



## ORIGINAL ARTICLE

# Amides as a model system of low molar mass algal organic matter. Influence on the adsorption of *p*-nitrophenol on activated carbon



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**Abstract** In this study, the adsorption equilibrium and diffusivity parameters of *p*-nitrophenol were estimated for water containing different concentrations of secondary amides. Commercial powdered activated carbon was used as an adsorbent. The external mass transfer coefficient ( $k_f$ ), the surface diffusion coefficient ( $D_s$ ) and the standard free Gibbs energy were calculated for *p*-nitrophenol in the presence of different secondary amide concentrations. The analysis established that there are correlations between structural parameters of amides, on the one hand, and diffusion and thermodynamic parameters for *p*-nitrophenol adsorption process, on the other. It was noticed that voluminous hydrophobic amides decreased the adsorption capacity of *p*-nitrophenol on activated carbon. On the basis of the results obtained for external mass transfer coefficients, it is assumed that amides cause the reduction of adsorption capacity of *p*-nitrophenol onto activated carbon by concentrating at the solid/liquid interface.

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## 1. Introduction

Understanding the mechanisms of the adsorption process has both a fundamental and technical importance. Determination of the

fundamental physical and chemical factors that influence the adsorption process can provide a better insight into the nature of all interactions possible between the adsorbent and the adsorbate in aqueous media. Further, a systematic study of interactions in heterogeneous adsorption systems provides valuable information for the design of technological processes.

Activated carbon is the most frequently used adsorbent in water treatment processes for removing both organic and inorganic pollutants. Numerous studies have shown that the adsorption efficiency of activated carbon depends on many factors, including the specific surface area, distribution of pore size, pollutant properties and the physical-chemical properties of the aqueous solution (Michael-Kordatou et al., 2015; Deliyanni et al., 2015).

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Natural organic matter (NOM) is a common constituent of surface and ground waters. NOM comprises a complex mixture of organic compounds with a wide range of molar masses and physical and chemical characteristics, depending on the NOM origin. Among these compounds, the most abundant ones are humic substances, while organic substances containing nitrogen as cell decomposition products (AOM-algal organic matter or EOM-extracellular organic matter), such as peptides, amino acids, or proteins, also cover a certain proportion of the total organic matter (Huang et al., 2009; Watt, 1966).

It is well-known that background NOM affects the removal of organic contaminants onto activated carbon. The effect of NOM on the change of the adsorption properties of an organic compound can be mainly explained by two mechanisms: direct competition for active sites on the adsorbent and the pore blocking effect caused by large NOM molecules (To et al., 2008; Quinlivan et al., 2003; Matsui et al., 2003; Summers et al., 1989).

The influence of NOM on the adsorption of organic pollutants on activated carbon has so far been mostly studied in natural water systems containing a mixture of high- and low-molecular mass compounds. Using amides as a model system of natural (algal) organic matter in multicomponent adsorption system was not studied so far. Also, there is very little information in the available literature regarding the adsorption of amides and peptides on activated carbon. Amides are adsorbed at the experimentally inaccessible "solid/liquid" interface making it difficult to obtain a molecular level understanding of amide interactions with solid surface (Arnold et al., 2008). However, more recent literature provides evidence for possible mechanisms for amide adsorption onto carbonaceous adsorbents. The adsorption of the specific long chain amides has been studied on graphite as an adsorbent (Arnold et al., 2008; Bhide et al., 2011). It has been shown that amides can form very stable monolayers on the surface of graphite, especially in the case of saturated amides. Additionally, it is evidenced that the adsorption of sulfonamide antibiotics on multiwalled carbon nanotubes occurs through formation of strong surface  $\pi$ - $\pi$  interactions (Ji et al., 2009). As for the adsorption of peptides, it was found that the adsorption capacity depends on the ionic strength and molecular weight (Kopecka et al., 2014). Furthermore, the influence of the electrostatic interactions and hydrogen bonding (H-bond) was observed for adsorption of some peptides on activated carbon (Hnatukova et al., 2011). Therefore, since both amide and peptides show affinity for adsorption on carbonaceous surfaces it seemed interesting to use amides as a model for AOM to investigate their influence on the adsorption of organic micropollutants on the activated carbon.

