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Adsorption of aromatic trace compounds from organic solvents on activated carbons—experimental results and modeling of adsorption equilibria

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Abstract Liquid phase adsorption is an important process for the removal of trace compounds from liquid matrices. Until today, research on liquid phase adsorption is less substantial than work on other thermal separation processes. The description of relevant mechanisms and interactions is difficult mainly because of lacking experimental data. This paper presents extensive isotherm measurements for the adsorption of organic trace compounds from organic solvents on activated carbons. A systematic variation of molecular structure of adsorptives and solvents enabled the identification of main structural factors dominating adsorption in these systems. The factors are polarity, extension and density of π electrons and sterical complexity. An analysis of the measured isotherms revealed incremental effects of functional groups and structural elements being characteristic for the adsorption capacities on activated carbons. Three consecutive empirical prediction models of adsorption equilibria are developed and compared. The empirical Freundlich equation appeared to be best suited for fitting the experimental data. The models apply an incremental concept permitting the calculation of adsorption isotherms on the basis of the structural increments of solvent and adsorptive molecules. The three models have a different extent of underlying data, a different number of parameters and a different range of application. The experimental data are predicted with satisfying accuracy for many engineering applications. The most sophisticated model has the most extensive range of application and manages on the smallest number of parameters.

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Symbols

$c_{i,0}$	Initial concentration of adsorptive i [mg adsorptive/L solvent]
$c_{i,eq}$	Equilibrium concentration of adsorptive i [mg adsorptive/L solvent]
K	Freundlich parameter [mmol adsorptive/kg adsorbent]
M_i	Molar mass of adsorptive i [g/mol]
M_{solv}	Molar mass of solvent [g/mol]
m_i	Weighed mass of adsorptive i [g]
n	Freundlich parameter [–]
ρ_{sol}	Solution density [g/L]
q_i	Adsorbent load [mmol adsorptive/kg adsorbent]
V_{sol}	Solution volume [L]
x_i	Molar fraction of adsorptive i [mol/mol]
K	Freundlich parameter [mmol adsorptive/kg adsorbent]
n	Freundlich parameter [–]
$N_{C,solv}$	Number of carbons atoms in the solvent hydrocarbon chain [–]
$N_{C,ads}$	Number of carbons atoms in the adsorptive hydrocarbon chain [–]

1 Introduction

Liquid phase adsorption is a thermal separation process which is known since the Antiquity. Fields of application, besides water processing, are for example the treatment of cases of poisoning and the cleaning of fats and oils (Robens 1994). In food industry liquid phase adsorption is used today

for the cleaning of sugar and alcoholic beverages (Singleton and Draper 1962; Gula and Paillat 2005). Other examples for industrial applications are the removal of the polymerization inhibitor 4-*tert*-butylcatechol from the monomer styrene on Al_2O_3 (River et al. 2002) and the adsorptive removal of water from organic solvents in the lower ppm- and ppb-range (Pahl et al. 2011).

Scientific investigations on liquid phase adsorption have been published by few authors who chiefly use water as a solvent. Karanfil and Dastgheib (2004) examined the adsorptive removal of trichloroethene from water by several activated carbons. They correlated the capacities to the proportion of micropores and hydrophilic surface groups. Shirgaonkar et al. (1992) measured the adsorption of 24 phenol derivatives with chloro, methyl and methoxy groups from water on activated carbons and fitted the data to the Freundlich equation. They found a strong dependence of adsorption on the nature of substitution.

The team of Le Cloirec investigated the removal of aromatic compounds from water by activated carbons. They varied the substituents to find relations with the adsorption capacities and tried to correlate molecular structure elements and molecular properties (QSPR) of phenol derivatives in aqueous solutions on the basis of molecular connectivity indices (MCI) in order to predict the adsorption equilibrium (Brasquet et al. 1999; Boulinguiez et al. 2008). The basic concept of MCI was developed by Randic (Kier and Hall 1986; Randic 1975). The concept describes the bond lengths of a molecule and the degree of branching by a matrix. Nirmalakhandan und Speece made a similar approach (Nirmalakhandan and Speece 1990).

