

# Kinetic and equilibrium study of the CO<sub>2</sub> adsorption on activated carbon

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**Abstract:** The presented research are concerned with the modelling of isotherms and chemical kinetics of mass transport for the CO<sub>2</sub> adsorption on activated carbon, taking place in the fluidized and fixed bed. To determine the nature of CO<sub>2</sub> binding under low-pressure conditions, adsorption complex and thermodynamic effects occurring during the process, four isothermal models were used: Langmuir, Freundlich, Temkin and Halsey. The evaluation of the factors affecting the course and rate of CO<sub>2</sub> binding was based on four kinetic models, i.e. pseudo-first-order (PFO), pseudo-second-order (PSO), intraparticle diffusion (IPD) and the Elovich model. The validation of mathematical models showed that the linearized Freundlich and Halsey isotherms models are best suited to empirical data. In the case of process kinetics, the analysis showed that the non-linearized pseudo-first-order model (PFO) proved to be unrivalled in fitting to experimental data. The comparison of two types of tested beds suggested faster kinetics for a fluidized bed, while a larger amount of CO<sub>2</sub> at equilibrium was adsorbed by the fixed bed.

**KEYWORDS:** ISOTHERMS, THERMODYNAMICS, KINETICS, MATHEMATICAL MODELING, COMPARISON OF LINEAR AND NON-LINEAR EQUATIONS

## 1. Introduction

The energy sector based on non-renewable energy sources, together with the associated global climate threat (greenhouse effect), the main causative factor of which is high carbon dioxide emissions to the atmosphere, searches for technologies enabling its reduction the most urgent goal in many industries [1, 2]. The adsorption process, against the background of the above issues, is quickly gaining popularity and is now widely used as a separation technique due to the potentially low energy consumption, increased CO<sub>2</sub> carrying capacity, minimal pressure drop and playing a large role in the future flexibility of the energy system. As a result, in the field of developing CO<sub>2</sub> adsorption technology, new materials with an extensive porous structure are searched for and a method of modifying those already available [3]. According to the literature, the most promising materials for CO<sub>2</sub> separation are activated carbons, and the amount of adsorbed gas depends on the porous structure, the properties of the chemical structure of their surface [3, 4]. Their performance can be determined based on the isotherms, which define the equilibrium state as a function of adsorbate pressure, and adsorption kinetics, which describe the amount of adsorbed gas as a function of time, until the equilibrium state is reached [3]. Therefore, the mathematical description seems to be an effective method of predicting the behaviour of given materials under various conditions, which is important for the effective design of adsorption systems as well as the scaling and optimization of the process.

## 2. Preconditions and means for resolving the problem

### 2.1. Review of mathematical models of the adsorption isotherms

#### Langmuir model

The equation given in 1916 by Langmuir presents an extremely accurate model of monolayer adsorption on a homogeneous (energetically homogeneous) microporous surface. The nonlinear equation of the Langmuir isotherm model takes the following form [5]:

$$q_e = q_m \frac{K_L \cdot P}{(1 + K_L \cdot P)} \quad (1)$$

where,  $q_e$  - amount of adsorbed substance at equilibrium per 1 gram of adsorbent [mg/g],  $q_m$  - maximum adsorption value [mol/g],  $K_L$  - equilibrium constant of adsorption,  $P$  - relative pressure of the adsorbate [Pa].

#### Freundlich model

The Freundlich isotherm model is the first and the best known empirical equation that describes the non-ideal, reversible process of monolayer and multilayer adsorption on the surfaces of

heterogeneous microporous adsorbents [6]. The equation of the Freundlich model in the nonlinear form takes the following form [6]:

$$q_e = K_F \cdot P^{\frac{1}{n_F}} \quad (2)$$

where:  $K_F$  - the empirical constant of the Freundlich isotherm related to the adsorbent capacity,  $P$  - relative pressure of the adsorbate [Pa],  $n_F$  - constant related to the affinity of the adsorbate to the adsorbent.

