

## Adsorption of selected herbicides from aqueous solutions on activated carbon

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**Abstract** The adsorption of MCPA and 2,4-D on the activated carbon Filtrasorb 300 was studied. The adsorption isotherms of herbicides from aqueous solutions were measured over a wide range of solute concentrations and at different temperatures. The experimental equilibrium data were analyzed by the Langmuir–Freundlich isotherm taking into account the energetic heterogeneity of adsorption system. The effect of temperature and herbicide properties on its uptake was discussed. The thermal analysis was applied in order to find the differences in herbicide interactions with carbon surface. The kinetic dependences were measured and the relations between solute properties and adsorption rate were discussed.

**Keywords** Herbicides adsorption · TG and DTA analysis · Adsorption equilibrium and kinetics

### Introduction

The contamination of surface and ground waters by pesticides is an important problem investigated over the years. Pesticides are group of inorganic and organic compounds that may pollute water due to their extensive application in agriculture. The harmful effect of these types of compounds

results from their generally high mobility and persistence in the aqueous media and to their toxicity. For example, 4-chloro-2-methylphenoxyacetic acid (MCPA) and 2,4-dichlorophenoxyacetic acid (2,4-D) are widely used herbicides which belong to the group of synthetic herbicides, the chlorophenoxy herbicides. They are commonly preferred because of their low cost and good selectivity. They may be used also in combination with other herbicides for the post-emergence control of broad-leaved weeds [1]. Mobility of MCPA and 2,4-D in natural environment may be attributed to their anionic form. Since anionic pesticides are very weakly retained by most of the soil components because of their structural negative charge, they remain dissolved in the soil solution and can rapidly move around leading subsequent contamination of surface and ground waters. They persist in the environment for several weeks [2]. These pesticides are classified, among other phenoxy acid herbicides, as possible human carcinogens (class 2B-carcinogen) by the International Agency for Research on Cancer, and have recently been reported to have long-term on reproductive functions such as mutagenicity [3]. Thus, the harmful influence of herbicides on human health and the environment results in stringent legislation being imposed on the purity of drinking water.

Regarding a wide variety of herbicides of different physical and chemical properties, it is difficult to apply a single method for their removal from water. Conventional water treatment processes such as filtration, disinfection, coagulation, and sedimentation have been reported to be more effective in removing less water soluble and easily degradable pesticides [4]. Ozone technology is a potentially attractive technique in waste water treatment, but in some cases the ozone degradation products can be equally harmful [5].

Another potential method for the removal of herbicides from water is adsorption. In order to find good adsorbents for

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the removal of pesticides from contaminated aqueous solutions many studies were conducted on various materials such as kerolite, Al-pillared clay, Fe–Al pillared clays, lignin, bentonite, zeolite, calcite, kaolinite, and  $\alpha$ -alumina [6–10]. However, the activated carbon materials are especially interesting adsorbents, because of their high capability of adsorbing various organic and inorganic compounds. Commercial activated carbons are usually derived from natural materials such as coconut shell, wood or coal and are manufactured to produce precise surface properties [11].

Activated carbon particle has a porous structure consisting of a network of interconnected macropores, mesopores, and micropores that provide a good capacity for the adsorption of adsorbate molecules due to high surface area. The surface chemistry of activated carbon such as the kind and concentration of adsorbent surface groups as well as its point of zero charge ( $\text{pH}_{\text{pzc}}$ ), the chemical characteristics of adsorbate, such as polarity, ionic nature, functional groups, and solubility and the properties of adsorption solution such as pH, concentration of adsorbate, the presence of other species determine the nature of bonding mechanisms as well as the extent and strength of adsorption. Electrostatic and van der Waals forces, H-binding, dipole–dipole interactions, ion exchange, covalent bonding, cation bridging, and water bridging can be responsible for adsorption of organic compounds in activated carbon [12–19].

In this study, the process of removal of the popular herbicides MCPA and 2,4-D from aqueous solutions by adsorption on granular activated carbons was investigated. The adsorption isotherms and the kinetic curves were measured experimentally and studied by applying conventional theoretical models. The data of thermal decomposition of pure activated carbon and carbon samples with adsorbed herbicides were also analyzed.

## Experimental

### Materials

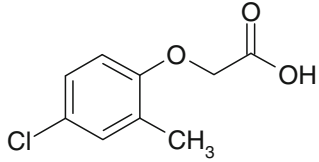
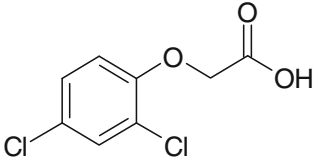
MCPA and 2,4-D of analytical reagent grade were obtained from Institute of Industrial Organic Chemistry in Warsaw and purchased from Sigma-Aldrich. The chemical structures and the most relevant physicochemical properties of the two herbicides are listed in Table 1.

The activated carbon F-300 (Chemviron Carbon, Feluy, Belgium) was chosen for adsorption experiment. Prior to use, the carbon F-300 was boiled for several days with redistilled water. The selected carbon F-300 is the adsorbent often used in the water treatment systems.