Abe and co-workers correlated the adsorbent loads of 93 aliphatic compounds at a particular equilibrium concentration on an activated carbon with a multitude of physical molecular parameters like molar mass, polarity, molar refraction, and molar forces of attraction (Abe et al. 1983).

Schürer and Peukert (2005) approximated Henry coefficients of adsorption isotherms for several systems at small concentrations by the COSMO-RS method (Klamt 1995) using the Hamaker constant. COSMO-RS employs density functional theory calculations to determine a polarity profile on the molecular surface as a basis for a computation of molecular interactions.

Chitra and Govind (1986) developed a group contribution model to calculate the Freundlich parameters K and n of aliphatic adsorptives. The thermodynamic model assumes an ideal liquid phase. The application of the model is limited because aromatic compounds are not implemented.

The most comprehensive work has been published by Ulbig and co-workers (Berti et al. 1999, 2000). Their method predicts the surface excess of binary mixtures using a UNIFAC-type group contribution model with the adsorbate-solid-solution theory (ASST). ASST models the adsorbate as an independent thermodynamic phase in equilibrium with the liquid bulk phase. The model parameters were fitted to experimental adsorption data of branched and non-branched alkanes, alcohols and aromatics on different adsorbents. The quantification of functional groups on activated carbons was done by Boehm titration (Boehm et al. 1964).

Despite significant progress in this field during the recent decades many aspects of liquid phase adsorption are not well understood. The main problem compared to other thermal separation processes like rectification (Gmehling 1985; Gmehling et al. 1977) and gas phase adsorption (Rudzinski and Everett 1992) is a lack of experimental data combined with the complexity of the interactions involved.

The objective of our work was to develop easy-to-use prediction models of adsorption isotherms for process engineering applications in the field of trace compound removal. As a firm basis for model fitting a large extent of consistent data is required which properly reflect the main factors exerting an influence on liquid phase adsorption.

A systematic variation of the adsorptive and solvent molecules was made in order to identify relevant molecular structure groups and quantify their influence on adsorption. This procedure suggests an incremental modeling approach which depicts the impact of the structural groups on adsorption capacity.

2 Experimental

2.1 Adsorption systems

In this work more than 350 isotherms for the adsorption of trace compounds were measured at 20 °C. 28 adsorptives, 48 solvents, and 6 activated carbons were employed in the experiments. The main focus of work was the variation of adsorptives and solvents.

As adsorptives aromatic compounds were chosen for several reasons. On the one hand these compounds are suitable to specifically vary their properties by changing the substituents at the ring. Derivatives with methyl, tertiary-butyl, methoxy, hydroxy, and benzyl alcohol groups were used for that purpose. On the other hand a good detectability in the trace range by liquid chromatography favors the use of these compounds.

In case of the solvents the functional groups and the length of the aliphatic chains were varied. Most solvents contained oxygen. The main solvents used were primary and secondary alcohols, ketones, esters, and methacrylates. The solvent carbon chains had between 1 and 6 methylene groups. Chain branching was examined for C4 and C5 alcohols as well as for esters and methacrylates.

In order to eliminate the influence of solubility on adsorption as far as possible measurements were only made

Table 1 Activated carbon properties

Adsorbent trade name	Raw material	BET surface	Iodine number	pH
PAK A 1420	Hard coal	1075 g/m^2	1000 mg/g	3.0
CGF 1-3/100	Hard coal	1400 g/m^2	990 mg/g	6.6
C40/4 AR	Hard coal	1250 g/m^2	1050 mg/g	9.4
DGF AX	Hard coal	1000 g/m^2	950 mg/g	7.4
DGF AR	Hard coal	1000 g/m^2	950 mg/g	9.2
DGK	Coconut	1250 g/m^2	1050 mg/g	9.2

for systems where the solubility of the adsorptives in the solvent was very similar, assuming that in this case the overall molecular interaction between adsorptive and solvent is also similar. As a result the effects discussed below are mainly due to interactions of functional groups of the adsorptive and solvent with the adsorbent at the surface.

The activated carbons used in the experiments are commercial products on a hard coal or coconut basis which are activated with steam and washed with acids. The activated carbons were obtained from *CarboTech AC GmbH*, Essen, and pre-treated for 5 hours at 200 °C prior to the experiments.

