

# Models of adsorption of natural contaminants from treated water for municipal purposes on powdered activated carbon

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## Abstract

The paper investigates whether time and doses of powder activated carbon (PAC) effect adsorption rates of organic contaminants from water and proposes a new model of volume adsorption. Depending on the nature of the organic compounds present in water, a general description of the adsorption process may require a linear combination of adsorption models running at different rates and at different parameters of adsorption isotherms. The model showed a good fit with the measured data and could be used in designing adsorption units at water or wastewater treatment plants. The proposed set of model equations enables to predict the effects of PAC adsorption in both plug flow reactors and homogeneous reactors.

**Keywords:** adsorption, powdered activated carbon, modeling of the adsorption process, water and wastewater treatment, organic substances, pollutants

## 1. Introduction

Adsorption on powdered activated carbon (PAC), generally carried out simultaneously with the coagulation, is an effective way to remove organic material from water (Najm, 1991; Altmann, 2015; Margot, 2013; Boehler, 2012). The parameters characterizing PAC adsorption include: PAC dose and a contact time between PAC and organic pollutants. The removal of organic pollutants is determined by conventional adsorption indicators i.e. changes in UV absorbance at 254 nm or removal of dissolved organic carbon (DOC). Natural waters treated for municipal use or wastewater treated with highly efficient treatment technologies are mixtures of organic compounds at different concentrations and affinities to the sorbent surface. Accordingly, removals of organic material from water or wastewater may proceed at different rates and with different efficiencies. It makes a description of the total adsorption kinetics complicated, especially when absorbance or DOC is used as a general measure of the organic content. In various studies, there is some information how to correlate adsorption effects and PAC doses, process times and concentrations of removed pollutants (Yunlong Luo, 2014; Zietzschmann, 2014; Nowotny, Epp, Sonntag, Fahlenkamp, 2007; Bonvin, 2016). However, an accurate evaluation of sorption of a pollutant from water or wastewater requires laboratory scale tests. Such tests determine the adsorption model parameters, which can be helpful during the design of water and wastewater treatment systems.

Generally the main kinetics models of adsorption contain drive modul which is difference between current adsorbate concentration and current equilibrium concentration resulting from the adsorption isotherm (Marczewski, 2010). These types of models are called first-order models. Such models result from Fick's law describing the speed of mass transfer through the phase boundary (Coulson, Richardson, 2009). Adsorption models taking into account the effects of coagulation of pollutants are also known (Szlachta, Adamski, 2009).

There are models in which the second order mechanism is used (Marczewski, 2010; Jin, Qian, 2017; Dinushika, Eeshwarasinghe, 2018; Chen 2011; Mahatheva, Kalaruban 2016a; 2016b; Riahi, Chaabane, Thayer, 2017; Arshadi, Amiri, Mousavi, 2014; Schwantes, 2016). These kind models work only in one direction of adsorbate transport, for example from solution to sorbent because the process drive module is always positive. So – during desorption these models are useless because the drive module does not change the sign. Such models are not suitable for modeling the work of adsorption columns at variable in time adsorbate concentration at the inflow to the column.

The use of the pseudo second order models leads to the illogicality in the description of mass transfer between solution and sorbent. It should be noted that the physical sorption process is a reversible process, and therefore pseudo second order models are considered to be incorrect. Even in the case of irreversible chemisorption, the component describing the diffusion mass transfer can't be modified.

There are several other models describing the adsorption kinetics such as: Elovich model (Dinushika, Eeshwarasinghe, 2018, Mahatheva, Kalaruban 2016a; 2016b), Thomas model (Mahatheva, Kalaruban 2016a; 2016b), Weber and Morrison model (Dinushika, Eeshwarasinghe, 2018), Bohart – Adams model (Nur, 2014), Yoon – Nelson model (Nur, 2014). Depending on the adsorption mechanism, the appropriate model is used.

The adsorption rate constants in the models mentioned above are treated as constants characteristic of a given type of adsorbent. According to the theory of mass transfer through the phase boundary: liquid – sorbent, the rate constants of adsorption are not constant because it should depend on the amount of sorbent and its specific outer surface. This will be demonstrated in this work.

The main aim of this work is presentation new model properly describes adsorption and desorption process. This new model tends to equilibrium concentrations, after infinite time, compatible with the concentrations

resulting from the adsorption isotherm. The model will be used to describe the adsorption of two fractions of organic matter described by the total concentration or UV absorbance at 254 nm. Fractions of organic substances usually adsorb at a different rate, which significantly hinders the modeling of the adsorption process.

## 2. Material and Methods

### Adsorption models for a volume system

The model described below discusses a concentration  $C$  of the adsorbate in a liquid phase. The UV absorbance at 254 nm is used to measure a dissolved organic matter. Since absorbance  $A$  is approximately proportional to a concentration  $C$  the models are also valid for absorbance ( $C$  can be replaced by  $A$  in the equations).

Mass exchange rates between a solution and a sorbent in a volume system are described by the set of equations (Coulson & Richardson, 2009; Bielski, 2011a; Bielski, 2011b; Adamski, Szlachta, 2011):

$$\frac{dm_c}{dt} = -k \cdot a_m \cdot m_{sorb} \cdot (C - C_i) \quad (1)$$

$$\frac{dm_a}{dt} = +k \cdot a_m \cdot m_{sorb} \cdot (C - C_i) \quad (2)$$

where:

- $C$  – adsorbate concentration in water [ $\text{g}/\text{m}^3$ ],
- $C_i$  – equilibrium concentration in water [ $\text{g}/\text{m}^3$ ],
- $m_c$  – mass of adsorbate in a solution [ $\text{g}$ ],
- $m_a$  – mass of adsorbate in sorbent [ $\text{g}$ ],
- $k$  – mass transfer rate constant across a water- sorbent interface [ $\text{m}/\text{s}$ ],
- $a_m$  – specific outer surface of sorbent particles [ $\text{m}^2/\text{g}$  of sorbent],
- $m_{sorb}$  – mass of sorbent [ $\text{g}$ ].

