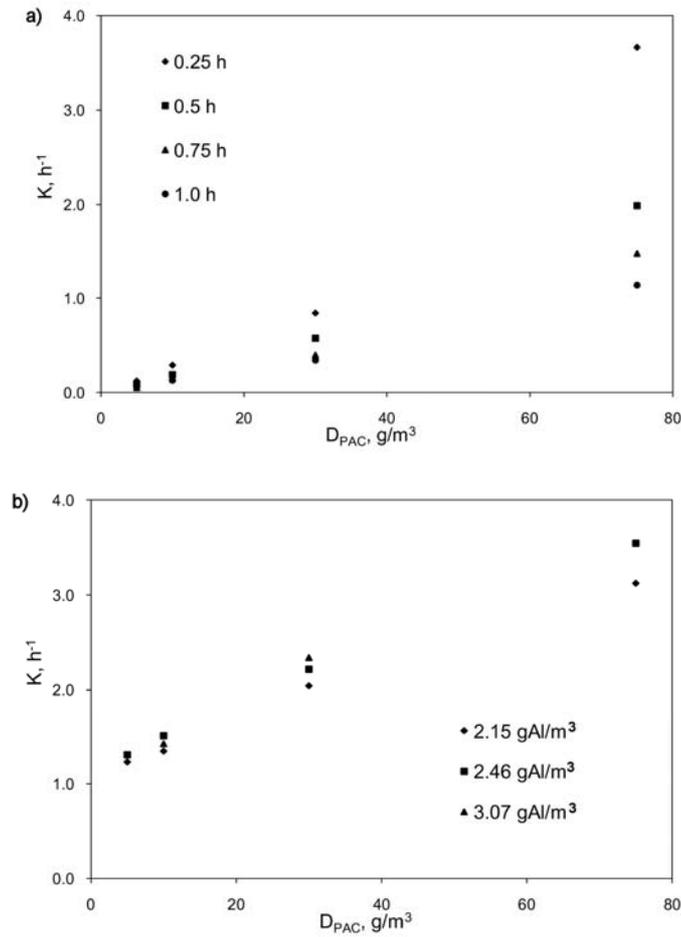
$$a = 1.10 \exp(0.076 \cdot D_C). \tag{21}$$

Fig. 2. Variations in the value of the coefficient *K* calculated in terms of equation (18):
(a) (RW+PAC), (b) (RW+C+PAC)

In relations (19)–(21), D_{PAC}, D_C and the calculated coefficient *K* are expressed in g/m^3, g Al/m^3, and h^{-1}, respectively. Regression coefficients were calculated by non-linear regression, by the least squares method in terms of the Levenberg–Marquardt algorithm. For the adopted exponential models of regression, very good agreement was obtained between experimental and predicted data.

The mathematical model was used to describe the efficiency of organic matter removal, which varied as a function of the coefficient of adsorbate mass transfer rate (*K*)