Table 1 shows some characteristic properties. The BET surface was calculated from gas phase isotherms of nitrogen at 77 K. The measurement of the iodine number and the pH value was conducted according to the guidelines of the American Water Works Association (1978). The main focus of this work was not a detailed examination of the adsorbents. However, different activated carbons were used to find out to what extent the results may be transferred to other activated carbon adsorbents.

2.2 Experimental work

The main part of experimental work contains the measurement of adsorption isotherms in a concentration range from 5 to 500 mg/L at 20 ± 1 °C. For each isotherm 10 to 15 points were measured. Replicate analyses were carried out for more than 60 % of all experiments. The equilibration time determined by preliminary kinetic tests was 2–72 h depending on the activated carbon.

The experimental setup was designed as a batch procedure. 400 to 800 mg of pre-treated (dried) activated carbon was weighed into dried 100 mL amber glass bottles which could be closed with a cap.

The solutions (solvent + adsorptive) had an initial adsorptive concentration $c_{i,0}$ from 800 mg/L to 1800 mg/L. According to the desired equilibrium concentration $c_{i,eq}$ different volumes of the solution were pipetted to the activated carbon samples in the glass bottles. The bottles were closed and shaken on a thermostated incubator until equilibrium was reached. Syringe filters were then used to separate the solution from the solids. Blind experiments without adsorbent excluded other reasons for the concentration decrease of the adsorptive like degradation processes.

Initial and equilibrium adsorptive concentrations were determined by HPLC. The mean relative deviation of the concentration measurement was about 1.5 % in the range from 20 mg/L to 2000 mg/L.

2.3 Isotherm fitting

Measured equilibrium concentrations $c_{i,eq}$ were converted in mole fractions x_i to discuss the results on a particle interaction basis:

$$x_i \approx \frac{c_{i,eq} M_{solv}}{\rho_{sol} M_i} \tag{1}$$

The unit of x_i is [µmol adsorptive i/mol solution]. It relies on the assumption that for the diluted systems investigated the mass and the molar mass of the solution is approximately equal to the mass and the molar mass of the solvent, respectively. The adsorbent load q_i was calculated by

$$q_i = \frac{(c_{i,0} - c_{i,eq}) V_{sol}}{M_i m_i} \tag{2}$$

For each system (adsorbent + adsorptive + solvent) a set of experimental data $\{x_i, q_i\}$ was obtained. The data were fitted to the Freundlich equation (Freundlich 1907) and the Langmuir equation (Langmuir 1918) by linear regression after linearization of the equations. For the Langmuir equation the Hanes-Woolf-variant was utilized (Schulthess and Dey 1996).

The quality of the fit of the non-linearized isotherms is described by the correlation coefficient r^2 and the mean fitting error, respectively. Table 2 summarizes the results for all isotherms. In nearly all cases the Freundlich equation was better for fitting than the Langmuir equation. Figure 1 illustrates this finding for the exemplary system 4-methoxyphenol/2-propanol/CGF 1-3/100.

3 Results and discussion

3.1 Extension and density of π-electrons

The extension of π-electrons in organic molecules represents the number of mostly conjugated double and triple bonds of a molecule which are formed by the overlapping of p-orbitals. The density of the π-electron cloud is determined by the inductive and mesomeric effects of neighbored atomic groups which may either cause an increase (+I-effect, +M-effect) or a decrease (−I-effect, −M-effect) of the electron density.

Table 2 Mean fitting errors and correlation coefficients of the isotherms

Adsorbent trade name	Number of isotherms	Mean fitting errors		Mean correlation coefficients r^2	
		Freundlich	Langmuir	Freundlich	Langmuir
PAK A 1420	83	2.8 %	10.0 %	0.990	0.948
CGF 1-3/100	206	2.2 %	7.7 %	0.985	0.952
C40/4 AR	28	2.5 %	9.9 %	0.992	0.958
DGF AX	16	1.8 %	7.1 %	0.997	0.966
DGF AR	15	2.6 %	9.0 %	0.982	0.962
DGK	15	1.8 %	8.4 %	0.998	0.951
total	363	2.4 %	8.3 %	0.988	0.952