The mass of adsorbate in a solution and in a sorbent may be written using a concentration  $C$  and an adsorption quantity  $a$ :

$$m_c = \frac{C}{\rho_w} m_u \epsilon_m \quad (3)$$

$$m_a = a \cdot m_u (1 - \epsilon_m) \quad (4)$$

- $\rho_w$  – water density ( $\sim 10^6 \text{g}/\text{m}^3$ ),
- $m_u$  – mass of a water – sorbent system [ $\text{g}$ ],
- $\epsilon_m$  – mass of water in a water-sorbent system,
- $a$  – adsorption quantity [ $\text{g}/\text{g}$  of sorbent].

Substituting formulas (3) and (4) to equations (1) and (2) a new formula for an adsorption model is obtained:

$$\frac{dC}{dt} \epsilon_m = -k \cdot a_m \cdot \frac{m_{sorb}}{m_u} \cdot \rho_w \cdot (C - C_i) \quad (5)$$

$$\frac{da}{dt} (1 - \epsilon_m) = +k \cdot a_m \cdot \frac{m_{sorb}}{m_u} \cdot (C - C_i) \quad (6)$$

Considering the system density  $\rho_u$ , equations (5) and (6) take a form:

$$\frac{dC}{dt} \varepsilon_m = -k \cdot a_m \cdot \frac{m_{sorb}}{m_u} \cdot \rho_u \cdot \frac{\rho_w}{\rho_u} \cdot (C - C_i) \quad (7)$$

$$\frac{da}{dt} (1 - \varepsilon_m) = +k \cdot a_m \cdot \frac{m_{sorb}}{m_u} \cdot \rho_u \cdot \frac{1}{\rho_u} (C - C_i) \quad (8)$$

Term  $\frac{m_{sorb}}{m_u} \cdot \rho_u$  is a sorbent dose  $D$  and then:

$$\frac{dC}{dt} \varepsilon_m = -k \cdot a_m \cdot D \cdot \frac{\rho_w}{\rho_u} \cdot (C - C_i) \quad (9)$$

$$\frac{da}{dt} (1 - \varepsilon_m) = +k \cdot a_m \cdot D \cdot \frac{1}{\rho_u} (C - C_i) \quad (10)$$

$D$  – sorbent dose [g of sorbent/m<sup>3</sup> of system],

$\rho_u$  – density of a water – sorbent system [g/m<sup>3</sup>].

Unless a sorbent dose  $D$  is not very high:  $\rho_u \approx \rho_w + D$ , while  $\varepsilon_m \approx \rho_w / (\rho_w + D)$ . Comparing formulas (9) and (10) results in an integral dependence:

$$-\frac{\varepsilon_m}{\rho_w} \int_{C_0}^C dC = (1 - \varepsilon_m) \int_{a_0}^a da \quad (11)$$

And its solution results in a state equation:

$$a = a_0 - \frac{\varepsilon_m}{\rho_w (1 - \varepsilon_m)} (C - C_0) \quad (12)$$

$C_0$  – initial adsorbate concentration [g/m<sup>3</sup> of water],

$a_0$  – initial adsorption quantity [g/g of sorbent].

A relation between the equilibrium concentration  $C_i$  and the actual adsorption quantity  $a$  results from adsorption isotherms:

- ▶ the Henry's isotherm:

$$C_i = \frac{a}{\Gamma} \quad (13)$$

- ▶ the Langmuir isotherm:

$$C_i = \frac{a \cdot b}{a_{\max} - a} \quad (14)$$

$\Gamma$  – Henry's constant [m<sup>3</sup> of water/g of sorbent],

$a_{\max}$  – maximum adsorption quantity (asymptote of the Langmuir isotherm) [g/g of sorbent],

$b$  – Langmuir isotherm's constant [g/m<sup>3</sup> of water].

When the adsorption equilibrium is described by the Henry's isotherm there is the analytical solution of equations (9) and (10). Substituting the equilibrium concentration  $C_i$  with (13) and using equation (12) a relationship (9) can be presented as:

$$\frac{dC}{dt} = -k \cdot a_m \cdot D \cdot \frac{\rho_w}{\rho_u} \cdot \frac{1}{\varepsilon_m} \left( C - \frac{a_0}{\Gamma} + \frac{\varepsilon_m}{\rho_w (1 - \varepsilon_m)} \frac{C}{\Gamma} - \frac{\varepsilon_m}{\rho_w (1 - \varepsilon_m)} \frac{C_0}{\Gamma} \right) \quad (15)$$

Assuming that:

$$\alpha = k \cdot a_m \cdot D \cdot \frac{\rho_w}{\rho_u} \cdot \frac{1}{\varepsilon_m} \quad (16)$$

$$\beta = \frac{a_0}{\Gamma} + \frac{\varepsilon_m}{\rho_w (1 - \varepsilon_m)} \frac{C_0}{\Gamma} \quad (17)$$

$$\omega = 1 + \frac{\varepsilon_m}{\rho_w (1 - \varepsilon_m)} \frac{1}{\Gamma} \quad (18)$$

then (15) has a form of:

$$\frac{dC}{dt} = -\alpha(C \cdot \omega - \beta) \quad (19)$$

Its solution at the initial condition:

$$C(t=0) = C_0 \quad (20)$$

is as follows:

$$C = \frac{\beta}{\omega} + \left( C_0 - \frac{\beta}{\omega} \right) \exp(-\alpha \cdot \omega \cdot t) \quad (21)$$