The objective of this study was to investigate the effects of eight structurally different amides, as models of low molecular mass AOM, on the adsorption kinetics and equilibrium of *p*-nitrophenol on activated carbon. We believe that the results of our work will be of interest to researchers interested in investigating the influence of NOM (especially AOM – algal organic matter or EOM – extracellular organic matter) on the adsorption of organic compounds onto carbonaceous materials which is not well understood. The understanding of the influence of NOM on adsorption processes is essential for assessing the efficiency of adsorption processes in water treatment technologies, as well as for understanding the influence of NOM on the behavior of organic pollutants in the environment.

## 2. Material and methods

### 2.1. Adsorbates and sorbent

The *p*-nitrophenol used in the research was purchased from Fluka ( $\geq 99,5\%$ ). Stock and work solutions of *p*-nitrophenol were prepared in phosphate buffer (pH 7.4) organic carbon free water ( $< 0.2$  mg TOC/L). Acylation of the corresponding amines with alkyl chloride, known as Schotten-Baumann reaction, was used to synthesize N-methylformamide (NMF),

N-ethylformamide (NEF), N-*t*-butylacetamide (NTBA), N,N-dimethylacetamide (NNDMA), N-*n*-butylbenzamide (NBB), N-2-phenylethylpropanamide (N2PP), N-hexylpropanamide (NHP), N-*n*-butylbenzamide (NMB). The purity of these N-monosubstituted amides was checked by gas chromatography (GC) and mass spectrometry (MS). Based on the GC/MS results, all the amides used in this work had a purity of 99.2% or better. The physical-chemical properties of the investigated secondary amides are listed in Table 1. Structural formulas of selected amides are shown in Fig. 1.

The powdered activated carbon (PAC) Norit SA 2 (Cabot Norit Nederland B.V) was used as the adsorbent. An Autosorb-iQ Surface Area Analyzer (Quantochrome Instruments, USA) was used for measurements of the average pore radius, the total pore volume and the micropore test. Samples were outgassed at 293 K for 5 h before running isotherms. The physical-chemical characteristics of the PAC used are listed in Table 2.

### 2.2. Kinetic and equilibrium adsorption experiments in single and binary systems

The powdered activated carbon was prepared as an adsorbent by drying at 378 K for 24 h. The adsorption equilibrium of *p*-nitrophenol on activated carbon was tested at a constant temperature of 298 K. The equilibrium and kinetics of the adsorption of a single-solute *p*-nitrophenol system were tested initially, which was followed by an investigation of the *p*-nitrophenol adsorption in the presence of the investigated amides (binary systems). In the single-solute system the concentration of *p*-nitrophenol was 5 mg/dm<sup>3</sup>. In the binary systems, the concentration of *p*-nitrophenol was the same, while the concentration of amides was 5, 50 and 100 mg/dm<sup>3</sup>.

Batch equilibrium experiments were performed on a rotary shaker at 180 rpm using 250 cm<sup>3</sup>-shaking flasks at room temperature for 180 min. After shaking, solutions were filtered through 0.45  $\mu$ m glass fiber filters and the absorbances were measured on a Shimadzu UV 1800 UV-VIS spectrometer at the characteristic wavelength (400 nm) in 1 and 2 cm cuvettes at 298 K. Synthetic pH adjusted (7.4) organic carbon free water ( $< 0.2$  mg/dm<sup>3</sup>) was used as a blank. All of the experiments were performed in duplicate. For all investigated amides the initial pH value and the pH value after the addition of the activated carbon suspension were in the range of 7.4–8.2 and did not change during the experiment.

**Table 1** Physical-chemical properties of the investigated amides.

Amide	Property*		
	Molar mass (g/mol)	$V$ ( $\text{\AA}^3$ )	$K_{OW}$
NMF	59.07	258.80	-0.99
NEF	73.09	313.73	-0.65
NNDMA	87.12	355.79	-0.54
NTBA	115.18	432.71	0.05
NHP	157.26	620.81	1.86
NMB	135.17	470.71	0.36
NBB	177.25	615.88	1.57
N2 PP	177.25	630.79	1.11

\* Calculated using Hyperchem v8.0 by semiempirical PM3 method.