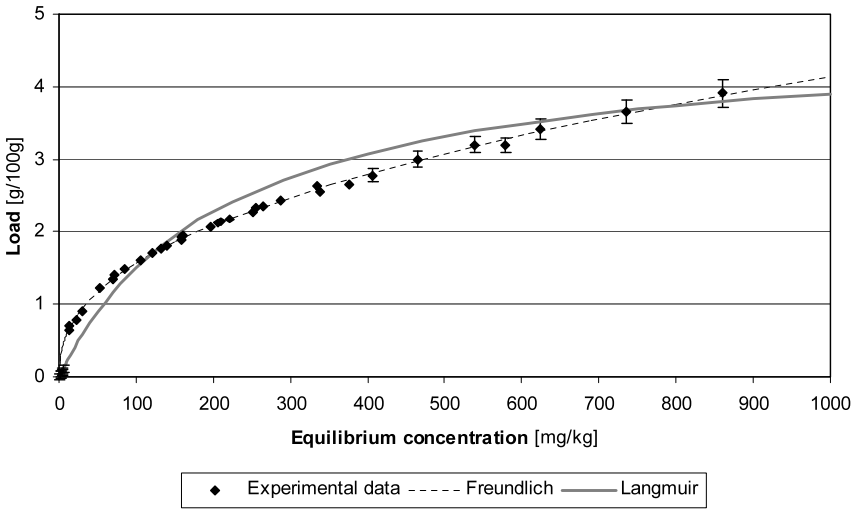


Fig. 1 Freundlich and Langmuir fitting for the adsorption of 4-methoxyphenol from 2-propanol on CGF 1-3/100

This work examines in detail these factors for both the solvents and the adsorptives. The experimental systems presented in the figures below are examples for a large number of systems which all show the effects discussed below in a very similar manner. In the following the influence of π-electron density is in the focus. This effect can be more clearly experimentally demonstrated than the effect of different extension of π-electrons because adsorptives with different π-electron extension (e.g. benzene and naphthalene derivatives) often have a significantly different solubility at the same time which may also affect adsorption.

For the solvents the adsorption behavior was investigated by experimental comparison of solvents differing only in the number of double bonds.

In case of the adsorptives first the detectability by the UV detector of the HPLC apparatus had to be ensured. Thus, UV active aromatic compounds were chosen. The density of the π-electrons was systematically varied by different kinds and numbers of substituents at the ring.

Adsorption isotherms for benzene, toluene, and *p*-xylene from alcohols on activated carbons were measured to describe the impact of methyl groups. The adsorptives only differ by the number of methyl groups. The solubility of the adsorptives in alcohols is very similar, which minimizes the impact of solubility on adsorption. Figure 2 compares the capacities for adsorption from methanol at an equilibrium concentration of 10^{-4} mol *i*/mol methanol. This concentration is the geometric mean of the covered range and should therefore be characteristic for the isotherm. Dividing the toluene load by the benzene load for all adsorbents yields 1.79 ± 0.08 on the average. The mean ratio of the *p*-xylene and toluene loads is 1.80 ± 0.06. An additional methyl group raises the loads of adsorption from methanol by about 80 %. For other alcohols the same trend is found. In case of ethanol the increase is about 60 %, for 1-propanol und 1-butanol it is 50 %. Branched alcohols show a raise of about 40 %. It is evident that an alkyl group makes an incremental contribution to the adsorption on activated carbons. The effect is attributed on the one hand to the interaction of the nonpolar alkyl groups with the mainly nonpolar carbon surface. On the other hand, we assume a contribution of the π-electron density increase by the +I-effect of the alkyl groups.

Figure 3 illustrates the impact of the inductive and mesomeric effect on the π-electron density by the adsorption of four aromatic compounds with different substituents from methanol on CGF 1-3/100. We observe a correlation between the load and the π-electron density of the adsorptives.