A ratio  $\frac{\beta}{\omega}$  is equal to the concentration  $C_r$  at the adsorption equilibrium achieved after time  $t \rightarrow +\infty$ :

$$\frac{\beta}{\omega} = \frac{a_0 \cdot \rho_w \cdot (1 - \varepsilon_m) + C_0 \varepsilon_m}{\Gamma \cdot \rho_w \cdot (1 - \varepsilon_m) + \varepsilon_m} \quad (22)$$

while from the mass balance for adsorbent:

$$(a_r - a_0) \cdot m_u \cdot (1 - \varepsilon_m) = (C_0 - C_r) \frac{1}{\rho_w} \cdot m_u \varepsilon_m \quad (23)$$

$a_r$  – adsorption quantity at the adsorption equilibrium [g/g of sorbent],  
 $C_r$  – concentration at the adsorption equilibrium [g/m<sup>3</sup> of water],

it can be concluded that for:  $a_r = \Gamma C_r$  (equation (13)):

$$C_r = \frac{a_0 \cdot \rho_w \cdot (1 - \varepsilon_m) + C_0 \varepsilon_m}{\Gamma \cdot \rho_w \cdot (1 - \varepsilon_m) + \varepsilon_m} \quad (24)$$

so:

$$\frac{\beta}{\omega} = C_r \quad (25)$$

Equation (21) was used to determine the product  $k \cdot a_m$ , which describes a substitute transfer rate constant across the water – sorbent interphase for the particular sorbent at the specific hydrodynamic conditions. To determine  $\alpha$  (equation (16)) a dose  $D$  was assumed as mass of sorbent introduced to a water volume (instead of a water/sorbent volume) since both volumes are almost the same.

If change of aqueous solution volume after a sorbent dose  $D$  was placed to the solution is slight, then formula:  $\frac{\rho_w}{\rho_u} \cdot \frac{1}{\varepsilon_m} \cong 1$  and  $D \cdot \frac{1}{\rho_u} \cdot \frac{1}{1 - \varepsilon_m} \cong 1$ .

In the case of other non-linear adsorption isotherms, equations (9) and (10) cannot be solved in analytical way and to calculate adsorbate concentrations in solutions and adsorption quantities they have to be integrated numerically. Using the Euler method, the adsorbate concentration  $C_j$  and adsorption quantities  $a_j$  at times  $t_j$  can be calculated from the following set of differential equations:

$$t_{j+1} = t_j + \Delta t \quad (26)$$

$$C_{j+1} = C_j - k \cdot a_m \cdot D \cdot \frac{\rho_w}{\rho_u} \cdot \frac{1}{\varepsilon_m} \cdot (C_j - C_{i,j}) \cdot \Delta t \quad (27)$$

$$a_{j+1} = a_j + k \cdot a_m \cdot D \cdot \frac{1}{\rho_u} \cdot \frac{1}{(1 - \varepsilon_m)} \cdot (C_j - C_{i,j}) \cdot \Delta t \quad (28)$$

using a general isotherm equation:

$$a_j = f(C_{i,j}) \quad (29)$$

$\Delta t$  – time step [s],  
(index  $j$  relates to following times  $t_j$ ).

Linear combination of adsorption models  
(a combined model)

In order to obtain the adsorption model as a linear combination of partial adsorption models, the author introduced the coefficient  $\alpha_x$  that described a fraction of organic substances  $C_0$  adsorbed according to the model (9), (10) and (13) with parameters  $(\Gamma)_1$  and  $(k \cdot a_m)_1$ . Fraction  $(1 - \alpha_x)$  will be adsorbed according to model (9), (10) and (13) but with parameters  $(\Gamma)_2$  and  $(k \cdot a_m)_2$ . Accordingly, the total concentration of adsorbate  $C$  is the sum of concentrations  $C_1$  and  $C_2$  of both fractions at time  $t$ . The initial concentrations of both fractions of adsorbate in a liquid phase:  $C_{01} = \alpha_x \cdot C_0$ ,  $C_{02} = (1 - \alpha_x) \cdot C_0$  are the initial condition for integration of equations (9) and (10). The initial adsorption quantity for both fractions is the same and equal to  $a_0$ . The total adsorption quantity  $a$  at time  $t$  is the sum of adsorption quantities  $a_1$  and  $a_2$  at time  $t$  for both fractions. The procedure is much simpler for model (21), because the overall adsorption quantity at time  $t$  can be calculated from equation (12) on the basis of the total concentration of the adsorbate  $C$  at time  $t$  and the initial concentration  $C_0$ . Linear combination of equation (21) may be expressed as:

$$C = \frac{\beta_1}{\omega_1} + \left( \alpha_x \cdot C_0 - \frac{\beta_1}{\omega_1} \right) \exp(-\alpha_1 \cdot \omega_1 \cdot t) + \frac{\beta_2}{\omega_2} + \left( (1 - \alpha_x) \cdot C_0 - \frac{\beta_2}{\omega_2} \right) \exp(-\alpha_2 \cdot \omega_2 \cdot t) \quad (30)$$

$\alpha_1$ ,  $\beta_1$ ,  $\omega_1$  – coefficients calculated from equations: (16), (17), (18) using parameters:  $(\Gamma)_1$ ,  $(k \cdot a_m)_1$

$\alpha_2$ ,  $\beta_2$ ,  $\omega_2$  – coefficients calculated from equations: (16), (17), (18) using parameters:  $(\Gamma)_2$ ,  $(k \cdot a_m)_2$

### 3. Experimental

Water samples used in the PAC adsorption studies

The study used natural water from the Rudawa river and two samples of tap water.

