

Adsorption equilibrium and kinetics of selected phenoxyacid pesticides on activated carbon: effect of temperature

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Abstract The temperature influence on equilibrium and kinetics of adsorption of 4-chlorophenoxyacetic and 3-bromophenoxypropionic acids from aqueous solutions on the Norit activated carbon was studied. The correlations between temperature and parameters characterizing adsorption process were found. Increase of rate of adsorption kinetics of phenoxy pesticides with temperature was observed. The rates of adsorption were best described and fitted by multi-exponential equation; simple approximate solution was obtained by using MOE equation (contribution of second order kinetics was always below 80 %). Intermediate quality of description and good correlation with temperature changes was attained for fractal-like MOE kinetics. Slightly worse results were obtained for rate coefficients estimated by MOE fitting. Model-independent adsorption half-times are proposed as the best single descriptor of the experimental kinetic data. Its temperature dependence is strongly correlated with rate coefficients.

Keywords Pesticide adsorption · Adsorption kinetics · Temperature dependences

1 Introduction

A major problem concerning the environment protection is pollution of waters and wastewaters with pesticides. Although the pesticide production adapts to more restrictive regulations concerning their registration and outlines determining the set on the market, these substances are still the threat to the living organisms because of toxicity, persistence, mobility and bioaccumulation (Foo and Hameed 2010; Lapworth et al. 2012; Ramalho et al. 2013). Moreover, the usage of pesticides is very intensive because they are an effective tool for increasing the food production.

As highly effective and neutral for the environment, the adsorption methods using activated carbon as adsorbent are widely applied. Thus, they constitute an important component of technologies for removal of contaminants from waters and wastewater (Salman and Al-Saad 2012). The adsorption process is complex and dependent on various factors like: structure and surface chemistry of activated carbon (type, concentration of surface groups), the chemical characteristics of adsorbate (polarity, ionic nature, functional groups, solubility) and the properties of adsorption solution (temperature, pH, concentration of adsorbate, presence of other species). The above mentioned factors determine the nature of bonding mechanisms as well as extent and strength of adsorption process (Hopman et al. 1995; Fontecha-Camara et al. 2008; Kim et al. 2005). The adsorption process is a multistage. Each stage is characterized by various types of adsorption kinetics. The slowest stage determines the rate of the whole process. In practical context it seems to be important to get knowledge and understanding of the relationship between the mentioned factors and adsorption efficiency in order to optimize the adsorption methods for water and wastewater

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treatment technologies. Due to scale and universal applications of the adsorption methods, even seemingly small increase of adsorption process efficiency from an environmental and economic point of view seems to be very useful in water purification systems.

The temperature dependences of sorption processes are of great importance in analysis of many natural systems which are subjected to strong temperature changes. Temperatures of waters or wastewaters to be subjected to technological treatment processes can vary in a wide range, depending on seasonal and daily changes. Since the adsorption of organic substances depends substantially on their solubility in water and this property is temperature dependent, the effect of temperature on adsorption is of great interest. Moreover, many other effects should be also taken into account.

Adsorption is a spontaneous process, in many cases it was found to be exothermic, thus, one would expect the adsorption reduction at raising temperature. This is confirmed in many studies of pesticide adsorption on carbon materials (Aksu and Kabasakal 2005; Fontecha-Camara et al. 2006; Pastrana-Martinez et al. 2009; Daneshvar et al. 2007). However, the opposite effects (Fontecha-Camara et al. 2006; Chingombe et al. 2006; Aksu and Kabasakal 2004; Dos Santos et al. 1998) or no relationship between temperature changes and the amount of adsorbed substance (Fontecha-Camara et al. 2006; Hamadi et al. 2004) were also found.

Various explanations of adsorption systems behavior have been proposed indicating exothermic or endothermic nature of process. Aksu and Kabasakal (2005) in the study of 2,4-D adsorption on powdered activated carbon noticed lower adsorption in equilibrium as temperature increases from 25 to 45 °C. Although differentiation in the amounts of adsorbed herbicide at raising temperature of the process was small, it was assumed that the process was exothermic. The results were attributed to the predominant role of surface bonds between organic substance and sorbent, and thus limited number of active sites. Fontecha-Camara et al. (2006) explained the negative trend for the amitrole adsorption on carbon fibers and cloths by the significant increase in solubility at raising temperature related to the hydrophobic interactions reduction. Additionally, it was pointed, that the oscillation energy increase in the adsorbed molecules gave them enough energy to overcome the attraction forces and to desorb to the solution. Analogous observations concerning the temperature dependence of the adsorption process were found for fluroxypyr (Pastrana-Martinez et al. 2009). Minor differentiation in removal of imidacloprid by granular activated carbon at different temperatures was observed by Daneshvar et al. (2007). An increase of 10°, from 25 °C within 90 min time period resulted in a minimal decrease in the pesticide removal efficiency. Such small differences in adsorption were related to energetic effect of the process.

Fontecha-Camara et al. (2006) studied the temperature changes of diuron adsorption on carbon fibers and cloths. The determined diuron adsorption capacity increased with the change of temperature in the range 15–45 °C, while at 35 and 45 °C the pesticide adsorption on the carbon fibers was at the same level. These results were explained by reduction of the herbicide mass transfer resistance in the system due to weakness of the hydrogen bonds between solvent, adsorbed substance and adsorbent. Increasing temperature favors the pollution particles dehydration and taking the flatter spatial conformation (Dos Santos et al. 1998). Flattening of the diuron particles means, they may have an easier access into micropores of adsorbent and possibility to diffuse into both phases. Additionally, increase of the diuron dipole moment leads to strengthening of the interactions with carbon material. Hamadi et al. (2004) in the paraquat adsorption study on the commercial carbon F-300 and on the carbon sorbent obtained by the pyrolysis and activation processes of used tires, did not recognize the adsorption/temperature dependence.

Chingombe et al. (2006) studied the temperature effect in the range 25–45 °C on the adsorption process of 2,4-D and benazoline on pure activated carbon F400 and after thermal modification. The results showed a positive temperature effect. The authors attributed it to endothermic nature of the adsorption systems, confirmed by values of the thermodynamic parameters at different temperatures. Similarly, Aksu and Kabasakal (2004) noticed a positive temperature effect in the case of 2,4-D adsorption on granular activated carbon. They supposed, the trend can be a result of pores size developing, activation of the adsorbent surface or creation of new active sites on the carbon surface by breaking existing bonds. Increasing temperature of the process could also enhance the mobility of 2,4-D ions from the solution bulk phase to the surface of adsorbent, expand the penetration within carbon structure and increase the intermolecular diffusion rate.

The temperature dependences of adsorption are investigated in many equilibrium experiments, however, such studies in the case of adsorption kinetics are rare (Azizian and Yahyaei 2006; Ho and Chiang 2001; Monash and Pugazhenthii 2009; Podkoscielny and Nieszporek 2011; Valenzuela-Calahorra et al. 2004, 2007). Thus, the aim of the presented paper is analysis of the influence of temperature both on adsorption equilibrium and kinetics. The experimental isotherms and concentration profiles were measured. The adsorption isotherms were investigated on the basis of the theory of adsorption on energetically heterogeneous solids. In order to analyze the rate dependences the multi-exponential and mixed-order equations, and diffusion models were used. Thermal analysis was applied to investigate the stability of surface complexes formed between herbicide and carbon.