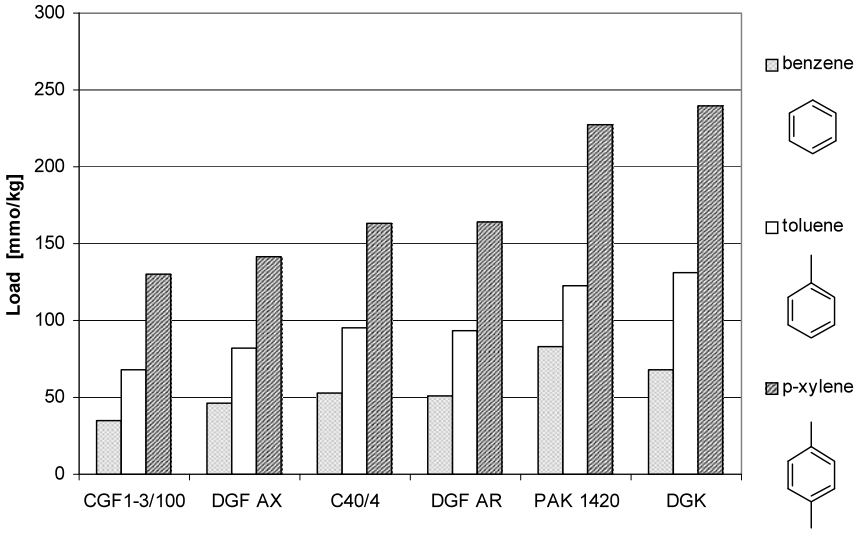


Fig. 2 Adsorbent load for benzene, toluene, and p-xylene at $c_{i,eq} = 10^{-4}$ mol i/mol methanol

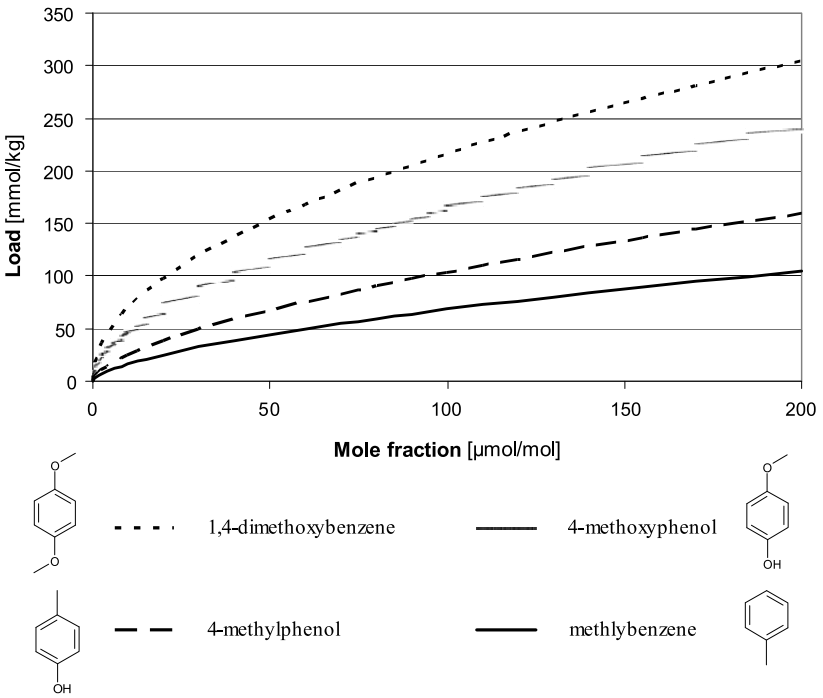


Fig. 3 Adsorption isotherms of aromatic compounds in methanol on CGF 1-3/100

1,4-dimethoxybenzene has the highest load as well as the highest π-electron density. The methoxy groups at the ring strongly increase the π-electron density by an +I-effect on the aromatic system. The +I-effect decreases in the order $H_3CO- > HO- > H_3C-$. In the same direction the loads are decreasing. The oxygen containing substituents have also an electron pushing +M-effect. More adsorption measurements with polysubstituted aromatics demonstrated the additive effects of these groups on adsorption.

The UV spectrum gives a first hint to the π-electron density of an adsorptive Fig. 4 shows the UV spectra of the adsorptives from Fig. 3. We observe a shift to longer wavelengths with increasing π-electron density.