### Adsorbent characterization

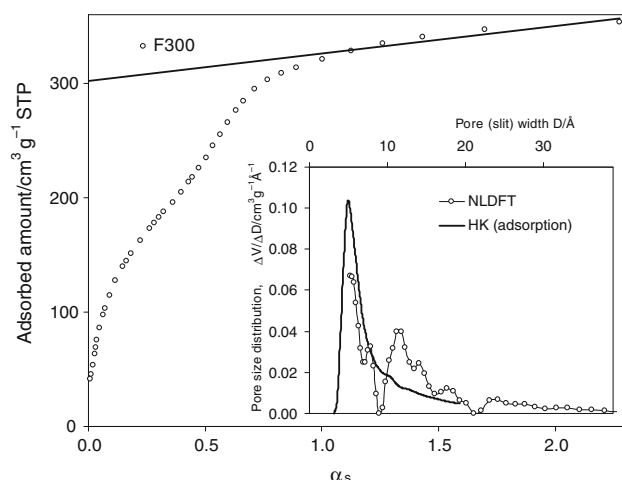
Nitrogen adsorption/desorption isotherms were measured at 77 K using AUTOSORB-1CMS apparatus (Quantachrome Instruments). Prior to adsorption measurements the carbon sample was degassed at 423 K. Parameters characterizing the properties of pore structure, e.g., the BET specific surface area ( $S_{\text{BET}}$ ) (estimated from the linear BET plot of adsorption data), the total ( $V_t$ ) (from the adsorption value at the relative pressure  $p/p_o \sim 0.98$ ), the external surface area ( $S_{\text{ext}}$ ), and micro pore volumes ( $V_{\text{mic}}$ ) (from the  $s$ -plot method by using the non-graphitized carbon black Cabot BP280 as a reference non-porous adsorbent [20]) were calculated from the obtained data. The pore size distributions (PSD) were estimated by using the AS1 software (Quantachrome Instruments) following the NLDFT (0.35–100 nm) and Horvath–Kawazoe (micropores) procedures for slit pores [21, 22]. The pore diameters were estimated from the PSD maxima (mode,  $D_{\text{mo}}$ ) and

**Table 1** Physicochemical properties of the MCPA and 2,4-D herbicides [47]

Common name	MCPA	2,4-D
IUPAC name	(4-Chloro-2-methylphenoxy)acetic acid	(2,4-Dichlorophenoxy)acetic acid
Structure		
Molecular weight/g mol <sup>-1</sup>	200.62	221.04
Ionization constant/pK <sub>a</sub>	3.07	2.73
Water solubility/mg L <sup>-1</sup>	825	680
Melting point/K	381–385	409–413
Boiling point/K	433	433

**Table 2** Textural characterization of activated carbon F-300

Specific surface area $S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	External surface area $S_{\text{ext}}/\text{m}^2 \text{ g}^{-1}$	Total pore volume $V_t/\text{cm}^3 \text{ g}^{-1}$	Micropore volume $V_{\text{mic}}/\text{cm}^3 \text{ g}^{-1}$	Pore size (hydraulic average) $D_h/\text{nm}$	Pore (slit) width by NLDFT		Pore (slit) width by HK	
					Mode $D_{\text{mo}}/\text{nm}$	PSD average $D_{\text{avg}}/\text{nm}$	Mode $D_{\text{HK,mo}}/\text{nm}$	PSD average $D_{\text{HK,avg}}/\text{nm}$
1098	66	0.56	0.47	1.99	0.52	1.89	0.50	0.77

**Fig. 1** The  $\alpha_s$ -plot and pore size distributions calculated for the activated carbon F-300 using the NLDFT and Horvath–Kawazoe procedures

PSD average ( $D_{\text{avg}}$ ). The values of these parameters obtained for the activated carbon F-300 are presented in Table 2, however, in Fig. 1 the  $\alpha_s$ -plot and PSD are presented.

#### Thermogravimetric measurements

Thermogravimetric analysis was performed in a derivatograph Q-1500 D (MOM, Hungary), with simultaneous recording of TG, DTG, and DTA curves in relation to temperature and time in quasi-isothermal conditions. The samples were heated at  $10 \text{ K min}^{-1}$  rate in the temperature range of 298–1273 K. Analyses were carried out on the carbon samples before and after herbicide adsorption.