2 Experimental

2.1 Chemicals and instruments

The experimental activated carbon RIB from Norit was used as adsorbent. Prior to experiment it was washed in concentrated HCl at elevated temperature (60 °C, 6 h) in order to remove partially the mineral impurities. Then, adsorbent was washed with distilled water and dried at 110 °C. Its structural characteristics were estimated from nitrogen adsorption/desorption isotherms: the BET specific surface area, S_{BET} , the total pore volume, V_t (calculated by using the standard methods), and the external surface area, S_{ext} , and the micropore volume, V_{mic} (α_s -plot) (Gregg and Sing 1982). The obtained structure parameters are given in Table 1. The surface charge density was calculated from the potentiometric titration measurements and the point of zero charge was obtained (Table 1). The value of $pH_{PZC} = 7.5$ indicates that at experimental conditions ($pH = 2$) the activated carbon was positively charged.

As adsorbates two herbicides from a group of phenoxyacids were chosen: 4-chlorophenoxyacetic acid (4-CPA) (analytical reagent grade, Sigma-Aldrich), and 3-bromophenoxypropionic acid (3-BrPP) (synthesized and purified in the Department of Organic Chemistry of Maria Curie-Skłodowska University). The physicochemical properties and structures of the herbicides are given in Table 2.

Thermal behavior of adsorbed 4-CPA on the activated carbon RIB was investigated using TG/DSC apparatus coupled with infrared spectroscopy (TG/DSC-IR) technique (STA 449 Jupiter F1, Netzsch, Germany). Temperature programmed desorption involved heating the carbon samples at a programmed heating rate to induce desorption of adsorbed species. The samples were heated at 10 °C min^{-1} rate in the temperature range 298–1173 K. Analyses were carried out for herbicide sample and for the carbon samples loaded with herbicide at different adsorbed amounts.

2.2 Adsorption studies

The equilibrium experiments were carried out by using the static method for 4-chlorophenoxyacetic acid (4-CPA) adsorption from aqueous solutions. The known amounts of adsorbent ($w = 0.04$ g) were contacted with 4-CPA solutions (100 ml) of known concentrations and pH adjusted to

2.2. The Erlenmeyer flasks with adsorption systems were placed in the incubator shaker (New Brunswick Scientific Innova 40R Model) and agitated at 110 rpm speed at established temperatures. The isotherms were measured for the temperatures: 298 and 318 K. After attaining equilibrium the solute concentrations were estimated by applying the UV–Vis spectrophotometer Cary 100 (Varian Inc., Australia).

The adsorbed amounts were calculated from the mass balance equation:

$$a_{eq} = \frac{(c_o - c_{eq}) \cdot V}{w} \quad (1)$$

where a_{eq} is the equilibrium adsorbed amount, c_o is the initial concentration of adsorbate solution, c_{eq} is the adsorbate equilibrium concentration, V is the solution volume, and w is the adsorbent mass.

The experimental adsorption isotherms were analyzed by using the Generalized Langmuir (GL) isotherm equation (Marczewski and Jaroniec 1983; Jaroniec and Marczewski 1984) derived in terms of the general theory of adsorption on energetically heterogeneous solids:

$$a_{eq}/a_m = \left[\frac{(Kc_{eq})^m}{1 + (Kc_{eq})^m} \right]^{m/n} \quad (2)$$

where a_m is the adsorption capacity, m and n are the heterogeneity parameters characterizing the shape (width) and asymmetry of adsorption energy distribution function ($m, n \in (0,1)$), K is the equilibrium constant describing the position of distribution function on energy axis. For specific values of heterogeneity parameters the GL equation reduces to simpler isotherms.

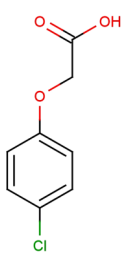
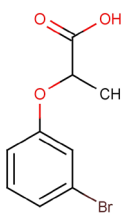
2.3 Kinetic studies

Kinetics measurements were conducted by using the UV–Vis spectrophotometer Cary 100 (Varian Inc., Australia) with a flow cell to cyclically measure a solute concentration in a closed system (Brandt et al. 2007; Marczewski 2007). The concentrations of studied pesticide solutions were chosen to be measured without additional dilution. The aqueous solutions of adsorbates of established initial concentration were contacted with a known amount of adsorbent in a thermostated vessel (thermostat Ecoline RE 207, Lauda, Germany). The solutions were stirred during the experiment by using a digitally controlled mechanical stirrer (110 rpm). Measurements were carried out at 278;

Table 1 Porous structure parameters and the value of pH_{PZC} characterizing RIB activated carbon (Derylo-Marczewska and Marczewski 1999)

Carbon	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{mic} (cm^3/g)	S_{ext} (m^2/g)	Granule size (mm)	pH_{PZC}
RIB	1190	0.64	0.53	70	0.5 × 5.0 cylindrical	7.5

Table 2 Physicochemical properties of the studied herbicides

Herbicide	Structure	M_w (g mol ⁻¹)	pK_a	c_s (mmol dm ⁻³)	Shape size (nm)
4-CPA (4-chlorophenoxyacetic acid)		186.59	3.14	4.8	Prolate 0.43 × 0.94
3-BrPP (3-bromophenoxypropionic acid)		245.07	2.71	2.9	Prolate 0.52 × 0.79

288; 298; 308; 318; 328 K; masses of adsorbent (w) and initial concentration of adsorbates (c_o) were constant.

For analysis of experimental concentration ~ time profiles several kinetic models and equations were applied. Mixed order equation (MOE) being a combination of first-order (FOE) and second-order (SOE) ones was proposed by Marczewski (2010a). This simple analytical equation describes well an intermediate, between FOE and PSOE, behavior of many experimental systems, thus, it may be treated as a model generalization of these relations. The integral form of MOE equation may be presented as follows:

$$\ln\left(\frac{1-F}{1-f_2F}\right) = -k_1t \quad (3)$$

where f_2 is the factor determining share of the second-order type kinetics in the whole process, k_1 is the rate constant, t is time, and F is the adsorption progress defined as:

$$F = \frac{a}{a_{eq}} = \frac{u}{u_{eq}}, \quad \text{where } u = \frac{c_o - c}{c_o} = 1 - \frac{c}{c_o}, \quad (4)$$

$$u_{eq} = \frac{c_o - c_{eq}}{c_o} = 1 - \frac{c_{eq}}{c_o},$$

In the above: c is the temporary solution concentration, a is the actual adsorbed amount, u is the relative change of adsorbate concentration, u_{eq} is the relative change of concentration determined at equilibrium (relative adsorbate uptake).

This equation may be considered as semi-empirical, as it is mathematically identical to the integrated Langmuir kinetic equation (IKL, Marczewski 2010b), later generalized to adsorption/desorption phenomena (gIKL, Marczewski et al. 2013). In IKL, equivalent of parameter f_2 is Langmuir equilibrium batch factor f_{eq} which is related to

the equilibrium conditions, $f_{eq} = \theta_{eq}u_{eq}$ where θ_{eq} is the relative adsorption an equilibrium (corresponding to Langmuir isotherm). For $f_2 = f_{eq} = 0$ the first-order kinetics will be obtained (always when adsorption is very small, $\theta_{eq} \ll 1$, or when concentration changes slightly, $u_{eq} \ll 1$). The second-order kinetics ($f_{eq} = 0$) will appear in Langmuir model only when simultaneously $\theta_{eq} \approx 1$ and $u_{eq} \approx 1$.

As very useful for description of typical experimental systems, the multi-exponential equation (m-exp) may be regarded (Marczewski 2007, 2008, 2010a, b; Marczewski et al. 2009). It may be treated as a series of parallel kinetic processes of the first-order type (for adsorption systems structurally and energetically heterogeneous) or approximate a series of follow up processes (e.g. inside the system of interconnected pores of differentiated sizes).

$$c = (c_o - c_{eq}) \sum_{i=1}^n f_i \exp(-k_i t) + c_{eq} \quad (5)$$

where $\sum_{i=1}^n f_i = 1$

$$a = a_{eq} - a_{eq} \sum_{i=1}^n f_i \exp(-k_i t), \quad (6)$$

In the above the coefficients f_i ($i = 1, 2, \dots, n$) determine a fraction of an adsorbate adsorbed with a rate characterized by k_i .