#### Temkin model

The Temkin model from 1940 is an experimental isotherm equation describing adsorption on a heterogeneous surface of a solid, taking into account the interaction between the adsorption complex, in which it ignores the exceptionally high and low values of the relative pressure of the adsorbate [6]. The equation of Temkin model in a non-linearized form takes the following form [6]:

$$q_e = B \cdot \ln(K_T \cdot P) \quad (3)$$

where:  $B$  - Temkin constant [-],  $K_T$  - equilibrium constant of adsorption [1/Pa],  $P$  - relative pressure of the adsorbate [Pa].

#### Halsey model

The Halsey isotherm model, similarly to the Freundlich model applies to the description of adsorption on heterogeneous adsorbent surfaces on which the heat of adsorption is distributed unevenly. However, in contrast to it [6], the authors of this work only characterize multilayer adsorption at a relatively large distance from the surface of the solid. The Halsey model equation in non-linearized form is represented as [6]:

$$q_e = e^{\frac{\ln(K_H) - \ln(P)}{n_H}} \quad (4)$$

where:  $K_H$  - equilibrium constant of adsorption [1/Pa],  $P$  - relative pressure of the adsorbate [Pa],  $n_H$  - Halsey model constant [-].

### 2.2. Review of mathematical models of adsorption kinetics

#### Pseudo-first-order model (PFO)

In 1898 the kinetic equation of the pseudo-first order model (PFO) was introduced by Lagergren. Of all the kinetic models, the PFO model is the simplest to describe the adsorption kinetics and adsorbent interactions, i.e. it can characterize the reversible interaction between the adsorbent and the adsorbate, which is more suitable for predicting the physisorption behaviour [7]. In differential form, the PFO model equation is determined as follows [7]:

$$\frac{dq(t)}{dt} = k_1 \cdot [q_e - q(t)] \quad (5)$$

where:  $t$  - time [min],  $q(t)$  - the amount of adsorbed adsorbate by the adsorbent mass as a function of time [mg/g],  $q_e$  - value of  $q$  in the state of adsorption equilibrium [mg/g],  $k_1$  - pseudo-first-order constant [g/(mg·min)].

#### Pseudo-second order model (PSO)

The kinetic pseudo-second-order (PSO) was proposed in 1995 by Ho. According to the PSO model, the adsorbate-adsorbent complex is caused by strong bonds, ensuring its better fit with the experimental data, when the adsorption process involves chemical bond interactions (chemisorption) [8]. In differential form, the above model is presented as follows [8, 9]:

$$\frac{dq(t)}{dt} = k_2 \cdot [q_e - q(t)]^2 \quad (6)$$

where:  $t$  - time [min],  $q(t)$  - the amount of adsorbed adsorbate by the adsorbent mass as a function of time [mg/g],  $q_e$  - value of  $q$  in the state of adsorption equilibrium [mg/g],  $k_2$  - pseudo-second-order rate constant [g/(mg·min)].

#### Intraparticle diffusion model (IPD)

In 1962, the intramolecular diffusion (IPD) model was developed by Weber and Morris based on Fick's second law. The main application of this model is to identify the next steps in the process mechanism, i.e. mass transfer during the adsorption process [10]. The IPD model is defined as the following linear equation [10]:

$$q(t) = k_i \cdot t^{\frac{1}{2}} + c_i \quad (7)$$

where:  $t$  - time [min],  $k_i$  - intraparticle diffusion constant [mg/(g·min<sup>1/2</sup>)],  $c_i$  - direct constant proportional to the thickness of the boundary layer [mg/g].

#### Elovich model

The Elovich kinetic model assumes that the real surface of the solid adsorbent is energetically heterogeneous, otherwise, it describes chemical adsorption on inhomogeneous surfaces. Therefore, it is often used to interpret the kinetics of second-order reactions [11], confirming the assumptions of the PSO model. In differential form, the above model is presented as follows [11]:

$$\frac{dq(t)}{dt} = \alpha \cdot e^{-\beta at} \quad (8)$$

where:  $t$  - time [min],  $\alpha$  - initial adsorption rate [mg/(g·min<sup>-1</sup>)],  $\beta$  - adsorption constant, related to the degree of surface coverage and activation energy for adsorption [mg/g].