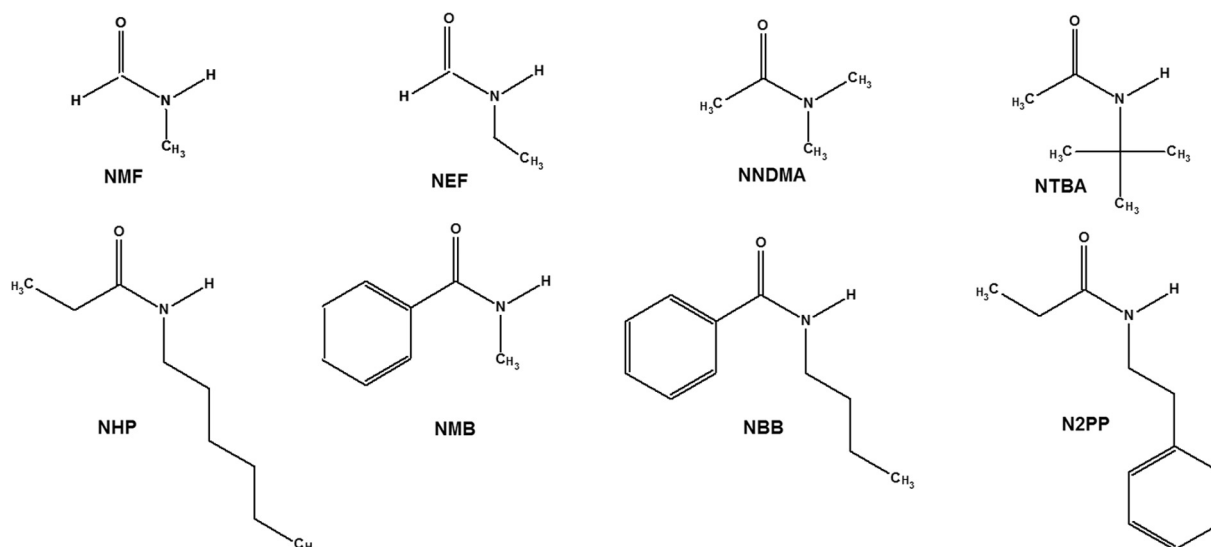


Figure 1 Structural formulas of selected amides.

Table 2 The physical-chemical properties of the adsorbent.

Property	
Iodine number	850
SSA BET (m <sup>2</sup> /g)	664
Average pore radius (Å)	18.5
Total pore volume (cm <sup>3</sup> /g)	0.39
Micropores (%)	32.3
Mesopores (%)	58.6
Macropores (%)	9.1

Prior to the investigation of the effect of the amide on the adsorption kinetics of *p*-nitrophenol, a set of tests was conducted to determine the impact of speed mixing on the kinetics of adsorption of *p*-nitrophenol. The tests were performed at 5 different stirring speeds (0, 50, 100, 240, 380 rpm). Based on the obtained values for film diffusion coefficients it was found that from the speed of 100 rpm stirring velocity has no more influence on the film diffusion.

The kinetic experiments were performed in a glass reaction vessel with a volume of 1 dm<sup>3</sup>. Previously prepared aqueous solution containing *p*-nitrophenol and amide (500 cm<sup>3</sup>) in the specific concentration ratio (1:1, 1:10, 1:20) was added into the reaction vessel and stirrer was turned on. Continuous mixing of the solution was maintained by means of a magnetic stirrer with a controlled number of revolutions. Kinetic experiment was started by addition of a certain amount of activated carbon suspension. Samples were taken at defined time intervals over a period of 180 min. After reaching certain time, the adsorbent was removed for determination of *p*-nitrophenol concentration. Filtration of samples was performed using 0.45 μm glass fiber filters and the absorbances were measured by a UV-VIS spectrometer at the characteristic wavelength (400 nm) in 1 and 2 cm cuvettes at 298 K. All experiments were performed in duplicate.

Solid-phase solute concentrations were calculated from a mass balance of solute between the solid and aqueous phases.

### 2.3. Data analysis

The simple film diffusion model and the HSDM model were applied in order to assess and compare external and internal diffusion coefficients of *p*-nitrophenol in the presence of different amides.