#### Equilibrium adsorption studies

Batch adsorption isotherms of MCPA and 2,4-D were performed using the classical static method. A stock solutions of  $800 \text{ mg L}^{-1}$  (MCPA) and  $600 \text{ mg L}^{-1}$  (2,4-D) were prepared by dissolving an appropriate amount of the herbicide in redistilled water. Initial solution concentrations of  $0.7\text{--}3.3 \text{ mmol L}^{-1}$  (MCPA) and  $0.4\text{--}2.2 \text{ mmol L}^{-1}$  (2,4-D) were prepared from the stock solutions. The carbon samples were heated in 393 K and kept in desiccator. About 50 mg of

the adsorbent were weighed in Erlenmeyer flasks, 5 mL of water were added to them and degassed under vacuum. Then, 25 mL initial solutions of MCPA or 2,4-D were added. The flasks were shaken for 14 days in the incubator shaker (New Brunswick Scientific Innova 40R Model). The shaker was set at a temperature of 288 K and 110 rpm speed. The same adsorption experiments were repeated at 298, 308, and 318 K. The equilibrium solute concentrations were measured by using the UV–Vis spectrophotometer Cary 100 (Varian Inc., Australia) at  $\lambda = 282$  and 278 nm for MCPA and 2,4-D, respectively. The adsorbed amounts of herbicides were calculated from the following mass balance equation:

$$a_{\text{eq}} = \frac{(c_0 - c_{\text{eq}}) \cdot V}{m} \quad (1)$$

where  $a_{\text{eq}}$  is the equilibrium amount adsorbed on the adsorbent ( $\text{mmol g}^{-1}$ ),  $c_0$  is the initial concentration of bulk fluid ( $\text{mmol L}^{-1}$ ),  $c_{\text{eq}}$  is the equilibrium concentration of the solution ( $\text{mmol L}^{-1}$ ),  $V$  is the volume of solution (L), and  $m$  is the weight of adsorbent (g).

In order to analyze the experimental data of organic solutes adsorption from aqueous solutions the linear form of well-known Langmuir–Freundlich (LF) isotherm equation, taking into account the energetic heterogeneity of solids [23], was chosen.

$$\ln[\theta/(1 - \theta)] = m \ln K + m \ln c_{\text{eq}} \quad (2)$$

In the above,  $\theta = a_{\text{eq}}/a_m$  is the relative adsorption of organic solute over the whole surface phase, where  $a_m$  is the adsorption capacity, the heterogeneity parameter  $m$  characterizes the shape (width) of adsorption energy distribution function, and the equilibrium constant,  $K$  describes the position of distribution function on energy axis. The adsorption capacity was determined from the carbon micropore volume and the molar volume of benzene.

#### Sorption kinetics

The samples for kinetic batch measurements were prepared by contacting 50 mg of activated carbon with 30 mL of the pesticide aqueous solution at concentration  $0.118 \text{ mmol L}^{-1}$  in magnetically stirred 50 mL Erlenmeyer flask connected through Teflon tubing to the flow cell in the UV/Vis spectrophotometer Cary 100. The 1.5 mL samples were

cyclically collected from the Erlenmeyer flask by peristaltic pump and returned to it. For each kinetic point entire absorbance spectrum was recorded and analyzed [24].

Lagergren developed the first equation for description of adsorption kinetics which is still commonly used [25]. This is the first order equation (FOE) with respect to concentration or, equivalently, the FOE with respect to adsorption (PFOE: pseudo-first order equation):

$$\frac{dc}{dt} = -k_1(c - c_{eq}) \quad (3a)$$

$$\frac{da}{dt} = k_1(a_{eq} - a) \text{ and } a = \frac{(c_0 - c)V}{m} \quad (3b)$$

where  $c$  is the temporary concentration,  $k_1$  is the kinetic rate coefficient, and  $t$  is time.

The integrated form of PFOE is called Lagergren equation:

$$\ln(a_{eq} - a) = \ln a_{eq} - k_1 t \quad (4a)$$

$$\ln(c - c_{eq}) = \ln(c_0 - c_{eq}) - k_1 t \quad (4b)$$

Lagergren equation 4a and 4b is useful mainly for data presentation and not for data fitting. Its usage results from the fact that various processes may be well described by different equations showing similar behaviour. Generally, Lagergren equation can describe the adsorption processes in which the changes of concentration are not very high. However, it may be also applied for analysis of the processes with strong variation of concentration if the adsorption isotherm is in the Henry region or is near equilibrium [26–29]. Moreover, Lagergren equation describes well practically any type of adsorption kinetics near its equilibrium (e.g., intraparticle diffusion [30, 31]).

The most widely used kinetic equation is the concentration dependent second order equation (SOE) and adsorption dependent pseudo-second order equations (PSOE) [29]:

$$\frac{dc}{dt} = -k_{2c}(c - c_{eq})^2 \quad (5a)$$

$$\frac{da}{dt} = k_{2a}(a_{eq} - a)^2 \quad (5b)$$

The PSOE [29] is commonly used as the linear dependence  $t/a$  vs.  $t$ .

$$\frac{t}{a} = \frac{1}{k_2 a_{eq}^2} + \frac{t}{a_{eq}} \quad (6)$$

Various physical models corresponding to the second order kinetics are summarized by Ho in the review [29]. In many studies it was shown that the second order kinetics may successfully approximate adsorption kinetics on strongly heterogeneous solids [32, 33].