### 2.3. Error functions as optimization criteria for adsorption modelling

To determine the adsorption process, its speed and the factors affecting it, equilibrium and sorption kinetics studies are required. To verify the theoretical assumptions of the process. The curves of mathematical models of isotherms or kinetics are fitted to the experimental data. The final choice between them is based on the comparison of one or more statistical criteria describing the degree of model compliance and the correct interpretation of their values [12]. This is a particularly important stage that allows to avoiding modelling errors that affect the correct recognition of the adsorption character. Coefficient of determination ( $R^2$ ), correlation coefficient ( $R$ ), error sum of squared deviations ( $ERRSQ$ ), average relative error ( $ARE$ ), chi-square test ( $\chi^2$ ), complex fractional error function ( $HYBRID$ ), Marquardt's percent standard deviation ( $MPSD$ ), the sum of absolute errors ( $EABS$ ) and relative standard deviation ( $\Delta q$ ) are some of the error functions used to model the adsorption process [12, 13]. The selection of the optimal model consists in minimizing each of these functions, except for  $R^2$  and  $R$ .

## 3. Results of discussion

### 3.1. Modeling of CO<sub>2</sub> adsorption isotherms

The experimental data used to model CO<sub>2</sub> isotherms includes the analysis of the adsorption capacity of activated carbon, where the amount of adsorbed CO<sub>2</sub> at equilibrium was measured depending on the change in its concentration in the volume of the gas mixture (1, 2, 3, 5, 10 and 15%), which corresponds to relative pressures: 0.01, 0.02, 0.03, 0.05, 0.1 and 0.15 atmospheres, at different adsorption temperatures. These are typical values for flue gas under low-pressure conditions, from which carbon dioxide is separated by the carbon adsorbents in the adsorption process. These data were derived from the work [15].

#### 3.1.1. Thermodynamic effects of the adsorption equilibrium

In order to thoroughly understand the thermodynamic phenomena occurring during the adsorption of CO<sub>2</sub> on activated carbon at equilibrium and to confirm the obtained assumptions from the analyzed isotherm models, the change of the standard free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were calculated from Van't Hoff linear equation. The interpretation of the obtained thermodynamic parameters clearly shows that the change of the standard free entropy and enthalpy are independent of the adsorption temperature. Moreover, the negative value of the change in the standard free entropy ( $\Delta S^0 < 0$ ) and enthalpy ( $\Delta H^0 < 0$ ) imply reduced randomness of the CO<sub>2</sub> - adsorbent system, CO<sub>2</sub> degree of freedom, adsorption capacity with temperature intensification, with the exothermic nature of the process. On the other hand, the change in the standard free energy ( $\Delta G^0 < 0$ ) provides information about the more favourable and more spontaneous nature of the process at lower temperatures.

Tab. 1. Comparison of thermodynamic parameters of CO<sub>2</sub> adsorption

$T$ [°C]	$\Delta G^0$ [kJ/mol]	$\Delta S^0$ [kJ/mol·K]	$\Delta H^0$ [kJ/mol]
18	-7.938	-0.0359	-18.384
40	-7.149		
70	-6.073		
100	-4.997		
130	-3.920		

#### 3.1.2. Analysis of the error functions of the adsorption isotherm models

To verify the correctness of linearized and non-linear isothermal models, as well as to determine the choice of the best-fit isotherm model to determine the nature of CO<sub>2</sub> binding, nine commonly used statistical error functions were used to examine the minimum distribution of discrepancies between the experimental and model data. In the case of the linearized form of the adsorption isotherm equations, where the linear regression by the least-squares method was used. The comparison of the obtained error functions reflects the fact that the Freundlich and Halsey isotherms are characterized by the highest values of the determination coefficients:  $R^2 = 0.983 \div 0.993$  with the lowest values ( $\Delta q$ ,  $ERRSQ$ ,  $EABS$ ,  $HYBRID$ ,  $MPSD$ ,  $ARE$ ,  $\chi^2$ ) which means that they are best able to describe the empirical data of CO<sub>2</sub> adsorption equilibrium compared to the Langmuir and Temkin isotherm. A full analysis of the error function of the linearized models is presented below:

$$\begin{aligned} R^2: & \text{Freundlich} = \text{Halsey} > \text{Langmuir} > \text{Temkin} \\ R: & \text{Freundlich} = \text{Halsey} > \text{Langmuir} > \text{Temkin} \\ \Delta q: & \text{Temkin} > \text{Langmuir} > \text{Freundlich} = \text{Halsey} \\ ERRSQ: & \text{Temkin} > \text{Langmuir} > \text{Freundlich} = \text{Halsey} \\ EABS: & \text{Temkin} > \text{Langmuir} > \text{Freundlich} = \text{Halsey} \\ HYBRID: & \text{Temkin} > \text{Langmuir} > \text{Freundlich} = \text{Halsey} \\ MPSD: & \text{Temkin} > \text{Langmuir} > \text{Freundlich} = \text{Halsey} \\ ARE: & \text{Temkin} > \text{Langmuir} > \text{Freundlich} = \text{Halsey} \\ \chi^2: & \text{Temkin} > \text{Langmuir} > \text{Freundlich} = \text{Halsey} \end{aligned}$$

Additionally, non-linearized forms of model equations were analyzed using non-linear regression. The obtained error analysis confirmed the best fit of the Freundlich and Halsey models in most of the

obtained error functions to the experimental data, where the Temkin model was characterized by the highest error values. A comparison was also made between the linear and non-linear forms of the best-fit isotherm models to select the most appropriate form of the equation to study the CO<sub>2</sub> adsorption equilibrium. The obtained results allowed us to conclude that the linear form of the Freundlich and Halsey adsorption isotherms better correlates with the empirical data. The course of curves of the linearized models is shown in Fig. 1., on the example of a temperature 18 °C (the choice was dictated by the highest adsorption capacity as a function of pressure).

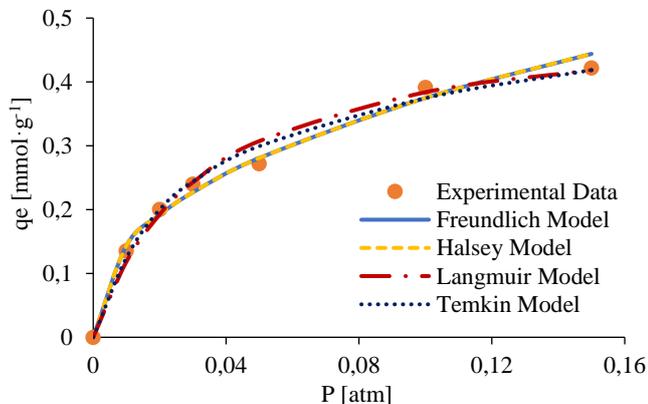


Fig. 1. Curves of linearized models vs. experimental points at 18 °C

### 3.2. Modeling of the kinetics of CO<sub>2</sub> adsorption's mass transport

The research on the kinetics of CO<sub>2</sub> adsorption on activated carbon in the form of a fluidized bed was carried out at the following temperatures: 18, 40, 70, 100 and 130°C, while for a fixed bed: 25, 50, 70 and 90°C - in both cases their initial concentration in the mixture gas (CO<sub>2</sub> + N<sub>2</sub>) was 10% by volume. These data were derived from the works [15, 16]. To study the kinetics of CO<sub>2</sub> adsorption on activated carbon in the form of a fluidized bed and a solid bed, four kinetic models were used to describe the different nature of the process, including: pseudo-first-order model (PFO), pseudo-second-order model (PSO), intramolecular diffusion (IPD) model and Elovich model. The IPD model was not included in the analysis, because it played the role of identifying the exact diffusion mechanism during adsorption. Analyzing the obtained values of the statistical error functions for the linearized model equations, the pseudo-second-order model (PSO) was characterized by the most accurate correlation with the experimental data, which would indicate chemisorption on the adsorbent surface.