The multi-exponential equation characterizes well the experimental systems in which the first fast stage is followed by slower adsorption stages. It may be fitted to many data when the other equations or models failed.

The model of intraparticle diffusion (IDM) was investigated by Crank (1975). Under the assumption of a spherical shape of adsorbent particles, and a variable adsorbate concentration in adsorption process one obtains:

$$F = 1 - 6(1 - u_{eq}) \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{p_n^2 Dt}{r^2}\right)}{9u_{eq} + (1 - u_{eq})^2 p_n^2}, \tag{7}$$

$$\tan p_n = \frac{3p_n}{3 + \left(\frac{1}{u_{eq}} - 1\right)p_n^2}$$

In the above: p_n are non-zero roots of a function $\tan p_n$, D is the effective diffusion coefficient, r is the adsorbent particle radius.

If the change of concentration during adsorption process is negligible ($c(t) \approx c_{eq} \approx c_o$, i.e. $u_{eq} \approx 0$) this equation is simplified to:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 Dt}{r^2}\right) \tag{8}$$

Independently of the uptake and other parameters, the Crank IDM model in the initial period of adsorption ($F < 0.3$) is reduced to Weber-Morris equation corresponding to the linear dependence of adsorbed amount on root of time ($F \sim t^{1/2}$).

Another, so called pore diffusion model (PDM) was proposed by McKay et al. (1996). It is based on additional assumptions: resistance during adsorbate transfer through surface layer, proportional penetration of adsorbate molecules into adsorbent granules, a sharp boundary between a space in which an adsorption equilibrium is established and a space without adsorbate:

$$\frac{dF}{d\tau_s} = \frac{3(1 - u_{eq}F)(1 - F)^{1/3}}{1 - B(1 - F)^{1/3}} \tag{9}$$

$$\tau_s = \frac{1}{6u_{eq}} \left\{ \left(2B - \frac{1}{b}\right) \ln \left[\frac{x^3 + b^3}{1 + b^3} \right] + \frac{3}{a} \ln \left[\frac{x + b}{1 + b} \right] \right\} + \frac{1}{b\sqrt{3}u_{eq}} \left\{ \arctan \left(\frac{2 - b}{b\sqrt{3}} \right) - \arctan \left(\frac{2x - b}{b\sqrt{3}} \right) \right\} \tag{10}$$

In the above: τ_s is the non-dimensional model time, $x = (1 - F)^{1/3}$, $b = (1/u_{eq} - 1)^{1/3}$, $B = 1 - Bi$, Bi is the Biot number defined as $Bi = K_f/D_p$, K_f is the external mass transfer coefficient, D_p is the effective pore diffusion.

McKay PDM model—unlike the IDM—reproduces initial linear *adsorption ~ time* dependence, however, due to simplifying assumptions of model the equilibrium is attained after a definite time, which is in contrary with experiment and another theories, which assume that a system may be very close to equilibrium but not exactly in it (Marczewski et al. 2013).

Haerifar and Azizian (2012) proposed new equation based on the fractal-like kinetic model which can be applied for analysis of complex adsorption systems. The fractal-like MOE (f-MOE) may be expressed as follows:

$$\ln \frac{1 - F}{1 - f_2 F} = -(k_1 t)^p \tag{11}$$

$$\text{if } f_2 < 1 \quad F = \frac{1 - \exp(-(k_1 t)^p)}{1 - f_2 \exp(-(k_1 t)^p)} \tag{12}$$

$$\text{if } f_2 = 1 \quad F = \frac{(k_2 t)^p}{1 + (k_2 t)^p} \tag{13}$$

In the above p is fractal coefficient usually close to 1. This equation was later applied to analysis of adsorption/desorption data of aromatic acids (Marczewski et al. 2013).

Many authors use different kinetic equations obtaining similar quality of fit despite quite divergent assumptions. This phenomenon was discussed e.g. by Plazinski et al. (2009) and Marczewski (2007, 2010a).

3 Results and discussion

The influence of temperature on adsorption equilibrium is presented in Fig. 1 for 4-CPA adsorbed from aqueous solution at pH = 2; the isotherms measured at 298 and 318 K are compared. The observed decrease of adsorption with temperature increase indicate the exothermic character of the process. This negative temperature effect may be explained by an increase of 4-CPA solubility in water with temperature increase; as a consequence it lowered its hydrophobicity and its relative affinity to the carbon surface. Moreover, an increase of oscillation energy in adsorbed molecules favors their desorption from carbon surface to solution. These results are similar to those obtained in analysis of other adsorption systems (Aksu and Kabasakal 2005; Fontecha-Camara et al. 2006; Pastrana-Martinez et al. 2009). However, the opposite temperature effect was also found for several experimental systems.

The experimental data for 4-CPA adsorption were analyzed by using the Generalized Langmuir equation (GL). The solid lines in Fig. 1 are best fit lines optimized by GL equation; one can find that this equation describes well the studied adsorption systems. Moreover, in Table 3 the values of GL equation parameters are presented. The values of heterogeneity parameter n equal to unity means that it is the Generalized Freundlich isotherm, a special case of GL equation, which is the best one for analysis of both adsorption systems. On the other hand, very small values of the second heterogeneity parameter, m , indicate high energetic nonhomogeneity of the systems studied. The common value of optimized adsorption capacities is 4.77; this value is slightly lower than 4.97 mmol/g estimated by using adsorbent porosity and adsorbate density data. It means that the optimized adsorption capacity is a reasonable value with physicochemical significance.

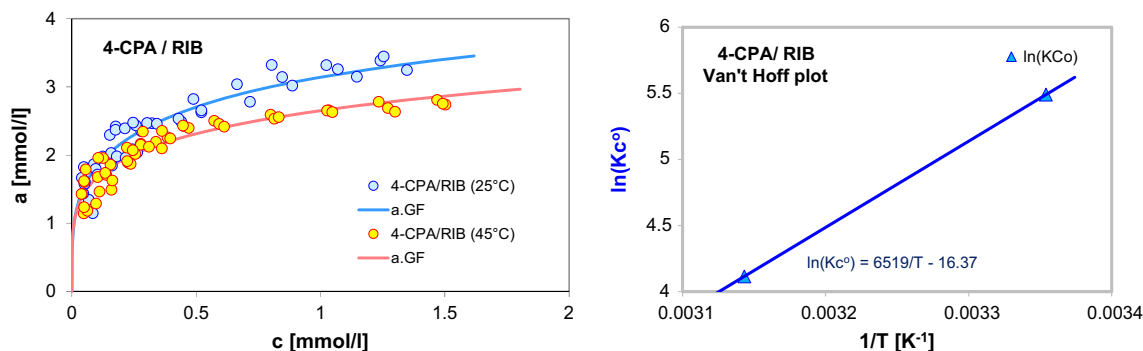


Fig. 1 The isotherms and van't Hoff plots for 4-CPA adsorption from aqueous solutions at 298 and 319 K (GL-fitted to experimental isotherm data—the solid lines) (Color figure online)

Table 3 Values of parameters of the generalized Langmuir (GL) isotherm equation characterizing the adsorption systems studied

Adsorption system	a_m	m	n	$\log K$	R^2	$SD(a)$
4-CPA/RIB (298 K)	4.77	0.26	1	-0.62	0.888	0.207
4-CPA/RIB (318 K)	4.77	0.21	1	-1.21	0.880	0.160