The quality of water from the Rudawa river was as follows: turbidity = 21.0 NTU, pH = 7.6, alkalinity = 190 g CaCO<sub>3</sub> / m<sup>3</sup>, dissolved oxygen (DO) = 7.9 g O<sub>2</sub> / m<sup>3</sup>, BOD = 3.9 g O<sub>2</sub> / m<sup>3</sup>, DOC = 3.9 g C / m<sup>3</sup> and absorbance 7.2 m<sup>-1</sup>.

The first tap water sample had turbidity of 0.1 NTU, pH = 7.4, alkalinity = 140 g CaCO<sub>3</sub> / m<sup>3</sup>, DO = 8.0 g O<sub>2</sub> / m<sup>3</sup>, DOC = 1.9 g C / m<sup>3</sup> and absorbance = 3 m<sup>-1</sup> while the second sample had pH = 7.5, alkalinity = 145 g CaCO<sub>3</sub> / m<sup>3</sup>, DO = 8.0 g O<sub>2</sub> / m<sup>3</sup>, DOC = 2.2 g C / m<sup>3</sup> and absorbance = 3.54 m<sup>-1</sup>.

Coagulant Flokor 1,2a was used for coagulation of natural water samples. Adsorption of organic material from water was carried out using powdered

activated carbon AKPA 22 [24].

### Adsorption on PAC

Before the adsorption study, natural water was coagulated with coagulant Flokor 1,2a, (dose of  $2 \text{ g Al / m}^3$ ) and let to settle for 0.5 h. During a 15 minute flocculation, water samples were mixed at a velocity gradient of  $G = 62 \text{ s}^{-1}$ . After this process water turbidity decreased to 1.2 NTU. Then water was poured into 6 beakers and PAC doses of 20, 40, 60, 80, 100 and  $120 \text{ g PAC / m}^3$  were added to water; the samples were mixed at a velocity gradient of  $G = 62 \text{ s}^{-1}$ . After 0.5, 2.0 and 24 hours, the samples were centrifuged for 5 minutes at 5000 rpm. The UV/254 nm absorbance was measured in the samples. Based on absorbance A, adsorption quantities were calculated as ratios of a difference between an initial absorbance and absorbance at the given PAC dose and the PAC dose. The results are represented by points ( $\blacklozenge$ ,  $\triangle$ ,  $\square$ ) in Fig. 3 and 6.

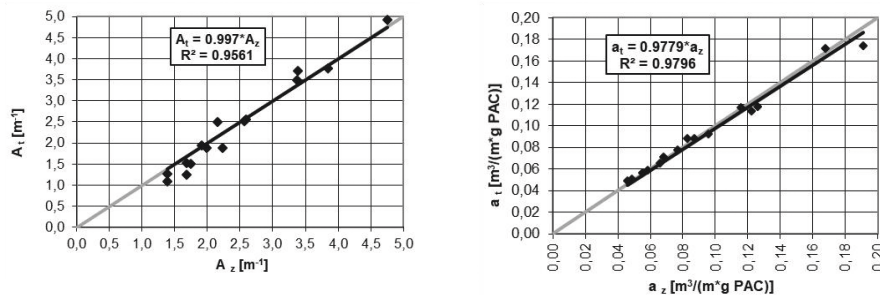
The tap water did not require any initial preparation.

The first tap water sample was poured into 5 beakers to which the following carbon doses were added: 20, 40, 60, 80 and  $100 \text{ g PAC / m}^3$ . The content of the beakers was mixed at a velocity gradient of  $G = 62 \text{ s}^{-1}$ . After 0.5, 2.5 and 24 h, the samples were centrifuged for 5 minutes at 5000 rpm and UV absorbance at 254 nm was determined. Based on absorbance A, adsorption quantities were calculated as ratios of a difference between an initial absorbance and absorbance obtained at the given PAC dose and the PAC dose. The results are represented by points ( $\blacktriangle$ ,  $\diamond$ ,  $\blacksquare$ ) in Fig. 9 and 12.

The second tap water sample was poured into 4 beakers, to which the following carbon doses were introduced: 20, 40, 60 and  $80 \text{ g PAC / m}^3$ . The content of the beakers was mixed with at a velocity gradient of  $G = 40 \text{ s}^{-1}$ . After 0.167, 0.333, 0.667 and 1 h the samples were centrifuged for 5 minutes at 5000 rpm and UV absorbance at 254 nm was determined. Based on absorbance A adsorption quantities were calculated as ratios of a difference between an initial absorbance and absorbance obtained at the given PAC dose and the PAC dose. The results are represented by points ( $\diamond$ ,  $\square$ ,  $\blacktriangle$ ,  $\bullet$ ) in Fig. 15 and 18.