#### 2.3.1. External (film) diffusion model

In the initial period of the adsorption process, due to the difference in the concentration of sorbate in the bulk liquid and at the external surface of the sorbent, a boundary layer (film) is formed on the surface of the sorbent. The driving force for mass transfer is a concentration gradient formed between the bulk solution and the external surface. Under an assumption that the sorbent particles are spherical, that the bulk concentration is uniform and that the internal diffusion is negligible in the initial period of the adsorption, the following equation (Mathews et al., 1976) can be made:

$$\frac{dC}{dt} = -k_f S_A (C - C_S) \quad (1)$$

where  $k_f$  is the external mass transfer coefficient,  $S_A$  represents a specific surface area of the sorbent,  $C$  concentration at the time  $t$ , and the  $C_S$  concentration at the external surface of the adsorbent particle. During the first short time period of adsorption process,  $C_S$  can be neglected, as it is practically zero. Integration with the boundary conditions  $C = C_0$ , where  $C_0$  is the starting concentration,  $C_t = 0$  at  $t = 0$  leads to:

$$\ln \frac{C_t}{C_0} = -k_f S_A t \quad (2)$$

$$S_A = \frac{6m_s}{d_p \rho_s} \quad (3)$$

where  $m_s$  is the mass of the adsorbent per unit volume of the adsorbate (kg/m<sup>3</sup>),  $d_p$  is the particle diameter (m) and  $\rho_s$  the particles density (kg/m<sup>3</sup>).

The external mass transfer coefficient  $k_f$  can be estimated from the initial slope ( $t \rightarrow 0$ ) of the curve  $\ln(C_t/C_0)$  versus  $t$ .

The external mass transfer coefficient  $k_f$  depends strongly on hydrodynamic conditions, and it is, therefore, necessary to determine the influence of the stirring velocity on the  $k_f$  value.

### 2.3.2. HSDM (Homogeneous surface diffusion model)

According to this model, the sorbent is considered a spherical homogeneous medium, while the driving force for mass transfer is the concentration gradient which is formed along the inner surface of the sorbent particles. Combining Ficks law and the particle geometry conditions produces the following equation:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_S \frac{\partial q}{\partial r} \right) \quad (4)$$

where  $D_S$  is the surface diffusion coefficient,  $q$  is the concentration of sorbate at a distance  $r$  from the center of the sorbent particle.

Calculating the surface diffusion coefficient  $D_S$  based on the HSDM model is not simple. The surface diffusion coefficient  $D_S$ , can be calculated by fitting experimental data on the basis of an empirical polynomial of the type (Zhang et al., 2009):

$$\bar{C} = A_0 + A_1 \ln T_B + A_2 (\ln T_B)^2 + A_3 (\ln T_B)^3 \quad (5)$$

where  $\bar{C}$  represents dimensionless concentration defined as

$$\bar{C} = \frac{C - C_e}{C_0 - C_e}, 0 \leq \bar{C} \leq 1 \quad (6)$$

The empirical coefficients  $A_i$  based on the Freundlich equation exponent  $n$  for different  $C_e/C_0$  ratios can be found in the literature (Worch, 2012). With known values of  $n$ ,  $C_e/C_0$  ratio, and coefficients  $A_i$ , a kinetic curve based on a polynomial equation (6), which best fits with the experimental data, may be constructed by changing the  $D_S$  values.

### 2.3.3. The thermodynamic parameters

The thermodynamic parameters can be determined from the single point distribution coefficient ( $K_d$ ). The single point distribution coefficient ( $K_d$ ) for a particular equilibrium concentration ( $C_e$ ) can be determined using the Freundlich isotherm:

$$K_d = K_F C_e^{n-1} \quad (7)$$

where  $K_F$  is the Freundlich equation coefficient. The adsorption distribution coefficient  $K_d$  can be used for calculating the standard free Gibbs energy from the following equation:

$$\Delta G^0 = -RT \ln K_d \quad (8)$$

Negative values of  $\Delta G^0$  indicate spontaneous adsorption.

## 4. Results and discussion

### 4.1. Amide impact on the diffusion kinetics of *p*-nitrophenol

Experimental kinetic curves for the systems investigated are shown in Fig. 2. The equilibrium adsorption capacity, external mass ( $k_f$ ) and surface diffusion ( $D_S$ ) coefficients for *p*-nitrophenol in the presence of investigated amides are presented in Table 3. The determination coefficients obtained for fitting the experimental kinetic data were in the range of 0.9217 to 0.9897. The coefficients were tested by Student's

( $n-2$ ) t-test, and it was found that the coefficients are statistically significant at the significance level of  $p \leq 0.05$ , i.e. with a certainty of 95%.