The values of coefficients of determination R^2 and the standard deviation SD are also given

By using van't Hoff equation $\frac{d \ln K_a}{dT} = \frac{\Delta H_a^\circ}{RT^2}$ and relation between adsorption equilibrium constant K_a and Gibbs free energy $\ln K_a = -\Delta G_a^\circ / (RT)$, and $\Delta G_a^\circ = \Delta H_a^\circ - T\Delta S^\circ$ we can estimate the values of thermodynamic functions: enthalpy, entropy and Gibbs free energy. In order to use experimental equilibrium constant K values we should rescale it with respect to standard conditions. It is typically done by using standard concentrations $c^\circ = 1 \text{ mol/l}$ (then $K_a = Kc^\circ$), one may also use molar or volume fractions, with e.g. pure component as reference state. If we take standard concentration as $c^\circ = 1 \text{ mol/l}$, we have:

$$\ln(Kc^\circ) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

By using these assumptions the following values from the plot $\ln(Kc^\circ)$ versus $1/T$ (Fig. 1) were obtained: $\Delta H^\circ = \Delta H_a = -54.2 \text{ kJ/mol}$, $\Delta S^\circ = -0.14 \text{ kJ/(mol K)}$, $\Delta G^{298} = -13.6 \text{ kJ/mol}$, $\Delta G^{318} = -10.2 \text{ kJ/mol}$. The negative value of enthalpy means that the process of 4-CPA adsorption is enthalpy favored, whereas entropy has low but negative value, partially negating the enthalpy effect, though the Gibbs free energy remains negative, which confirms process spontaneity. However, one should remember, that the equilibrium constant in GF isotherm is related to the minimum adsorption energy of the GF distribution (Jaroniec and Marczewski 1984; Marczewski

et al. 1988), i.e. to the weakest adsorption sites. It means that the average site will be characterized by much higher values of K , $-\Delta H$ and $-\Delta G$.

The kinetic dependences were measured and analyzed for 4-chlorophenoxyacetic acid (4-CPA) and 3-bromophenoxypropionic acid (3-BrPP) adsorption on RIB carbon at a wide temperature range. Basing on analysis of the Bangham plots (Aharoni et al. 1979) it is possible to identify a sorption mechanism (see Supplementary material, Fig. S1). The initial slopes are close to 1.0 and in a time range 20 to 1000 min their values are within 0.77–0.85 (4-CPA) and 0.70–0.83 (3-BrPP), showing that pure IDM mechanism (slope ~ 0.5) cannot be applied. Thus equations allowing for linear initial time rate dependence should be favored.

In further analysis various kinetic equations and models were applied. In Fig. 2 the experimental data for 4-CPA adsorption are presented as the concentration and adsorption profiles. In order to improve data clarity, initial parts of kinetic plots were enlarged. We may clearly see that the initial kinetic curves are always linearly dependent on time. Strong dependence of adsorption kinetics on temperature is observed; adsorption rate strongly increases with temperature increase. The solid lines were obtained by fitting multi-exponential equation (see Table 4). By using fitted parameters, adsorption half-times ($t_{0.5} = t(F = 0.5)$) were determined.

In order to analyze temperature dependences of kinetic data either Arrhenius or Eyring relations are used (Eyring 1935a, b; Laidler and King 1983, Peterson 2000). Arrhenius absolute rate theory suggests that:

$$k_{rate}(T) \approx A \exp(-E^*/RT) \quad (15)$$

where E^* is the activation energy and A is pre-exponential factor related to the frequency of collisions.

Later several researchers (including Tolman, Wigner, Polanyi) were working on this simple theory, and in 1935 Eyring (1935a, b) and independently Evans and Polanyi (1935) derived a new equation:

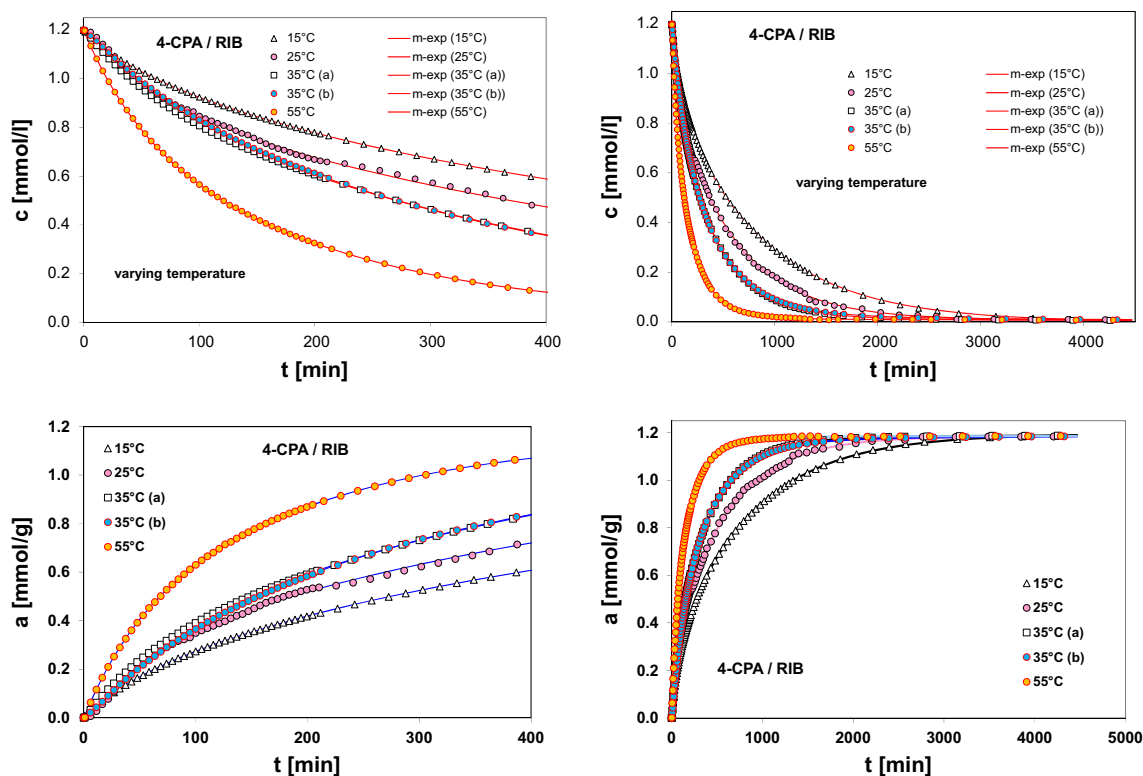


Fig. 2 The comparison of concentration and adsorption profiles measured for 4-CPA adsorption from aqueous solutions at various temperatures (entire curves and initial parts). *Solid lines* represent multi-exponential best fits (Color figure online)

Table 4 Adsorption kinetics of 4-CPA on RIB carbon—optimized parameters of m-exp Eq. (5)