Azizian [34] proved that the kinetic equation being the foundation and justification of the Langmuir isotherm,

explains both the first order and second order equations as boundary cases of Langmuir kinetic model (activated rate theory, ART). The former corresponds to weak adsorption and low adsorption uptakes (small change of concentration), whereas the latter describes situation where adsorption is strong and uptake is close to 100%. The full solution of Langmuirian kinetics given by Azizian was analytical, but complicated and thus impractical.

Recently, Marczewski [35] presented application of a simple analytical equation corresponding to the linear combination of first and second order rate equations (mixed first and second-order rate equation, MOE).

With regard to the mathematical properties of the standard linear form of pseudo-second order Eq. 6 it is very useful in fitting equilibrium adsorption  $a_{eq}$  for various kinetic data. An alternative linear plot of PSOE [29] (an analog of Scatchard plot for Langmuir isotherm) may be helpful to show if the model itself is truly applicable in such a case.

$$a = a_{eq} - \frac{1}{k_{2a} a_{eq}} \frac{a}{t} \quad (7)$$

Marczewski et al. [36–38] applied the multi-exponential equation (m-exp), which may be treated as an approximation of a series of parallel first order processes (also structural or energetic heterogeneity) or a series of follow-up processes (e.g., in pores with constrictions). It was successfully used for analysis of various experimental kinetics data. The m-exp may be treated as a kind of generalization of Lagergren equation.

$$c = c_0 \left( \sum_{i=1}^n A_i \exp(-k_i t) + A_0 \right) \text{ where } A_0 = c_{eq}/c_0 \text{ and } \sum_{i=1}^n A_i + A_0 = 1 \quad (8a)$$

$$c = (c_0 - c_{eq}) \sum_{i=1}^n f_i \exp(-k_i t) + c_{eq} \text{ where } f_i = A_i/(1 - A_0) \text{ and } \sum_{i=1}^n f_i = 1 \quad (8b)$$

$$a = a_{eq} - a_{eq} \sum_{i=1}^n f_i \exp(-k_i t) \quad (8c)$$

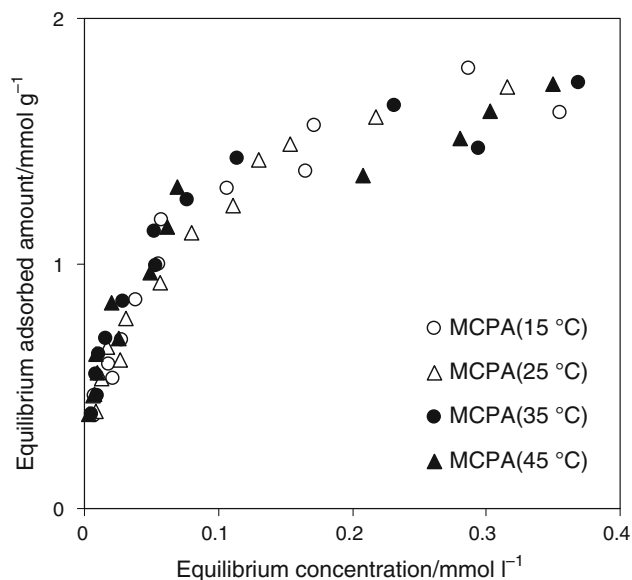
In the above equations  $n$  is number of exponential terms,  $A_0$  describes relative equilibrium concentration, and other  $A_i$  parameters describe fraction of the adsorbate in the system (i.e., solution + adsorbent) following kinetics with a particular kinetics coefficient  $k_i$ . On the other hand coefficient  $f_i$  describes fraction of total adsorbed amount corresponding to the rate coefficient  $k_i$ .

Equation 8a–8c may describe well experimental systems, where the initial process with fast adsorption rate is

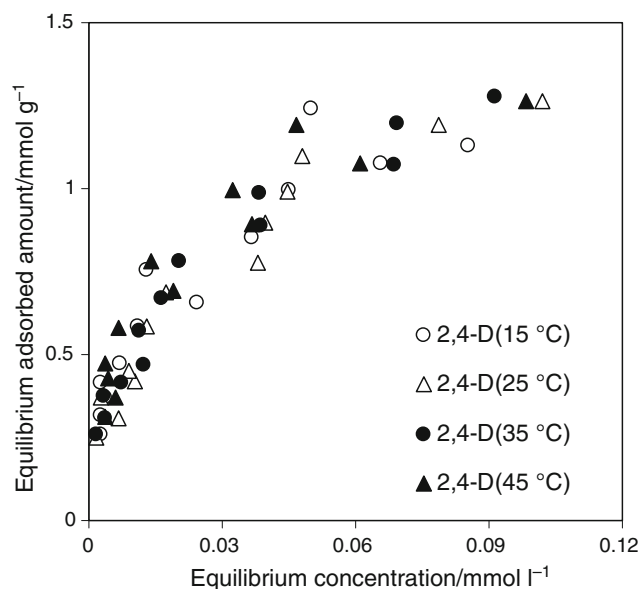
followed by a series of slower and slower processes, which may be expected, e.g., for porous adsorbents with non-uniform pore structure or a complicated pore network with varying accessibility of smaller and larger pores. This  $(2n + 1)$ -parameter equation fits very well many experimental data sets that could not be described by the first or second order model. Even the equation with only two exponential terms usually describes data better than any of the aforementioned simple equations.