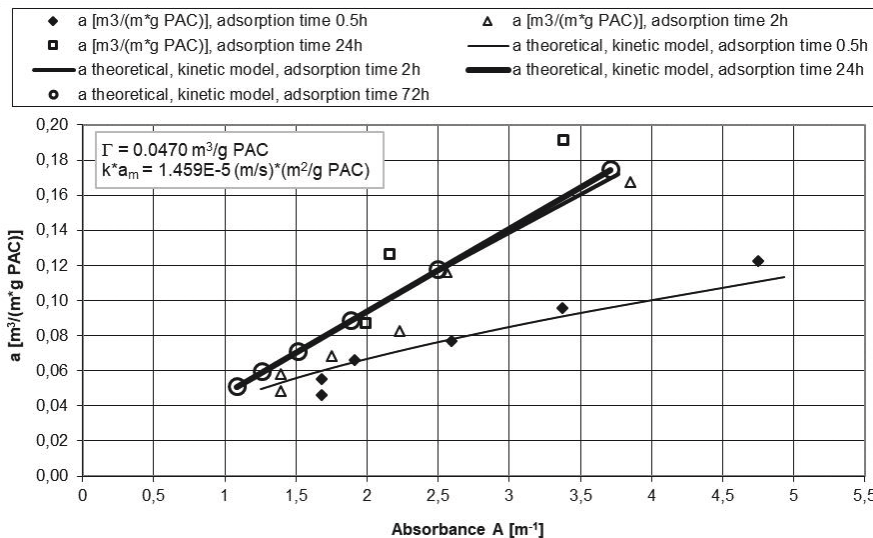
## 4. Results and Discussion

The model (6), (10) described the adsorption process well for all the samples, if only the process time was shorter than 2.5 h (Figs. 1–18); for adsorption processes lasting 24 hours a combined model was a better option. Generally, in the model (21), (12) the average relative errors of the model fit to the measured data ranged from 0.020 to 0.093 for absorbance A and from 0.041 to 0.098 for adsorption quantity a, in all cases (Figs. 1, 2, 7, 8, 13 and 14); they slightly exceeded the average relative errors of the combined model fit, which stayed in the range of 0.020–0.054 for absorbance A and in the range of 0.022 – 0.062 for adsorption quantity a (Figs. 4, 5, 10, 11, 16 and 17). Reduction of relative errors is accompanied by higher squared correlation coefficients  $R^2$  and trend line coefficients approaching unity. Differences in relative errors are not large, but even a small reduction of a relative error has a significant effect on a state line of a water/sorbent system determined at a given adsorption moment. Comparing the line  $a(A)_t$  at the moment it can be stated that the model (21), (12) does not “split” adsorption effects between process times 2h and 24h (Fig. 3) or 2.5 h and 24 h (Fig. 9) while the combined model divides the lines  $a(A)_t$  for these time pairs (Figs. 6 and 12). Therefore, the combined model describes better long mass exchange processes because absorbance measures the amount of numerous organic substances in natural water or wastewater. The substances are adsorbed at different rates and exhibit different affinities to the sorbent surface. The ones that are adsorbed slowly will show measurable adsorption effects only after long process hours. For the natural water sample and the first tap water sample

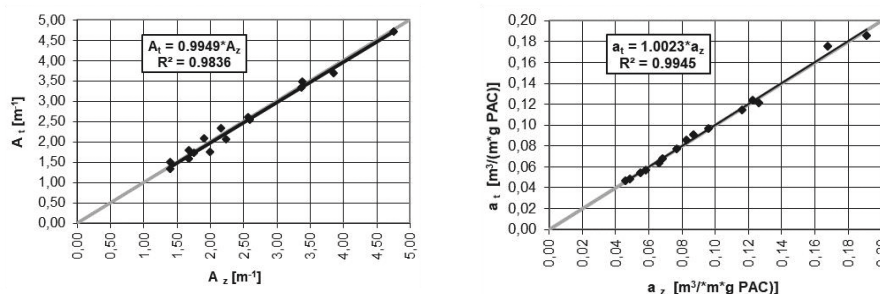


**Fig. 1.** Goodness of fit of theoretical absorbance  $A_t$  calculated from the model to measured  $A_z$ ; (model (21), water from the Rudawa river, relative error 0.093)

**Fig. 2.** Goodness of fit of theoretical adsorption quantity  $a_t$  to measured  $a_z$  (equations (21) and (12); water from the Rudawa river, relative error 0.041)

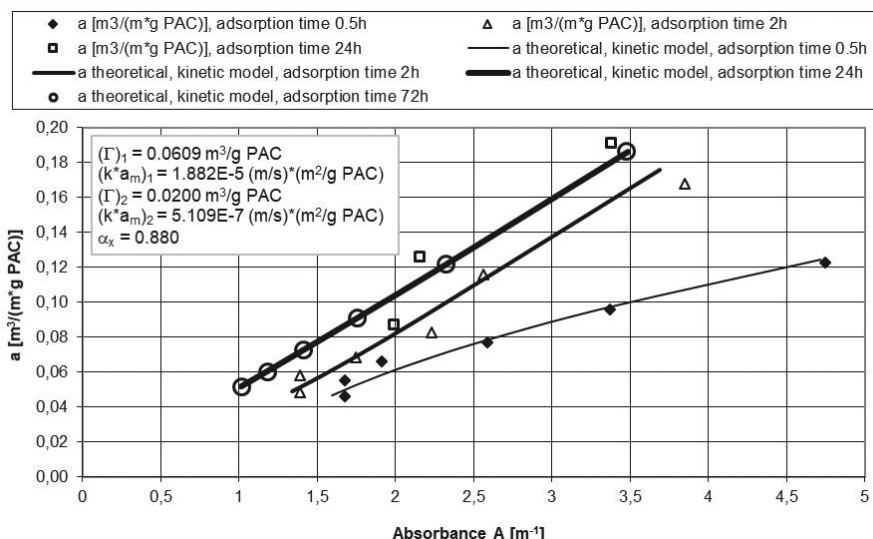


**Fig. 3.** Adsorption quantity  $a$  vs. absorbance  $A$  at different adsorption times (equations (21) and (12), water from the Rudawa river)



**Fig. 4.** Goodness of fit of theoretical absorbance  $A_t$ , calculated from the model, to the measured  $A_z$  (a combined model based on equation (21), water from the Rudawa river; relative error 0.048)