System (°C)	$f_1, \log k_1$	$f_2, \log k_2$	$f_3, \log k_3$	u_{eq}	$t_{0.5}$ (min)	SD(c)/c ₀ (%)	1-R ²
15	0.046; -1.44	0.189; -2.13	0.765; -2.94	1	387.4	0.096	9.5 × 10 ⁻⁶
25	0.233; -1.81	0.767; -2.77		0.9934	255.7	0.713	5.0 × 10 ⁻⁴
35 (a)	0.163; -1.74	0.796; -2.57	0.041; -3.01	0.9956	200.5	0.053	2.5 × 10 ⁻⁶
35 (b)	0.204; -1.99	0.761; -2.57	0.035; -3.16	0.9937	202.9	0.143	1.8 × 10 ⁻⁵
55	0.260; -1.67	0.702; -2.26	0.039; -2.74	0.9932	89.6	0.113	1.3 × 10 ⁻⁵

$$k_{rate}(T) = \frac{kT}{h} Q(T) \exp(-E^*/RT) \tag{16}$$

where k is the Boltzmann constant, h is Planck constant and $Q(T)$ is a temperature dependent function related to the partition functions of the molecules. After rearrangement we obtain:

$$\frac{k_{rate}(T)}{T} \approx q_T \exp(-E^*/RT). \tag{17}$$

As we can see those 2 equations actually differ in treatment of the pre-exponential factor—despite that, if some data set is linear in one of the plots it is usually linear in the other one, because the changes of the exponential factor are much larger. However, in order to use any of

those two approaches, one has to define the rate constant. Whereas it is a simple matter for chemical reactions, it becomes a problem for adsorption kinetics, especially if system porosity and energetic heterogeneity is involved. Then the rate constant definition will depend on the model or equation employed. Thus we propose to use model-independent and experimentally determinable adsorption half-time, $t_{0.5}$, instead of model dependent rate coefficient to find temperature dependence of adsorption kinetics. Moreover, for many kinetic equations simple relations with rate parameters exist (e.g. for f-MOE and MOE: $t_{0.5} = [\ln(2 - f_2)]^{1/p} / k_1$ - if $p = 1$ we have MOE, if $f_2 = 0$ we have FOE and f-FOE; for f-SOE and SOE: $t_{0.5} = 1/k_2$; for MPFO: $t_{0.5} = (\ln 2 - \frac{1}{2}) / k_1$). As we can see,

typical relation is $t_{0.5} = B/k_{rate}$ (where B is model dependent constant) whereas for other ones half-times must be obtained numerically (m-exp, PDM, IDM etc.). Thus we may also expect that logarithm of half-time will be a linear function of reciprocal temperature

$$\ln t_{0.5} \approx \ln B - \ln A + \frac{E^*}{RT} \quad (18)$$

or will be near-linear function of reciprocal temperature

$$\begin{aligned} \ln(t_{0.5}T) &\approx \ln B - \ln q_T + \frac{E^*}{RT} \quad \text{and} \\ \ln t_{0.5} &\approx \ln B - \ln(q_T T) + \frac{E^*}{RT} \end{aligned} \quad (19)$$

Thus we can see, that we may easily replace rate coefficients by adsorption half-times and obtain the same thermodynamic constants. For backwards compatibility we may calculate rate constants by using model-specific rate constant relation with adsorption half-time.

In Fig. 3 dependence of logarithm of half-times on $1/T$ for 4-CPA adsorption is presented (their values were estimated by using best-fitted parameters of multi-exponential equation); this dependence has a clearly linear character. It allows to estimate the adsorption activation energy as 28.1 kJ/mol.

As optimization of other equations IDM (see Fig. S2, S3 in Supplementary material), PDM (see Fig. S5) as well as MOE and f-MOE (below), produced much worse fit, we should prefer to derive thermodynamic data by using the proposed method instead of any of the corresponding fitted rate constants.

Regarding the complexity of the studied systems the fractal-like kinetic model was also used for analysis of 4-CPA kinetic data. In Fig. 4 the kinetic data are compared with the fitted lines representing f-MOE. Fit quality was satisfactory (deviation were smaller than for MOE), but much worse than for multi-exponential equation. Even

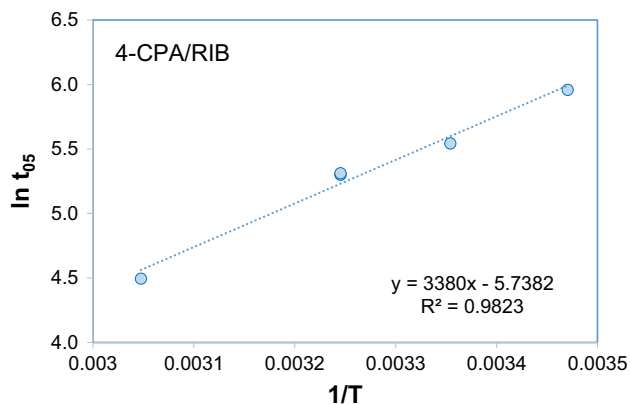


Fig. 3 The dependence of logarithm of half-times (derived from m-exp best fits) on $1/T$ for 4-CPA adsorption from aqueous solutions at various temperatures

though fractal-like MOE may describe certain type of deviations from Langmuirian kinetics, it is less flexible than multi-parameters equations like m-exp.

In Fig. 5 the dependences of fractal parameter p as well as logarithms of rate parameters: rate constant, k_f , k_f/T , and half-time, $t_{0.5}$ (evaluated from fitted f-MOE parameters), on $1/T$ for 4-CPA adsorption are shown. These dependencies have a linear character in agreement with the analysis shown above. Fractal parameter grows with temperature (approximately linear decay with increasing reciprocal temperature). Logarithms of adsorption half-times and negative logarithms of rate constants and constants divided by temperature grow linearly with reciprocal temperature (decrease with temperature) with almost identical slopes (E^*/R). By comparing thus calculated activation energies we see that the value determined from half-time data (27.9 kJ/mol) is intermediate of Arrhenius (28.9 kJ/mol) and Eyring (26.3 kJ/mol) plots and very similar to the value 28.1 kJ/mol estimated by using fitted m-exp parameters (Fig. 3).

In Table 5 all performed optimization for 4-CPA/RIB kinetic data are compared (Tables S1, S2, S5, S6 and S10 with IDM, MOE, f-MOE and PDM parameters are in Supplementary material). By far the best description is obtained for m-exp, then PDM and finally f-MOE equations. Fitting by using IDM is worse than even a simple Lagergren equation.

In Fig. 6 experimental kinetic curves for 3-BrPP adsorption are presented as the concentration and adsorption profiles versus time and time^{1/2} and initial parts of kinetic plots were enlarged to emphasize characteristic data behavior. Similarly to 4-CPA the initial part of kinetic curves is linear in a time scale and highly non-linear in Weber-Morris coordinates. Similar to 4-CPA strong increase of adsorption rate with increase of temperature is observed. The solid lines were obtained by fitting multi-exponential equation (see Table 6).

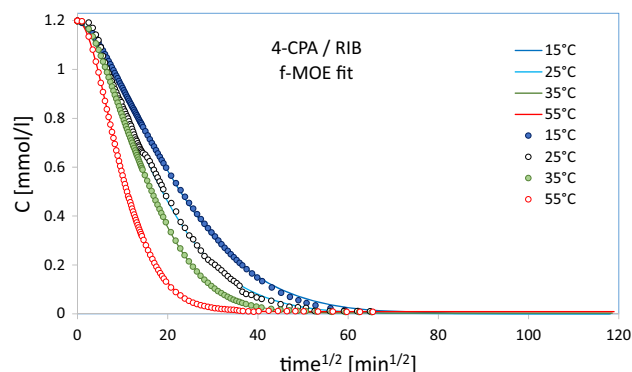


Fig. 4 Concentration profiles of 4-CPA adsorption on RIB in $t^{1/2}$ scale. Lines are fractal-like MOE (f-MOE) fits (Color figure online)