## Results and discussion

To study the process of removal of chlorophenoxy herbicides from aqueous solutions on microporous activated carbon F-300, the equilibrium adsorption isotherms for 2,4-D and MCPA were measured at different temperatures. In Figs. 2 and 3 the adsorption isotherms of 2,4-D and MCPA measured at 288, 298, 308, and 318 K are compared. In the case of both systems slight temperature effect is observed—adsorption of MCPA and 2,4-D increase slightly with increasing temperature. Such a behaviour of adsorption systems may be a result of superposition of various effects. The increase of adsorption with temperature indicates endothermic character of adsorption, it could also be due to the enhanced mobility of 2,4-D and MCPA ions from the bulk solution towards the adsorbent surface and extent of penetration within adsorbent structure overcoming the activation energy barrier and enhancing the rate of intraparticle diffusion [5]. This trend may be also attributed to creation of some new active sites on the adsorbent surface due to bond rupture. The opposite trend of adsorption



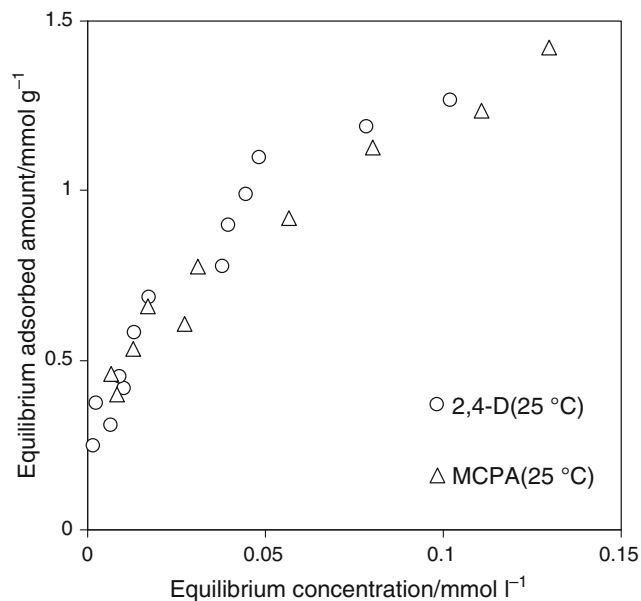
**Fig. 2** Comparison of isotherms of MCPA adsorption from aqueous solutions on the activated carbon F-300 at different temperatures



**Fig. 3** Comparison of isotherms of 2,4-D adsorption from aqueous solutions on the activated carbon F-300 at different temperatures

decreasing with temperature increase may be interpreted by exothermic character of adsorption process, increase of solubility resulting in adsorption decrease, and increase of oscillation energy of herbicide molecules resulting in desorption from surface phase to bulk phase.

In Fig. 4 the static isotherms of 2,4-D and MCPA at 298 K are compared. Over the whole concentration range and at various temperatures higher 2,4-D adsorption is observed, however, the differences between adsorption uptakes are not significant. It is well-known that



**Fig. 4** Comparison of isotherms of MCPA and 2,4-D adsorption from aqueous solutions on the activated carbon F-300 at 298 K

effectiveness of organics adsorption depends on solubility of the compound; solubility being an equivalency of the adsorbate hydrophobicity is the main driving force in adsorption of organic substances on carbonaceous materials—the less soluble the substance, the more likely it is to be adsorbed. Thus, in the case of studied herbicides, 2,4-D showing lower solubility has higher affinity towards activated carbon, its hydrophobic interactions with carbon should be stronger. Apart from solubility/hydrophobicity of adsorbate in the analysis of its affinity towards adsorbent surface the other factors should be taken into account: the properties of adsorbed substance—molecular size and form—ionic or neutral, properties of functional groups, the properties of adsorbent—structure and surface characteristics, and the conditions of conducting the adsorption process—solution pH, ionic strength, and temperature [39, 40]. Comparing the adsorption of two studied herbicides of aromatic character on the same carbon and at the same conditions only the differences in their properties should be regarded. Both herbicides are differentiated by nature and position of substituent groups influencing their solubility and adsorptivity. On the basis of donor–acceptor complex mechanism the differences in both adsorbates with carbon surface may be explained involving carbonyl oxygen of the carbon surface as donor and the aromatic ring of the pesticides as an acceptor [40, 41]. It may be expected that the electron-withdrawing groups, which deactivate the ring, would promote adsorption through complex formation via donor–acceptor mechanism. It is known that chloride and

acid substituents deactivate the ring due to inductive effect [42].