On the basis of the obtained values for the adsorption capacity it can be estimated that the secondary amides with the lower molar mass and less voluminous substituents (NMF, NEF, NNDMA, NTBA) show no significant influence on the adsorption capacity of *p*-nitrophenol, whereas for amides with the voluminous substituents (NHP, NMB, NBB, N2PP) a decrease in adsorption capacity with increasing concentration of the amide in the system can be noticed.

A similar trend is observed for film diffusion coefficient values  $k_f$  of the investigated amides. Namely, more voluminous amides (having higher molar mass) significantly affect the reduction of the  $k_f$  value. Furthermore, it can be observed that this effect increases with the concentration of the amide. These experimental facts can lead to the assumption that the increase in amide concentration causes an increase in the thickness of the boundary diffusion film layer. Based on literature data, it can be assumed that the amides are concentrated on the of water/carbon interface and thus affect the external diffusion phase of the process (Arnold et al., 2008; Bhide et al., 2011). Namely, for some peptide surfactants it was found that an increase in hydrophobic tail chain length enhances the hydrophobic affinity, resulting in the increase of the adsorbed amount (Pan et al., 2010) Also, a correlation of work of adhesion (decrease in water solution surface tension) and carbon loading was established for some pollutants (de Ridder et al., 2013).

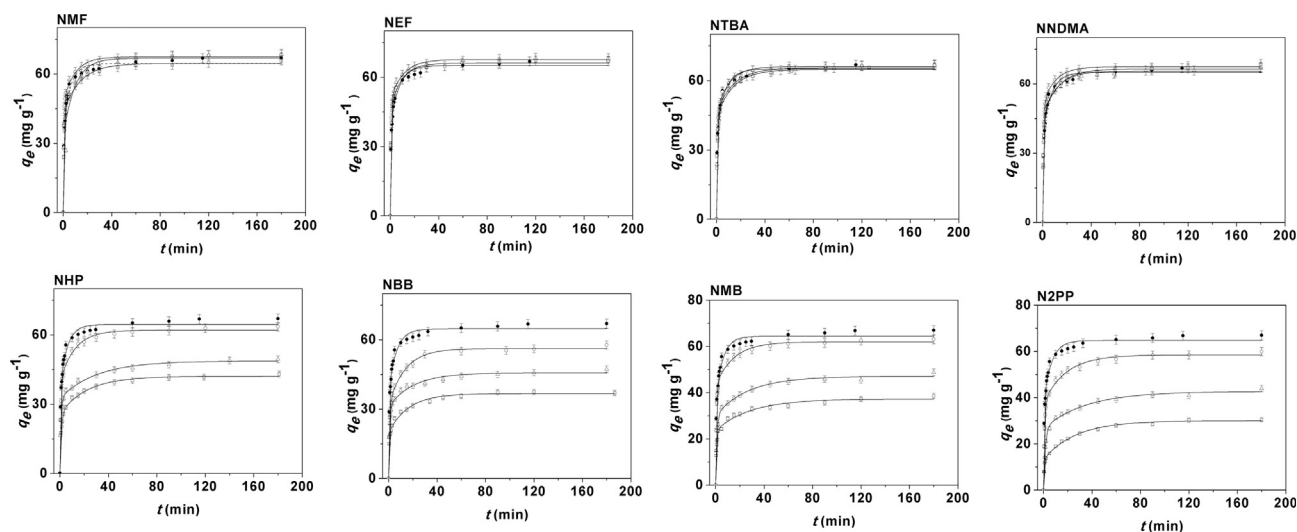
The values obtained for the coefficient of internal diffusion  $D_S$  are all of the same order of magnitude and not significantly different for the *p*-nitrophenol adsorption with and without the presence of amides.

Based on the differences observed for the  $k_f$  and  $D_S$  values, it can be assumed that some of the investigated amides affect the external rather than the internal diffusion step of the adsorption process. Differences in the values for external and internal diffusion coefficients may be a result of various factors. In literature it can be found that some high molar mass model substances (poly(styrene sulfonate)) have impact on reducing the  $D_S$  coefficient of atrazine for several orders of magnitude (Li et al., 2003). Adsorption from multicomponent aqueous solutions (system phenols-cresol) is a surface diffusion-controlled process (Mijangos et al., 2001). An increase in the effective diffusion coefficients can occur also due to the *in situ* formation of complex species (Bautista-Toledo et al., 2014). The effects of natural organic matter loading and an aging powdered activated carbon slurry are responsible for a decrease of the  $D_S$  value for atrazine (Lebeau et al., 1999).