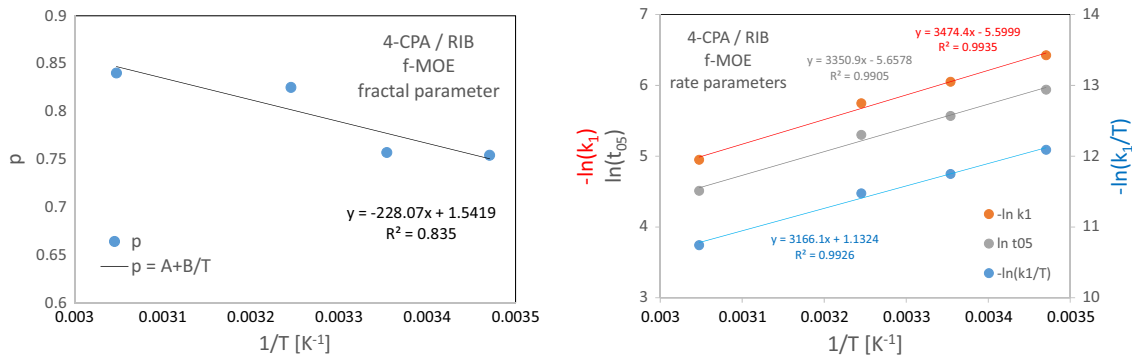


Fig. 5 The temperature dependence of fractal parameter p and rate parameters of fractal-like MOE equation for 4-CPA adsorption from aqueous solutions (Color figure online)

Table 5 Comparison of fitting quality for 4-CPA on RIB and various kinetic equations

System (°C)	m-exp (5) SD(c)/c ₀ (%)	MOE (5) SD(c)/c ₀ (%)	f-MOE (12) SD(c)/c ₀ (%)	IDM (7) SD(a)/a _{eq} (%)	IDM (8) SD(a)/a _{eq} (%)	PDM (9) SD(c)/c ₀ (%)
15	0.096	1.424	0.639	11.67	4.17	0.245
25	0.713	1.672	1.214	12.18	4.09	0.895
35 (a)	0.053	0.757	0.373	13.21	4.78	0.479
35 (b)	0.143	0.228	0.506	13.84	5.72	0.288
55	0.113	0.244	0.471	11.83	3.93	0.308

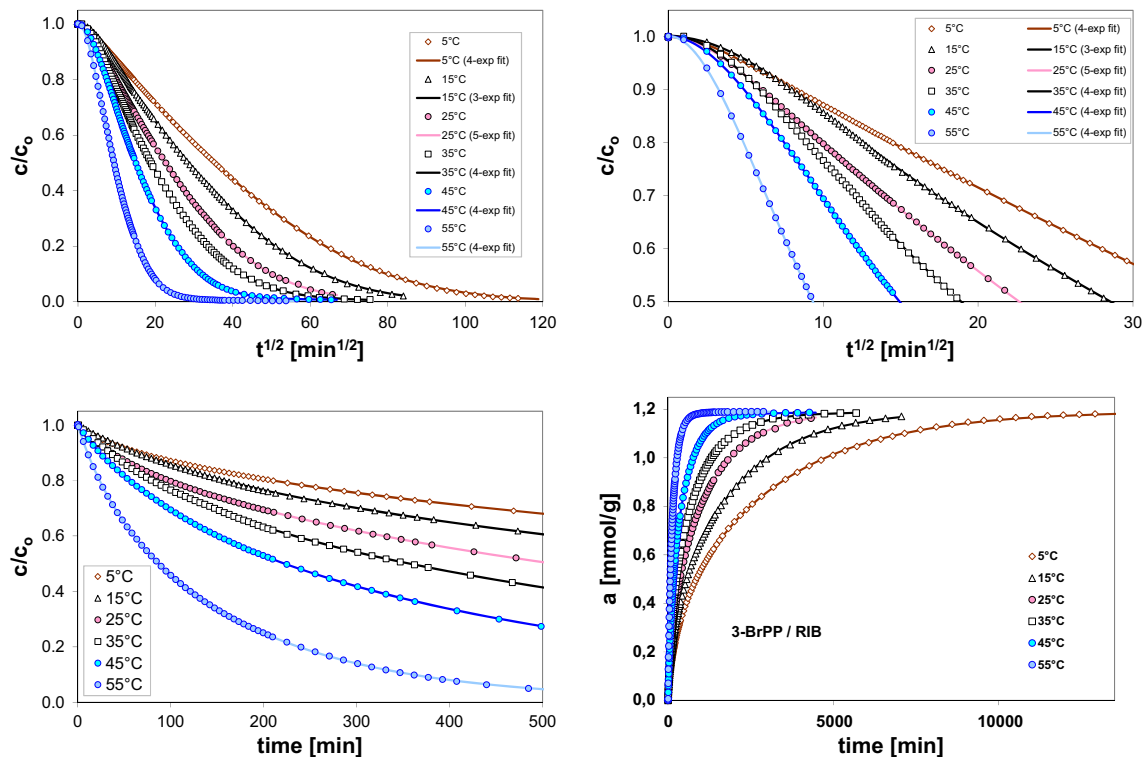


Fig. 6 The comparison of concentration and adsorption profiles measured for 3-BrPP adsorption from aqueous solutions at various temperatures (entire curves and initial parts). *Solid lines* represent multi-exponential best

fits. Concentration profile is drawn vs. $t^{1/2}$ to show incompatibility with IDM model, whereas adsorption and initial concentration profiles are plotted in linear time scale (Color figure online)

In Fig. 7 dependence of logarithm of 3-BrPP adsorption half-times on reciprocal temperature is shown (half-time values estimated by using best-fitted parameters of multi-exponential equation)—like for 4-CPA this dependence is linear and allows to estimate adsorption activation energy as 31.5 kJ/mol.

Figure 8 compares experimental 3-BrPP data and fitted IDM curves in Weber-Morris coordinates. Full IDM model (Eq. 17) was first used with very low quality of fit (typically $SD(c)/c_0$ was $\sim 10\%$), which showed that this model cannot describe such data. However, the simplified IDM model (Eq. 18) (alternatively, Eq. 17 with disassociated c_{eq} and u_{eq} parameters) was used much more successfully, though the fitting quality (Supplementary material, Fig. S2 for 4-CPA and S3 for 3-BrPP) remained much below m-exp, f-MOE (below Fig. 9 and Fig. S4) or McKay (Supplementary material, Fig. S5) fitting.

In the following Fig. 9 experimental data of 3-BrPP adsorption is compared with f-MOE-fitted kinetic curves. Though the fit quality was worse than for multi-exponential equation, it was quite satisfactory for such a simple equation. Its simplicity makes its optimized parameters relatively stable and allows to use them to derive some synthetic parameters, e.g. temperature dependences.

In Fig. 10 the dependences of fractal parameter p as well as logarithms of rate parameters: rate constant, k_1 , k_1/T , and half-time, $t_{0.5}$ (evaluated from fitted f-MOE parameters), on $1/T$ for 3-BrPP adsorption are shown. Estimated fractal parameter grows with temperature (approximately linear decay with increasing reciprocal temperature). Logarithms of adsorption halftimes and negative logarithms of rate constants and constants divided by temperature grow linearly with reciprocal temperature (decrease with temperature) with almost identical slopes (E^*/R). By comparing thus calculated activation energies we see that the value determined from half-time data (30.4 kJ/mol) is intermediate of Arrhenius (31.8 kJ/mol) and Eyring (29.3 kJ/mol) plots and smaller than the value 31.5 kJ/mol estimated from m-exp fitted parameters (Fig. 7). However, those values for 3-BrPP are by $\sim 10\%$ (2.5–3.0 kJ/mol) larger