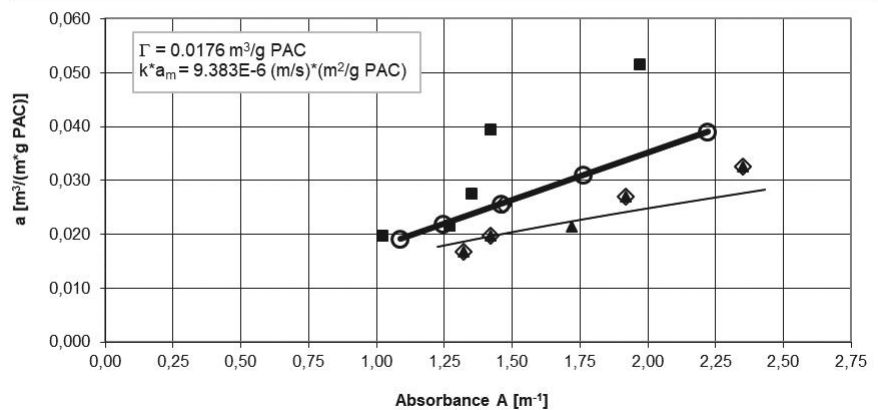
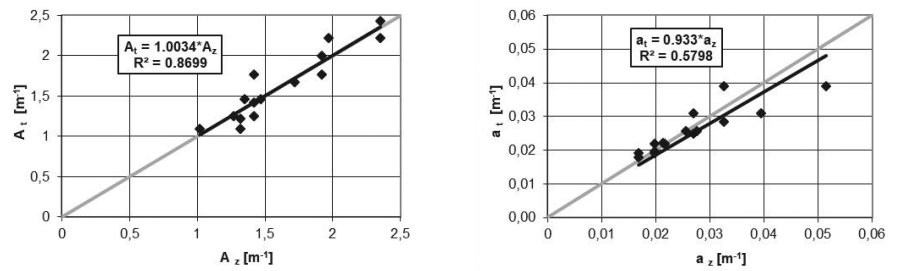
**Fig. 5.** Goodness of fit of theoretical adsorption quantity  $a_t$  to measured  $a_z$  (a combined model based on equations (21), (12), water from the Rudawa river; relative error 0.022)



**Fig. 6.** Adsorption quantity  $a$  vs. absorbance  $A$  at different adsorption times (a combined model based on equations (21) and (12), water from the Rudawa river)

**Fig. 7.** Goodness of fit of theoretical absorbance  $A_t$ , calculated from the model, to measured  $A_z$  (model (21), the first tap water sample; relative error 0.077)

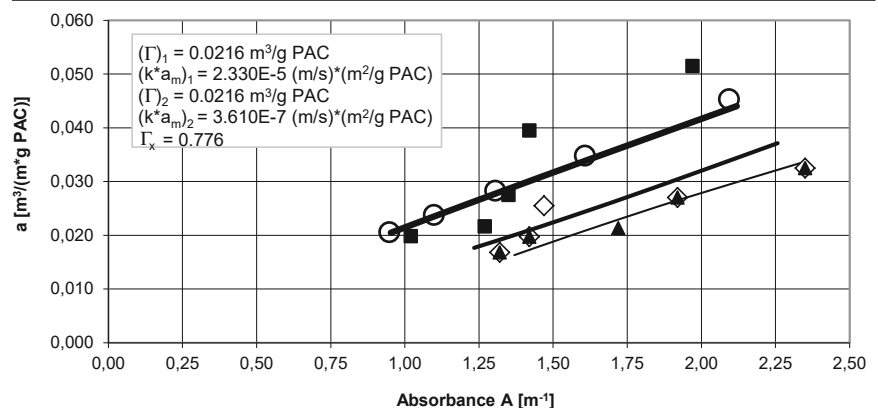
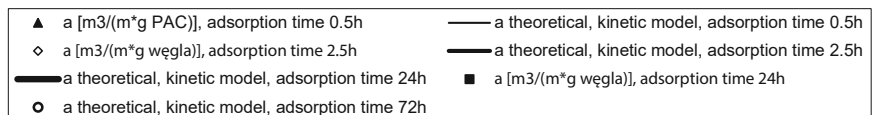
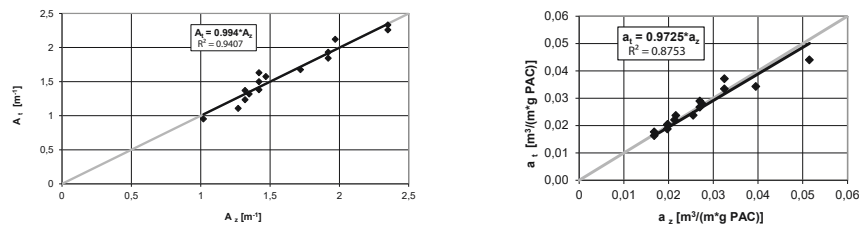
**Fig. 8.** Goodness of fit of theoretical adsorption quantity  $a_t$  to measured  $a_z$  (equations (21) and (12), the first tap water sample; relative error 0.098)



**Fig. 9.** Adsorption quantity  $a$  vs. absorbance  $A$  at different adsorption times (equations (21) and (12), the first tap water sample)

**Fig. 10.** Goodness of fit of theoretical absorbance  $A_t$ , calculated from the model, to measured  $A_z$  (a combined model based on equation (21), the first tap water sample; relative error 0.054)

**Fig. 11.** Goodness of fit of theoretical adsorption quantity  $a_t$  to measured  $a_z$  (a combined model based on equations (21) and (12), the first tap water sample; relative error 0.062)