in the treatment train where adsorption was both conducted separately and combined with coagulation. The equations derived permitted the efficiency of DOC removal to be related to time and to the adsorbent dose (equations (17) and (19)), when use was made of PAC adsorption alone. When the treatment train involved the coagulation–adsorption process, DOC removal efficiency was related to time and to the dosage of both adsorbent and coagulant (equations (17), (20) and (21)). Figure 3 shows how the efficiencies of DOC removal obtained experimentally (expressed in relative values) compare with those attained from calculations.
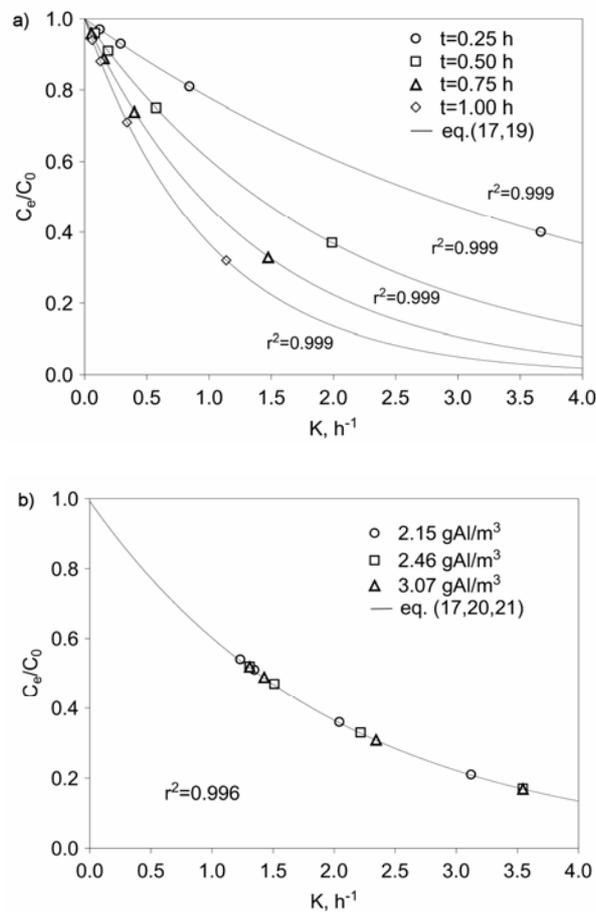

Fig. 3. Comparison between observed and predicted results for
(a) (RW+PAC) and (b) (RW+C+PAC)

The relations of (19) to (21) are applicable to the following ranges of D_{PAC}, D_C and time:

$$5 \text{ g/m}^3 \leq D_{\text{PAC}} \leq 75 \text{ g/m}^3,$$

$$2.0 \text{ g Al/m}^3 \leq D_C \leq 3.0 \text{ g Al/m}^3,$$

$$0 \leq t \leq 1.0 \text{ h}$$

as well as to the following extent of raw water pollution:

$$3.0 \text{ g C/m}^3 \leq \text{DOC} \leq 4.0 \text{ g C/m}^3.$$

5. CONCLUSIONS

The mathematical model proposed describes a simultaneous process of coagulation and adsorption and relates the variations in the efficiency of dissolved organic matter removal (measured in terms of DOC) to time, as well as to the PAC and coagulant doses applied. The final form of the model is:

$$C_e = C_0 \exp\left[-1.1 \exp\left(0.076 \cdot D_C\right) \exp\left(0.013 \cdot D_{\text{PAC}}\right) \cdot t\right].$$

When adsorption is carried out as a single process, the efficiency of DOC removal is related to time and adsorbent dose, and can be described by the following equation:

$$C_e = C_0 \exp\left[-0.171 \exp\left(0.033 \cdot D_{\text{PAC}}\right) \cdot t\right].$$

The comparison of the DOC removal efficiencies obtained by calculations and experiments has revealed a high consistency of observed and predicted data, as can be inferred from the value of the coefficient of determination, which varies between 0.996 and 0.999. The empirical formulae derived for the coefficient of adsorbate mass transfer rate (K) preserve their accuracy in the D_{PAC}, D_C and time ranges used in the technological investigations performed.

The findings reported are applicable to the optimization of technological trains where the process of PAC adsorption is conducted simultaneously with the coagulation process. The mathematical models offer the possibility of controlling the course of the process efficiently and of enhancing the removal of natural organic compounds from the water being treated.

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MATEMATYCZNY MODEL ADSORPCJI NA PWA
I JEGO ZASTOSOWANIE W TECHNOLOGII WODY

Zaprezentowano model matematyczny opisujący skuteczność usuwania związków organicznych metodą sorpcji na pylistym węglu aktywnym realizowaną jako wydzielony proces i symultanicznie z koagulacją. Zaproponowany model opisuje efektywność usuwania frakcji organicznych mierzonych stężeniem rozpuszczonego węgla organicznego, zmieniającą się w funkcji czasu, dawki adsorbentu i dawki koagulantu. Wyprowadzono wzory empiryczne pozwalające obliczyć wartość współczynnika szybkości przenoszenia masy adsorbatu, które zachowują swoją dokładność w zakresie przeprowadzonych badań technologicznych.