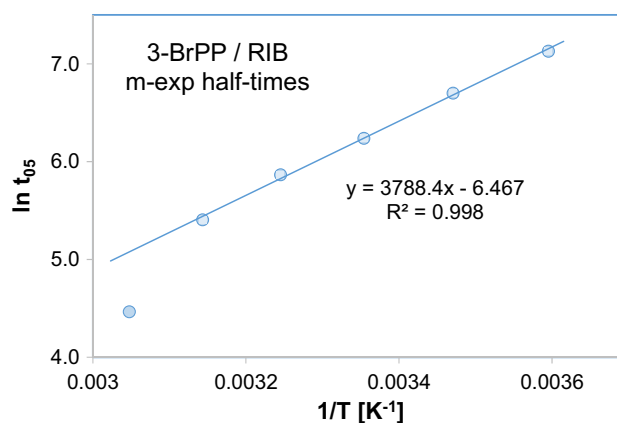


Fig. 7 The dependence of logarithm of half-times (derived from m-exp best fits) on $1/T$ for 3-BrPP adsorption from aqueous solutions at various temperatures

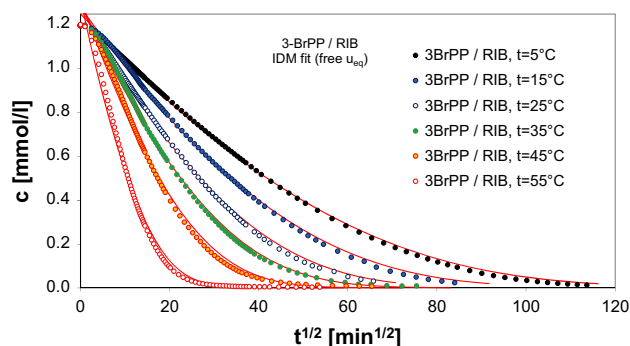


Fig. 8 Concentration profiles of 3-BrPP adsorption on RIB in $t^{1/2}$ scale (Weber-Morris plot). Lines are intraparticle diffusion model (IDM) with dissociated uptake and equilibrium concentration (equation for $c = \text{const}$) (Color figure online)

than for 4-CPA adsorption, which may be related to its larger size and differences in chemical properties.

In Table 7 all performed optimization for 3-BrPP/RIB kinetic data are compared (Tables S3, S4, S7, S8 and S9 with IDM, MOE, f-MOE and PDM parameters are in Supplementary material). Like in the case of 4-CPA, by far the best description is obtained for m-exp, then PDM and

Table 6 Adsorption kinetics of 3-BrPP on RIB carbon—optimized parameters of m-exp Eq. (5)

System (°C)	$f_1, \log k_1$	$f_2, \log k_2$	$f_3, \log k_3$	$f_4, \log k_4$	u_{eq}	$t_{0.5}$ (min)	$SD(c)/c_0$ (%)	$1-R^2$
5	0.031; -1.37	0.082; -2.07	0.180; -2.75	0.707; -3.51	1	1248.9	0.122	1.4×10^{-5}
15	0.117; -2.02	0.164; -2.57	0.719; -3.31		1	812.6	0.128	1.8×10^{-5}
25	0.079; -1.61	0.158; -2.27	0.273; -2.91	0.490; -3.16	1	512.2	0.087	8.6×10^{-6}
35	0.027; -1.59	0.219; -2.09	0.492; -2.83	0.262; -3.09	0.996	352.9	0.132	1.6×10^{-5}
45	0.016; -1.19	0.231; -1.98	0.739; -2.68	0.014; -3.79	1	222.5	0.073	4.7×10^{-6}
55	0.026; -1.17	0.180; -1.63	0.785; -2.23	0.009; -3.37	1	87.0	0.094	9.0×10^{-6}

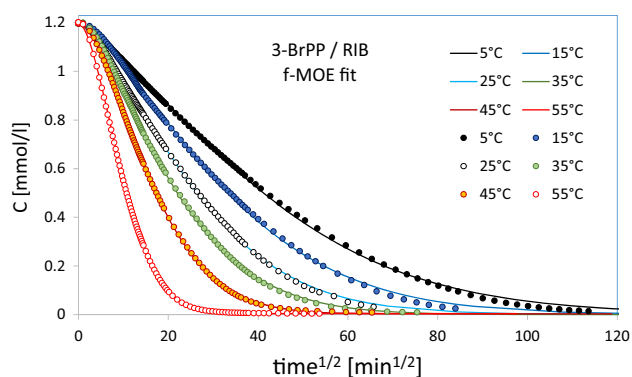


Fig. 9 Concentration profiles of 3-BrPP adsorption on RIB in $t^{1/2}$ scale. Lines are fractal-like MOE (f-MOE) fits (Color figure online)

finally f-MOE equations, while fitting by using IDM is plainly unacceptable.

Thermal analysis is a useful tool for investigating the stability of surface complexes. In Fig. 11 the TG, DTG and DSC curves measured for the pure 4-CPA (a) and the carbon loaded with various amounts of adsorbate: 0.5 mmol/g (4-CPA(1)/RIB) (b) and 2.06 mmol/g (4-CPA(2)/RIB) (c), are presented. Analyzing these dependences for pure herbicide one can observe two endothermic peaks above its melting point which is about the

temperature range of 157–159 °C. They are connected with a structure of the herbicide like the existence of aromatic ring and multiple bond. The first peak at 167 °C is hardly visible on the DTG curve (which corresponds to a small mass loss) but well defined on the DSC curve. The second peak at 269 °C is predominant (the mass loss about 98 %). Endothermic character of peaks indicates that no decomposition occurs in the evaporation of the herbicide.

The processes of thermal degradation of the activated carbon loaded with a given amount of herbicide show two or three stages. For the adsorbate/adsorbent system with the smaller adsorbed amount 0.5 mmol/g, the minimum located at about 60 °C is found, that is related to removing hygroscopic and physisorbed water. The process is endothermic as it results from the DSC curve. With increasing temperature the exothermic small bimodal peaks with minima at 207 and 237 °C (Fig. 1b) or single wide and distinguished peak with minimum at 218 °C (Fig. 1c) are observed. The processes of herbicide thermodesorption and volatile products of the adsorbate melting release occur. Comparing the mass loss in the temperature range 150–320 °C (3.73 and 13.92 % for 4-CPA(1)/RIB and 4-CPA(2)/RIB, respectively) differentiation about four times is obtained which is consistent with the differences in capacities of given systems.