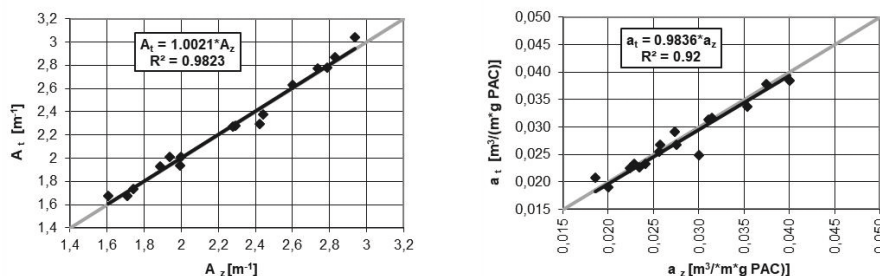


**Fig. 12.** Adsorption quantity  $a$  vs. absorbance  $A$  at different adsorption times (a combined model based on equations (21) and (12), the first tap water sample)

fractions of slowly adsorbed substances were  $(1-\alpha_x)$  0.12 and 0.224 of the initial absorbance value. The values of  $(k \cdot a_m)_1$  for slowly adsorbed substances were about two orders of magnitude lower than  $(k \cdot a_m)_1$  for rapidly adsorbed substances; for slowly adsorbed substances they were  $\{5.109\text{E-}7, 3.610\text{E-}7\}$  (m/s)  $\cdot$  (m<sup>2</sup>/g PAC) while for rapidly adsorbed ones  $\{1.882\text{E-}5, 2.330\text{E-}5\}$  (m/s)  $\cdot$  (m<sup>2</sup>/g PAC) (Figs. 6 and 12). The Henry's adsorption coefficients  $(\Gamma)_2$  for slowly adsorbed substances were lower than or equal to the coefficients  $(\Gamma)_1$  for rapidly adsorbed substances (Figs. 6 and 12). This means that the slowly adsorbed substances exhibited the same or lower affinity to the sorbent.

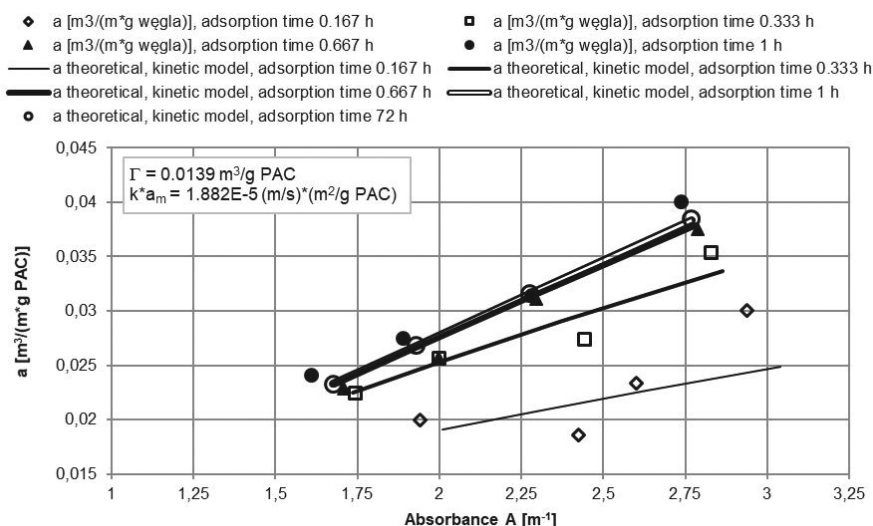
The differences between the model (21), (12) and the combined model are much smaller for shorter adsorption times (Figs. 15 and 18) and both models seem to be sufficiently accurate to serve technological and design purposes. It should be noted, however, that  $(k \cdot a_m)_2$  for a slowly adsorbed fraction is still about two orders of magnitude smaller than  $(k \cdot a_m)_1$  for a rapidly adsorbed fraction (Fig. 18).

For all samples water samples  $(k \cdot a_m)_1$  as well as  $(k \cdot a_m)_2$  were similar (Fig. 6, 12 and 18); the points ( ) marked the state line of a (A) water – sorbent system for 72 h. Figs. 6 and 12 show that after 24 hours of adsorption, the state line of the a (A) system is the same as for 72 h. It means that the adsorption equilibrium is practically reached after 24 h. After additional calculations it can be stated that the actual equilibrium in a natural water sample can be reached after 18 h (Fig. 6) while in the first tap water sample after approximately 22 h (Fig. 12). For the second tap water sample, the adsorption equilibrium is reached already after 0.9 h (Fig. 18). It is difficult to anticipate the actual time required to reach the adsorption equilibrium without previous simulation calculations, because even small changes in the combined model parameters result in major time changes. In the model (21), (12) such predictions are easier to make since  $k \cdot a_m$  is the only factor affecting the equilibrium time.