### 4.2. Amide impact on the equilibrium adsorption of *p*-nitrophenol

Table 4 presents the Freundlich isotherm parameters ( $K_F$  and  $n$ ), the single point distribution coefficient ( $K_d$  at concentration of 2.5 mg/dm<sup>3</sup>) and the standard free Gibbs energy change ( $\Delta G$ ) for *p*-nitrophenol (single systems) and *p*-nitrophenol in the presence of different concentrations of the investigated amides (binary systems).

Adsorption isotherms of *p*-nitrophenol in the absence and in the presence of different concentrations of the investigated amides are shown in Fig. 3.



**Figure 2** Kinetics of the adsorption of *p*-nitrophenol in the presence of investigated amides (●—*p*-nitrophenol, ○—5 mg/dm<sup>3</sup> of amide, △—50 mg/dm<sup>3</sup> of amide, □—100 mg/dm<sup>3</sup> of amide).

**Table 3** The external mass ( $k_f$ ) and surface diffusion ( $D_s$ ) coefficients for *p*-nitrophenol with and without the presence of investigated amides.

	$c$ (mg/dm <sup>3</sup> )	$q_e$ (mg/g)	$k_f \cdot 10^7$ (min <sup>-1</sup> )	$D_s \cdot 10^{13}$ (m <sup>2</sup> /min)
<i>p</i> -nitrophenol-pNP	5	65.78	2.55	8.23
N-methylformamide-NMF	5	68.11	2.77	9.76
	50	68.26	2.52	8.74
	100	65.36	2.06	8.79
N-ethylformamide-NEF	5	64.90	2.86	8.53
	50	67.40	2.78	9.31
	100	65.93	2.87	8.68
N,N-dimethyl acetamide-NNDMA	5	67.17	2.62	9.03
	50	65.05	2.06	8.40
	100	65.87	2.15	8.45
N-tert-butylacetamide-NTBA	5	65.77	2.44	8.68
	50	64.73	2.03	8.68
	100	64.13	2.15	8.52
N-hexylpropanamide-NHP	5	61.39	1.95	8.37
	50	46.39	1.32	8.90
	100	40.58	0.60	8.11
N-methylbenzamide-NMB	5	62.76	2.03	9.96
	50	47.14	1.18	9.97
	100	37.94	0.99	9.69
N-n-butylbenzamide-NBB	5	55.60	1.47	9.98
	50	44.39	1.44	9.35
	100	35.99	1.17	9.78
N-2-phenylethyl propanamide-N2PP	5	59.18	1.55	9.43
	50	42.33	0.61	9.39
	100	30.37	0.59	9.56

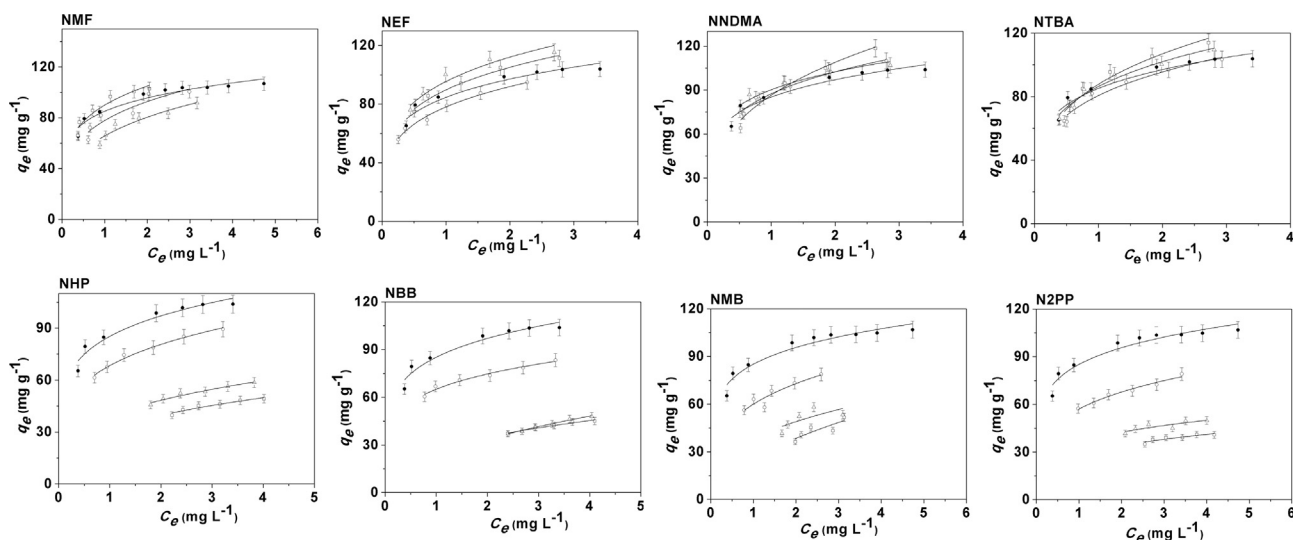
As it can be expected on the basis of kinetic experiments, the adsorption equilibrium of *p*-nitrophenol is affected much more by the more voluminous amides. The group of amides with less voluminous substituents (NMF, NEF, NNDMA, NTBA) showed a negligible influence on the adsorption capacity of *p*-nitrophenol, whereas voluminous amides (NHP, NMB, NBB, N2PP) affect the adsorption capacity reduction