However, in the case of the modelling results of the non-linearized models, the error functions of the PFO model are defined as the best fit, characterized by the lowest values ( $\Delta q$ ,  $ERRSQ$ ,  $EABS$ ,  $HYBRID$ ,  $MPSD$ ,  $ARE$ ,  $\chi^2$ ), with the highest coefficients of determination  $R^2 = 0.999$  compared to the PSO and Elovich models, at any temperature (for the fixed and fluidized bed conditions). Based on the results of fitting linearized and nonlinear models, it can be concluded that they are quite diverse. To determine which form of the PFO model best correlates with the experimental data, they were confronted with each other:

$$R^2: PFO(\text{non-linear}) > PFO(\text{linear})$$

$$R: PFO(\text{non-linear}) > PFO(\text{linear})$$

$$\Delta q: PFO(\text{linear}) > PFO(\text{non-linear})$$

$$ERRSQ: PFO(\text{linear}) > PFO(\text{non-linear})$$

$$EABS: PFO(\text{linear}) > PFO(\text{non-linear})$$

$$HYBRID: PFO(\text{linear}) > PFO(\text{non-linear})$$

$$MPSD: PFO(\text{linear}) > PFO(\text{non-linear})$$

$$ARE: PFO(\text{linear}) > PFO(\text{non-linear})$$

$$\chi^2: PFO(\text{linear}) > PFO(\text{non-linear})$$

The above observations suggested that using the non-linear regression method there is no problem with transforming the non-linearized form of the equations into linear forms. In addition, converting a nonlinear equation to a linear form can change its error distribution. That phenomenon is best illustrated by fitting the PFO model curve to the experimental data e.g. for a fluidized bed at 18°C (Fig. 2.).

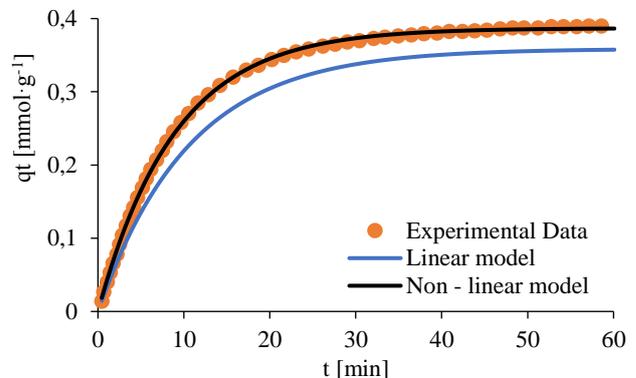


Fig. 2. Model curve vs. experimental points - PFO model at 18 °C for the fluidized bed

Additionally, Fig. 3. and Fig. 4. show the course of curves of non-linearized models for two types of beds at 70 °C (a common process temperature), as those that better correlate with the experimental data than their linear equations.

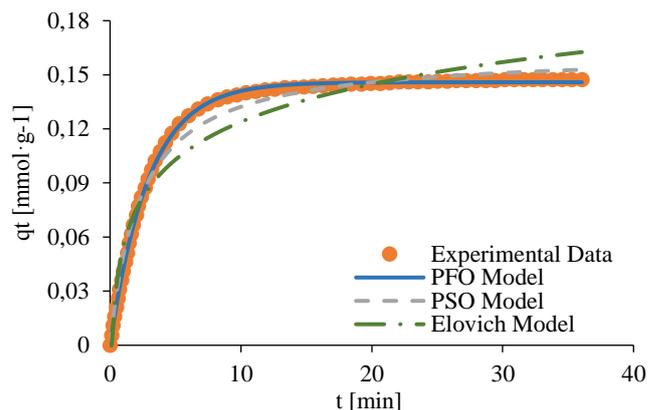


Fig. 3. Curves of non-linearized models vs. experimental points for the fluidized bed

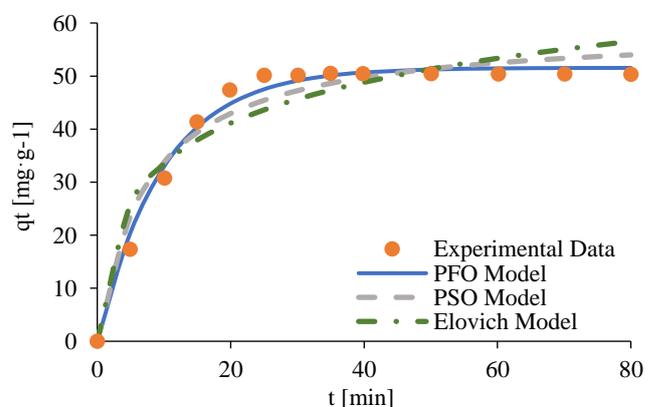


Fig. 4. Curves of non-linearized models vs. experimental points for the fixed bed