**Fig. 13.** Goodness of fit of theoretical absorbance  $A_1$  calculated from the model, to measured  $A_2$  (model (21), the second tap water sample; relative error 0.020)

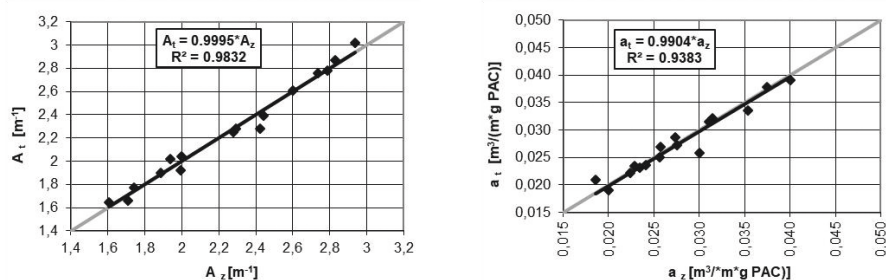
**Fig. 14.** Goodness of fit of theoretical adsorption quantity  $a_1$  to measured  $a_2$  (equations (21) and (12), the second tap water sample; relative error 0.042)



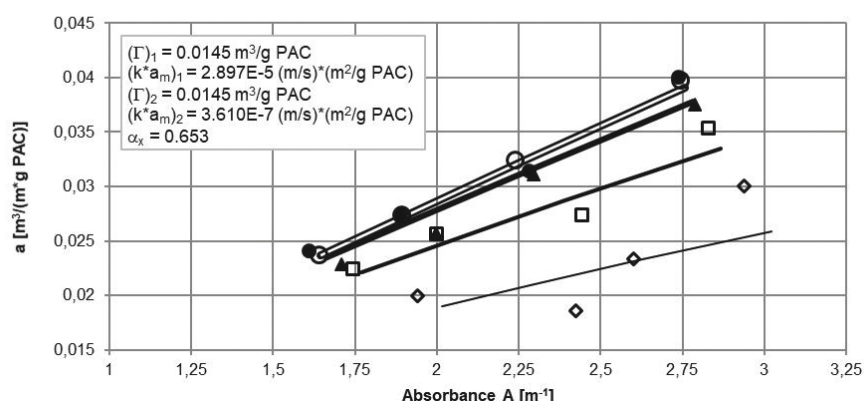
**Fig. 15.** Adsorption quantity  $a$  vs. absorbance  $A$  at different adsorption times (equations (21) and (12), the second tap water sample)

**Fig. 16.** Goodness of fit of theoretical absorbance  $A_t$ , calculated from the model, to measured  $A_z$  (a combined model based on equation (21), the second tap water sample; relative error 0.020)

**Fig. 17.** Goodness of fit of theoretical adsorption quantity at to measured  $a_z$  (a combined model based on equations (21) and (12), the second treated tap sample; relative error 0.039)



- ◆  $a$  [ $\text{m}^3/(\text{m}^3 \text{ węgla})$ ], adsorption time 0.167 h
- ▲  $a$  [ $\text{m}^3/(\text{m}^3 \text{ węgla})$ ], adsorption time 0.667 h
- $a$  theoretical, kinetic model, adsorption time 0.167 h
- $a$  theoretical, kinetic model, adsorption time 0.667 h
- $a$  theoretical, kinetic model, adsorption time 72 h
- $a$  [ $\text{m}^3/(\text{m}^3 \text{ węgla})$ ], adsorption time 0.333 h
- $a$  [ $\text{m}^3/(\text{m}^3 \text{ węgla})$ ], adsorption time 1 h
- $a$  theoretical, kinetic model, adsorption time 0.333 h
- $a$  theoretical, kinetic model, adsorption time 1 h



**Fig. 18.** Adsorption quantity  $a$  vs. absorbance  $A$  at different adsorption times (a combined model based on equations (21) and (12), the second tap water sample)

The author also verified whether the adsorption rate was proportional to the sorbent dose  $D$ . The studies described in (Szlachta, Adamski, 2009) indicated a disproportionate effect of dose  $D$  on the adsorbate mass transfer rate constant across the water-sorbent phase; a power dependence of a dose  $D$  in equations (6) and (10) did not significantly improve the model fit to the measured data in the samples. It means that the mass exchange rate increases proportionally to the sorbent dose  $D$  and the mass exchange surface is also proportional to the sorbent dose to the first power.

## 5. Conclusions

The mathematical model of PAC adsorption in a volume system describes quite well the results obtained during several hours of adsorption of organic substances from treated natural water.

A new model of PAC adsorption of organic substances from natural water was proposed.

The model is a linear combination of two mathematical models referring to two groups of substances adsorbed at different rates and showing a different affinity for PAC. The model was called a combined model.

For long adsorption times (over 12 h) it is recommended (in justified cases) to use the combined model to calculate adsorption of organic substances in natural water.

It was verified that the PAC adsorption rate of organic matter from natural water was proportional to the dose of sorbent to the first power.

The developed models allow to determine the time required to reach the adsorption equilibrium.

Models can be used to design units for PAC adsorption of organic substances from natural waters.

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## Modele adsorpcji naturalnych zanieczyszczeń z uzdatnionej wody do celów komunalnych na sproszkowanym węglu aktywnym

### Streszczenie

Artykuł bada, w jaki sposób czas i dawki proszku węgla aktywnego (PAC) wpływają na szybkość adsorpcji zanieczyszczeń organicznych z wody, i proponuje nowy model adsorpcji objętościowej. W zależności od charakteru związków organicznych obecnych w wodzie ogólny opis procesu adsorpcji może wymagać liniowej kombinacji modeli adsorpcji działających z różnymi prędkościami i przy różnych parametrach izoterm adsorpcji. Model, na którym przeprowadzono badania, wpasował się w przykładowe dane, więc można go wykorzystać do projektowania jednostek adsorpcyjnych w oczyszczalniach wody lub ścieków. Proponowany zestaw równań modelowych pozwala przewidzieć skutki adsorpcji PAC zarówno w reaktorach z przepływem tłokowym, jak i reaktorach homogenicznych.

**Słowa kluczowe:** adsorpcja, sproszkowany węgiel aktywny, modelowanie procesu adsorpcji, uzdatnianie wody i ścieków, substancje organiczne, zanieczyszczenia