with increasing concentrations. Accordingly, the values obtained for the free Gibbs energy changes indicate a less spontaneous adsorption process of the *p*-nitrophenol in the presence of the group of more voluminous amides.

Furthermore, the calculated values of diffusion and thermodynamic parameters of adsorption of *p*-nitrophenol have been correlated with structural parameters of the amide:

**Table 4** Equilibrium adsorption parameters of *p*-nitrophenol in the absence and in the presence of different concentrations of the investigated amides.

	$c$ (mg/dm <sup>3</sup> )	$K_F$ ((mg/g)/(mg/dm <sup>3</sup> )) <sup>n</sup>	$n$	$K_d$ (dm <sup>3</sup> /g)	$\Delta G$ (kJ/mol)
<i>p</i> -nitrophenol	5	84.88	0.196	39.74	-8.9
N-methylformamide-NMF	5	77.54	0.260	39.35	-8.9
	50	65.21	0.304	34.46	-8.6
	100	93.95	0.301	49.51	-9.5
N-ethylformamide-NEF	5	78.12	0.236	38.79	-8.9
	50	95.61	0.232	47.25	-9.4
	100	89.75	0.229	44.23	-9.3
N,N-dimethyl acetamide-NNDMA	5	87.34	0.232	43.24	-9.2
	50	89.97	0.194	42.91	-9.2
	100	86.27	0.344	47.29	-9.4
N-tert-butylacetamide-NTBA	5	80.51	0.252	40.56	-9.1
	50	86.28	0.248	43.31	-9.2
	100	87.57	0.301	45.95	-9.4
N-hexylpropanamide-NHP	5	68.17	0.242	34.04	-8.6
	50	36.18	0.337	20.69	-7.4
	100	26.04	0.416	17.06	-6.9
N-methylbenzamide-NMB	5	60.11	0.278	30.98	-8.4
	50	36.92	0.399	21.28	-7.4
	100	25.72	0.577	17.45	-6.9
N-n-butylbenzamide-NBB	5	65.11	0.197	31.19	-8.4
	50	23.45	0.521	15.11	-6.6
	100	13.10	0.841	15.20	-6.6
N-2-phenylethyl propanamide-N2PP	5	57.23	0.244	28.62	-8.2
	50	35.93	0.238	17.87	-7.1
	100	27.89	0.280	14.42	-6.5

**Figure 3** Adsorption isotherms of *p*-nitrophenol in the absence and in the presence of investigated amides at different concentrations (●—*p*-nitrophenol alone, ○—5 mg/dm<sup>3</sup> of amide, △—50 mg/dm<sup>3</sup> of amide, □—100 mg/dm<sup>3</sup> of amide).

the molecular volume  $V$ , the octanol-water partition coefficient  $\log K_{ow}$  value. The coefficients were tested by Student's ( $n-2$ )  $t$ -test, and it was found that some of coefficients are statistically significant at the significance level of  $p \leq 0.1$ , i.e. with a

certainty of 90%. The obtained correlations are presented in Table 5.

The following correlation can be observed: the volume and octanol-water partition coefficient correlated positively.

**Table 5** Obtained correlation coefficients for adsorption parameters of *p*-nitrophenol and structural parameters of amides.