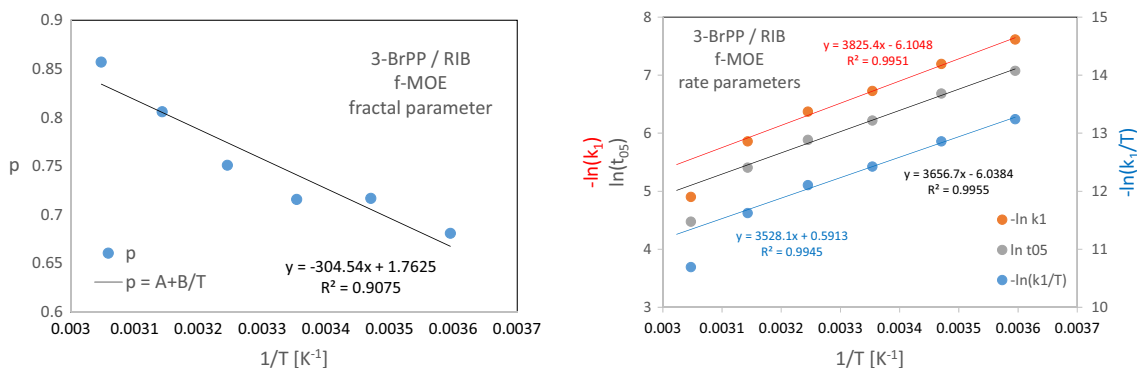
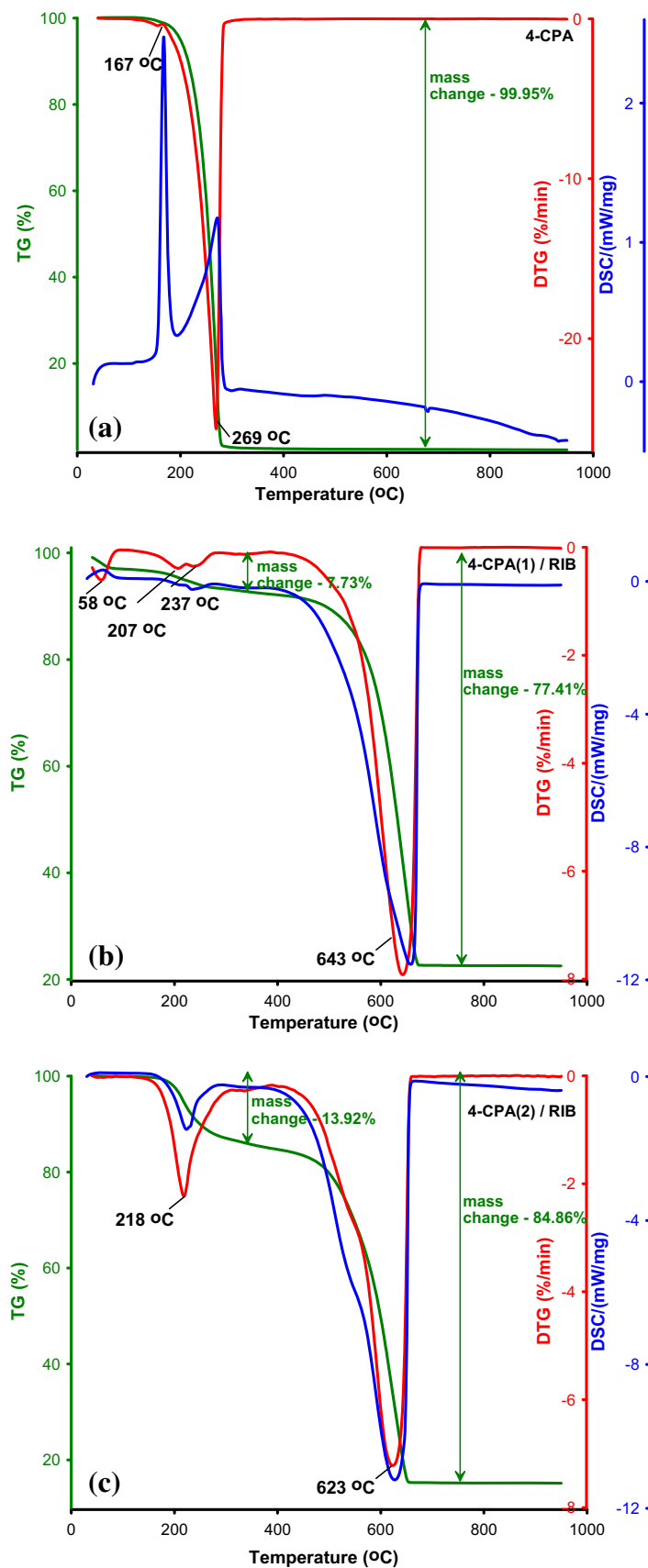


Fig. 10 The temperature dependence of fractal parameter p and rate parameters of fractal-like MOE equation for 3-BrPP adsorption from aqueous solutions (Color figure online)

Table 7 Comparison of fitting quality for 3-BrPP on RIB and various kinetic equations

System (°C)	m-Exp (5) SD(c)/c ₀ (%)	MOE (3) SD(c)/c ₀ (%)	f-MOE (12) SD(c)/c ₀ (%)	IDM (7) SD(a)/a _{eq} (%)	IDM (8) SD(a)/a _{eq} (%)	PDM (9) SD(c)/c ₀ (%)
5	0.122	2.113	1.053	10.43	2.50	0.269
15	0.128	1.886	0.827	10.35	3.76	0.240
25	0.087	1.699	0.610	10.45	3.53	0.253
35	0.132	1.087	0.637	11.84	4.13	0.325
45	0.073	0.655	0.398	12.84	4.60	0.302
55	0.094	0.401	0.267	12.26	4.10	0.350

Fig. 11 TG, DTG and DSC curves measured for the pure 4-CPA (a) and for the carbon with adsorbed herbicide (adsorbed amount 0.5 mmol/g) (b) and (adsorbed amount 2.06 mmol/g) (c)



In the temperature range 400–690 °C the exothermic process of carbon surface and bulk oxidation takes place (minimum at 623 or 643 °C). Width and asymmetry of a corresponding peak result from complexity of the processes. The mass loss for this predominant stage is approximately 70 %. Oxidation of bulk activated carbon is related to oxygen diffusion into the micropores. Comparing the main peak for 4-CPA(1)/RIB with the one for 4-CPA(2)/RIB one can observe shift towards lower temperatures on the DTG curves. This indicates the changes of thermal stability of the systems.

4 Conclusions

In the paper the influence of temperature on adsorption equilibria and kinetics was studied for two herbicides: 4-chlorophenoxyacetic acid (4-CPA) and 3-bromophenoxypropionic acid (3-BrPP). The equilibrium studies were undertaken for 4-CPA adsorption from aqueous solutions at 298 and 318 K on activated carbon. Decrease of 4-CPA adsorption with temperature increase was observed and explained by a decrease of its hydrophobicity (increase of solubility in water) with temperature increase and an increase of oscillation energy in adsorbed molecules which favored their desorption from adsorption phase to bulk one.

The experimental equilibrium data were well described by the Generalized Freundlich, a special case of the Generalized Langmuir equation. The small values of heterogeneity parameter confirm high nonhomogeneity of the studied system. From the temperature dependences the values of thermodynamic functions were estimated: enthalpy (negative value), entropy (negative but low value), Gibbs free energy (negative value), which show that the process of 4-CPA adsorption is enthalpy favored and it is spontaneous.

The kinetic measurements were performed for 4-CPA and 3-BrPP at a wide temperature range and the experimental data were analyzed by using the fractal-like kinetic model, f-MOE, PDM, and MOE models as well as the multi-exponential equation. Bangham plots revealed that the adsorption kinetics do not follow the pure IDM mechanism, thus, the equations allowing for linear initial time rate dependence were better for analysis of the studied systems. Strong dependences of adsorption kinetics on temperature were found; adsorption rates increased with temperature for all studied systems.

The kinetic temperature dependences were analyzed by using the Arrhenius and Eyring relations. In order to avoid the problems with defining the rate constant for the adsorption systems showing structural and energetic heterogeneity the usage of model-independent and experimentally determinable adsorption half-time, instead of

model dependent rate coefficient was proposed. The simple analytical relations of half-time with rate parameters were applied for several kinetic equations (f-MOE, MOE, FOE, f-FOE, f-SOE, SOE, MPFO). Analysis of temperature dependences of adsorption kinetics confirmed, that simple and consistent results may be obtained by using Arrhenius or Eyring plot and employing model-independent logarithms of adsorption halftimes instead of logarithms of rate constants. Differences between activation energies obtained by using Arrhenius and Eyring plots were not higher than 10 % if rate constants were used, whereas activation energies estimated by using adsorption halftimes were very close to the average of the two methods. The best results in analysis of kinetic data were obtained for multi-exponential equation. Simple approximate solution were obtained by using McKay's PDM model or much simpler fractal-like MOE or MOE equations (contribution of second order kinetics was always below 80 %).

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