### 3.3. Comparison of a fluidized bed and a fixed bed

In order to finally compare the researched beds in the form of activated carbon, the kinetic model best suited to the experimental data was selected, i.e. the non-linearized pseudo-first-order (PFO)

(Tab. 2). As it results from the kinetic modelling, the parameters of the PFO model indicate that for the fluidized bed the adsorption process is much faster. The kinetic constant of the adsorption rate is characterized by higher values with increasing temperature than in the case of the fixed bed. On the other hand, the amount of adsorbed CO<sub>2</sub> at equilibrium for a fixed bed is greater than that adsorbed in the fluidized bed.

Tab. 2. Parameters of the non-linearized PFO model

$T$ [°C]	Parameters of the non-linearized PFO model for a fluidized bed		$T$ [°C]	Parameters of the non-linearized PFO model for a fixed bed	
	$q_{e,mod}$ [mmol · g <sup>-1</sup> ]	$k_1$ [min <sup>-1</sup> ]		$q_{e,mod}$ [mmol · g <sup>-1</sup> ]	$k_1$ [min <sup>-1</sup> ]
18	0.387	0.111	25	2.610	0.0568
40	0.253	0.188	50	1.742	0.0763
70	0.146	0.340	70	1.172	0.102
100	0.0960	0.554	90	0.820	0.132
130	0.0741	0.724	—	—	—

The obtained dependencies correspond closely with the theoretical knowledge. The use of a fluidized bed intensifies the mass exchange between the gas mixture passed and the solid particles of active carbon, through a large surface of interfacial contact and good mixing of the material with the gas phase, which accelerates the adsorption process. However, the effectiveness of the contact of the gas mixture with the fluidized bed is often seriously compromised, in particular by agglomeration of the bed solids at higher temperatures, which has been identified for the two types of beds studied [14]. This phenomenon causes heterogeneity of the material and is characterized by the formation of cracks and channels in its structure, through which the gas phase tends to bypass the adsorbent particles. In practice, the working capacity defined for a short adsorption time is preferable to the equilibrium capacity, which is confirmed by many studies in this field [14].

#### 4. Conclusion

The modelling of adsorption isotherms in the first stage of the work concerned the analysis of the adsorption capacity of active carbon, where the amount of adsorbed CO<sub>2</sub> at equilibrium was measured depending on the change in its partial pressure. According to the statistical analysis, it was found that the Freundlich and Halsey isotherms best correlate with the experimental data in the entire temperature range, due to the highest coefficient of determination ( $R^2$ ) - close to one, with the lowest values of the rest of the function errors, which proves the occurrence of the phenomenon of physical adsorption on Finally, the thermodynamic analysis showed that CO<sub>2</sub> adsorption is a spontaneous process at lower temperatures, where the disruption and randomness of the CO<sub>2</sub> - activated carbon system decreases with increasing temperature, and the process is exothermic by nature, which confirmed the preliminary interpretation of the measurement points and assumptions of the models Freundlich and Halsey.

In the second stage of the research work, the kinetics of the adsorption mass transport was modelled based on measurements of the amount of adsorbed CO<sub>2</sub> as a function of time, from the gas mixture N<sub>2</sub>+CO<sub>2</sub> in a different temperature range, for a fluidized bed and a fixed bed. The obtained model parameters suggested that the initial adsorption rate was increasing, and the amount of adsorbed CO<sub>2</sub> at equilibrium decreased proportionally to increasing temperatures. A comparative statistical analysis of linearized and nonlinearized forms of kinetic models showed that the best fit to the experimental data for two types of deposits was obtained for the non-linearized pseudo-first order (PFO) model. Obtaining such relationships suggests that chemisorption did not play a significant role in shaping the mechanism of the kinetics of CO<sub>2</sub> adsorption on activated carbon.

Finally, two types of the studied beds were compared for the best-fitted model, i.e. non-linearized pseudo-first-order (PFO), where the values of kinetic parameters were interpreted by literature knowledge in the context of intensifying the adsorption method of carbon dioxide separation. The set of parameters suggested faster kinetics for the fluidized bed, while the greater amount of CO<sub>2</sub> in equilibrium was adsorbed by the fixed bed.

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