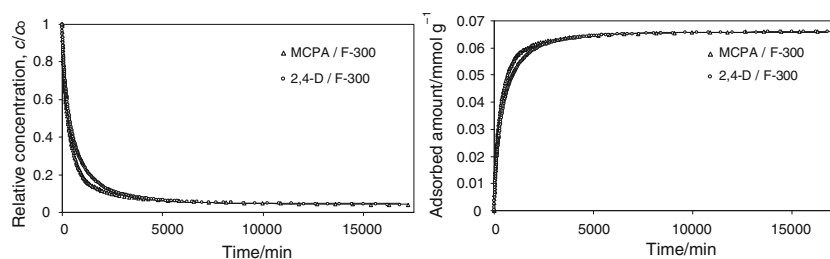
In Table 3 the parameters of LF equation obtained by line fitting procedure (2) are compared for all experimental systems: the heterogeneity parameter  $m$ , the equilibrium adsorption constant  $K$ . In all cases we observe good agreement between the experimental points and fitted lines, which is confirmed by  $R^2$  values. All adsorption systems show strong heterogeneity effects evidenced by low values of heterogeneity parameter. The values of adsorption equilibrium constant are higher for 2,4-D confirming it higher adsorption affinity.

The results of kinetic experiments are shown in Fig. 5 as the relative concentration ( $c/c_0$ ) and relative adsorption progress ( $a/a_{eq}$ ) data for MCPA and 2,4-D at 293 K. The kinetic processes for MCPA (smaller and easier soluble) are clearly faster than in the case of 2,4-D. This effect may result in apparently higher adsorption of MCPA in applications where the granular F-300 is used with limited contact time. The data were fitted by using the standard PFO (4a and 4b) and PSO (6) equations. The results of fitting to the PFOE were not satisfactory, whereas the results for PSOE are shown in Fig. 6 plotted in two-time ranges. The plots display linearity at higher adsorption times (close to the equilibrium), however, in the initial part (below 200 min) the plots are non-linear. The alternative linear PSOE plot (7) (not shown) emphasizes only partial conformation to the PSOE model.

**Table 3** The parameters of Langmuir–Freundlich equation 2 calculated by using line fitting procedure

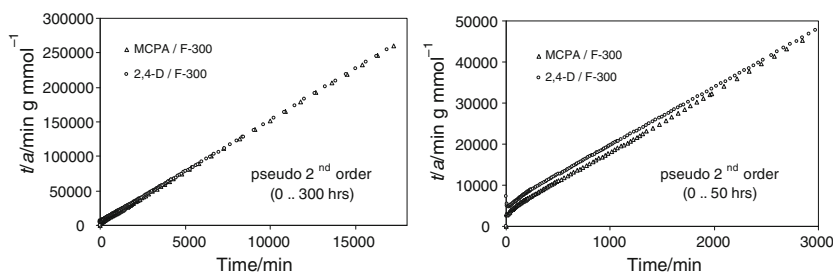
Temperature	Adsorbate	Log of adsorption equilibrium constant $\log K$	Heterogeneity parameter $m$	Correlation coefficient $R^2$
15 °C	2,4-D	0.08	0.44	0.924
	MCPA	0.06	0.50	0.958
25 °C	2,4-D	0.05	0.47	0.926
	MCPA	0.06	0.49	0.975
35 °C	2,4-D	0.08	0.48	0.966
	MCPA	0.02	0.43	0.956
45 °C	2,4-D	0.08	0.45	0.906
	MCPA	−0.04	0.39	0.958

**Fig. 5** Comparison of kinetic adsorption curves (left: relative concentration, right: relative adsorption progress) for MCPA and 2,4-D on the activated carbon F-300 at 298 K. Lines correspond to the fitted multi-exponential Eq. 8a–8c (Table 4)





**Fig. 6** Comparison of standard linear PSOE plots (6) for adsorption kinetics of MCPA and 2,4-D on the activated carbon F-300 at 298 K shown for two-time ranges (300 and 50 h)



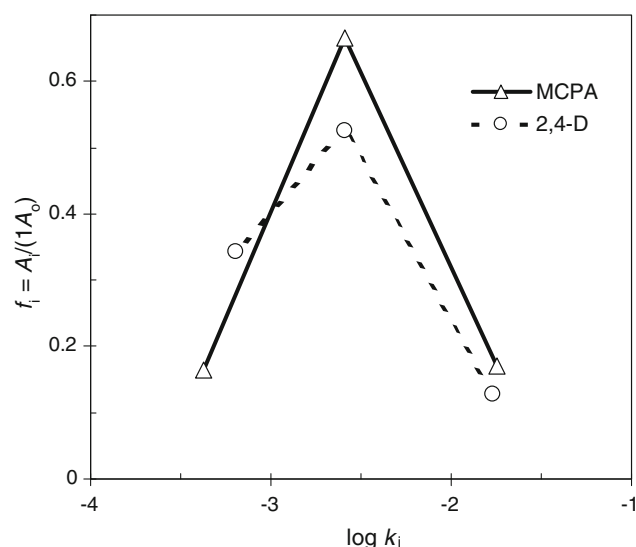
**Table 4** The parameters of multi-exponential kinetic Eq. 8a–8c