	Adsorption parameters of <i>p</i> -nitrophenol <sup>a</sup>									Amide parameters <sup>a</sup>	
	$\Delta G_5$	$\Delta G_{50}$	$\Delta G_{100}$	$k_{f5}$	$k_{f50}$	$k_{f100}$	$D_{S5}$	$D_{S50}$	$D_{S5}$	$V$	$\log K_{OW}$
$\Delta G_5$	1	0.932	0.955	-0.485	-0.653	-0.724	0.441	0.726	-0.089	0.878	0.842
$\Delta G_{50}$		1	0.996	-0.179	-0.856	-0.876	0.457	-0.137	-0.932	<b>0.943</b>	0.457
$\Delta G_{100}$			1	-0.258	-0.817	-0.854	0.522	0.521	-0.143	<b>0.944</b>	<b>0.922</b>
$k_{f5}$				1	-0.331	-0.179	-0.073	-0.931	-0.204	-0.020	0.059
$k_{f50}$					1	0.969	-0.352	0.044	0.371	<b>-0.930</b>	<b>-0.947</b>
$k_{f100}$						1	-0.207	-0.065	0.526	<b>-0.950</b>	<b>-0.940</b>
$D_{S5}$							1	0.305	0.704	0.367	0.412
$D_{S50}$								1	0.266	0.315	0.256
$D_{S100}$									1	-0.314	-0.265
$K$										-0.968	-0.987
$V$										1	0.994
$\log K_{ow}$											1

The bolded coefficients represents significant correlations.

<sup>a</sup>  $\Delta G$  in kJ/mol,  $k_{f5,50,100}$  in  $\text{min}^{-1}$ ,  $D_{S5,50,100}$  in  $\text{m}^2/\text{min}$ ,  $V$  in  $\text{\AA}^3$ .

Moreover, significant correlations were also observed between all amide parameters and external diffusion constants  $k_f$ . Furthermore, a positive correlation of the volume and the octanol-water partition coefficient indicate that more voluminous, more hydrophobic amides reduce the possibility of binding *p*-nitrophenol on activated carbon.

As for the established correlation with the external diffusion coefficient, it can be assumed that more voluminous and less polar amides have impact on the increase of thickness of the outer film and reduce the capacity of the adsorbed *p*-nitrophenol. In other words, the less polar amide molecules concentrated at the boundary layer of polar and non-polar phase (water/carbon), thus creating an external film that remains stable despite the relatively high stirring velocity. Decrease of external diffusion can be also explained by NOM accumulation on the outer carbon surface and by increasing viscosity and thickness of the external layer (Carter and Weber, 1994).

In literature about multicomponent adsorption systems, a decrease of the absorption capacity of some of the components is usually explained mainly by two phenomena: the effect of direct competition for active sites on the adsorbent and the effect of blocking of the pores. According to the obtained results, it could be estimated that the effect of pore blockage is responsible for the reduced adsorption of *p*-nitrophenol in the presence of an amide.

The pore size distribution of the adsorbent and the molar mass fractions of NOM molecules show the most significant impact on the adsorption process of organic pollutants. Many studies indicated that a direct competition for available adsorbent sites is the dominant mechanism if the pores are large enough to admit micropollutants and NOM molecules. Also, if the pores are wide enough to pass only micropollutants and not NOM molecules, then the pore blocking mechanism is dominant (Pelekani and Snoeyink, 1999). In this study, powdered activated carbon with an average pore size of 20  $\text{\AA}$  was used. This average pore size can be classified as a lower mesopore. Based on the mean molecular weight of amide molecules and the medium pore size it can be estimated that the pore blocking mechanism is responsible.

As far as the inability of making more significant estimations is concerned, it can be concluded that the research needs to be expanded for the purpose of better distinguishing the

impact of amides on the diffusion parameters of *p*-nitrophenol at this concentration level. It is necessary to use more structurally/electronic different amides as model systems and also to perform experiments on water matrices with a wider range of amide concentrations.

## 5. Conclusion

In this paper it is shown that lower secondary amides may serve as model systems of low molar mass natural organic matter. Obtained differences in equilibrium and kinetic diffusivity parameters showed that voluminous and less polar amides decreased the adsorption capacity of *p*-nitrophenol on activated carbon. It is assumed that this effect is stronger on the external phase diffusion compared to internal.

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