Kinetic system	Equation term no. <i>i</i>	Logarithm of rate coefficient, log <i>k<sub>i</sub></i>	Coefficient <i>A<sub>i</sub></i>	Coefficient <i>f<sub>i</sub> = A<sub>i</sub>/(1–A<sub>0</sub>)</i>	SD <sup>a</sup>
MCPA/F-300	0	–	0.044	–	0.0035
	1	–1.75	0.163	0.171	
	2	–2.59	0.636	0.665	
	3	–3.37	0.156	0.164	
2,4-D/F-300	0	–	0.048	–	0.0042
	1	–1.77	0.123	0.129	
	2	–2.59	0.501	0.525	
	3	–3.20	0.328	0.343	

<sup>a</sup>  $SD = \frac{1}{c_0} \sqrt{\sum_{i=1}^L (c_i - c(t_i))^2 / (L - (2n + 1))}$  where *L* is the number of experimental points

In Table 4 the results of fitting kinetics data of adsorption of MCPA and 2,4-D on F-300 carbon to the multi-exponential Eq. 8a–8c are presented, whereas the theoretical lines are compared with experimental data in Fig. 5. Moreover, in Fig. 7 the plot of parameter spectrum presents in a concise form both similarities and differences of MCPA and 2,4-D kinetics—faster kinetics for MCPA

corresponds to the higher share of kinetic constants with higher magnitudes, however, the general shape of both spectra is similar for both systems. This plot also explains why the PFOE fitting does not succeed—pure first order kinetics would correspond to a single point or—due to experimental errors—a narrow spectrum, whereas in the case of both systems the highest term share is 0.5–0.64 and the distribution of kinetic constants is not narrow.

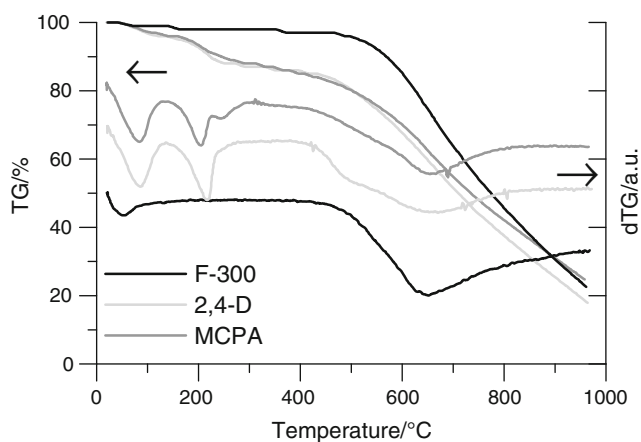
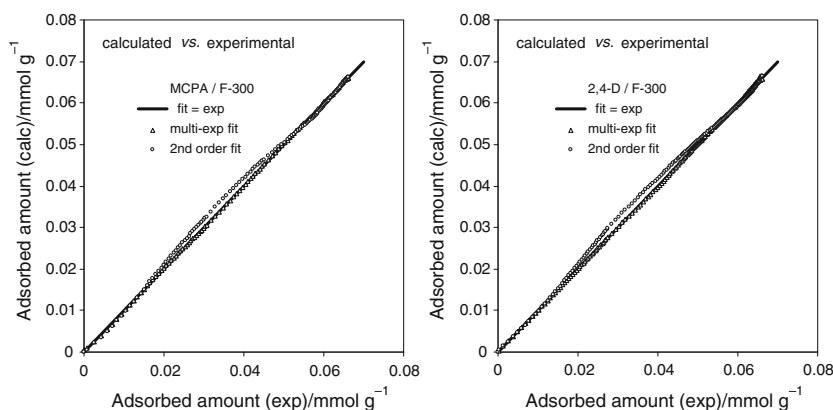


**Fig. 7** Parameter spectrum for multi-exponential Eq. 8a–8c fitted to the MCPA and 2,4-D adsorption kinetics on F-300 carbon (Table 4)

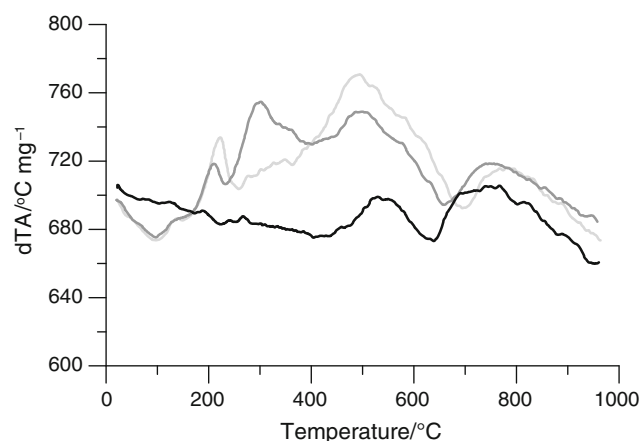
In Fig. 8 the quality of fit for both equations is compared. The thick solid lines correspond to the perfect fit of theoretical equation to the data and points correspond to the actual experimental data fitted according to both equations. Almost perfect fit for m-exp is obvious while the deviations for PSOE are also evident.

Thermogravimetry is a useful technique for investigations of adsorption interactions [43]. Thermal analysis of activated carbon F-300 before and after herbicide adsorption allowed to study the thermal stabilities of surface complexes. Temperature programmed desorption involved heating the carbon sample at a programmed heating rate to induce desorption of adsorbed species. The obtained profiles are presented in Figs. 9 (TG, DTG) and 10 (DTA) for all samples: the pure carbon F-300, and the carbons with adsorbed MCPA and 2,4-D. The TG curves show well defined weight losses along with the total weight losses corresponding to about 80 wt% of sample masses, which indicates that mostly of carbon samples are burning out at

**Fig. 8** Comparison of experimental (exp) and optimized (calc) kinetic adsorption curves for MCPA (left) and 2,4-D (right) on the activated carbon F-300 at 298 K. Triangles correspond to the optimized multi-exponential kinetic curves (Eq. 8a–8c, Table 4), circles are calculated according to the PSOE (Eq. 7, Fig. 5) and solid lines show perfect fit



**Fig. 9** Comparison of TG and DTG curves measured for the pure carbon F-300 (black line), carbon with adsorbed 2,4-D (light grey line) and carbon with adsorbed MCPA (dark grey line)



**Fig. 10** Comparison of DTA curves measured for the pure carbon F-300 (black line), carbon with adsorbed 2,4-D (light grey line) and carbon with adsorbed MCPA (dark grey line)

temperatures below 1270 K. On the curves measured for pure carbon one can observe three stages of thermal decomposition. The minimum located at low temperatures in the case of all samples indicate desorption of hygroscopic

and physisorbed water. This endothermic process is seen on DTA curve, and is revealed as the first peak in DTG curve. At higher temperatures water adsorbed by hydrogen bonds on the oxygen surface groups is released. In the temperature range 400–650 °C the exothermic process of pure carbon surface oxidation takes place as is evidenced by the maximum on DTA curve at 550 °C. However, for higher temperatures (650–950 °C) further oxidation of carbon, connected with oxygen diffusion into the micropores [44] is observed; this process is revealed as a wide exothermic peak on DTA curve. The profiles for carbon with adsorbed herbicide show new peaks centred at 490 K for 2,4-D/F-300, 480 and 515 K for MCPA/F-300 samples. They were not detected before adsorption, thus, they are assigned to the herbicide physisorbed on the carbon surface. As reported in the paper [45] the peaks at the temperature around 500 K are related to the dehydration of two adjacent carboxyl groups. Moreover, on the DTA curve for MCPA/F-300 a large peak appears around 570 K; these changes in DTA profiles for both samples are the result of the difference in substituent groups at aromatic ring of the studied herbicides. At temperatures lower than 670 K desorption of carbon oxygen complexes occurs simultaneously with chemisorption of oxygen by the carbon surface [46]. However, when the temperature increases the oxidation of the sample surface occurs more and more rapidly with the maximum at about 770 K. At a temperature of about 870 K the whole surface of carbon is already oxidized while inside the carbon mass the pyrolysis process begins to occur. With further increase in temperature the rate of oxygen diffusion into small pores of carbon particles increases and internal combustion occurs rapidly.

## Conclusions

Slight temperature effect is observed in adsorption of MCPA and 2,4-D as a result of superposition of various effects: energetic effect of adsorption process, changes in



mobility of adsorbate ions from the bulk solution towards the adsorbent surface, changes of the rate of intraparticle diffusion, creation of some new active sites on the adsorbent surface, increase of solubility, increase of oscillation energy of herbicide molecules which resulted in desorption from surface phase to bulk phase. Higher affinity of 2,4-D towards activated carbon results from its lower solubility, thus, from stronger hydrophobic interactions with carbon surface. Despite stronger adsorption of 2,4-D the kinetics of MCPA is faster what in practical applications with limited contact time may result in apparently higher adsorption of MCPA. This effect may be attributed to its slightly smaller molecule. The kinetics of both adsorbates is best described by the m-exp, whereas PSOE may be used close to the equilibrium.

The course of thermal decomposition for both pesticides adsorbed on activated carbon is similar. On the thermodesorption curves measured for pure carbon one can observe three stages of thermal decomposition: desorption of hygroscopic and physisorbed water, surface oxidation, further oxidation of carbon, connected with oxygen diffusion into the micropores. In comparison to pure carbon the profiles for carbon with adsorbed herbicide show new peaks which can be assigned to the herbicide physisorbed on the carbon surface. The changes observed in DTA profiles for both carbon samples with adsorbed herbicide result from the difference in substituent groups at aromatic ring.

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