The π-electron effect may also be illustrated by a solvent variation (see Fig. 5). The load for the adsorption of 4-methoxyphenol from 1-propanol **1** on CGF 1-3/100 and PAK 1420 is 3 times higher than the load for the adsorption of 4-methoxyphenol from the solvent 2-propen-1-ol **2**. Since adsorptive and solvent compete for the adsorption sites this implies that 1-propanol **1** adsorbs weaker than 2-propen-1-ol **2**. As seen in Fig. 5, these solvents only differ by one double bond. A similar comparison was made of isobutyric acid esters and methacrylates, as for example isobutyric acid ethyl ester **3** and ethyl methacrylate **4** (Gräf et al. 2010). The adsorptives were several monophenol ethers. Adsorption from solvents without a double bond was higher by a

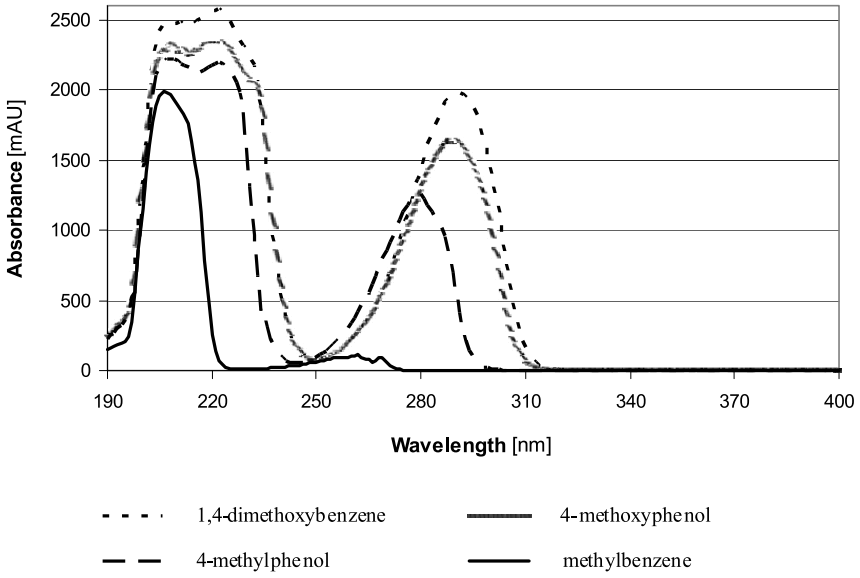


Fig. 4 UV spectra of aromatic compounds

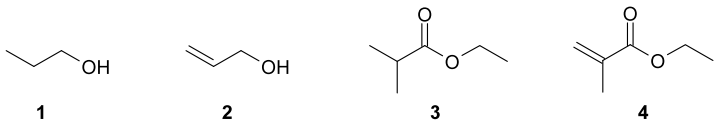


Fig. 5 Structure formulas of solvents

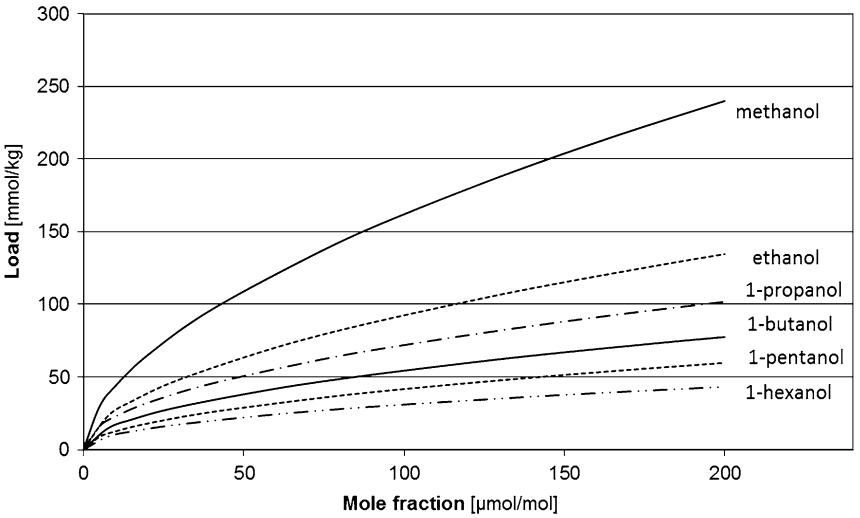


Fig. 6 Adsorption isotherms of 4-methoxyphenol in primary alcohols on CGF 1-3/100

factor of 3 to 4 compared to adsorption from solvents with a double bond due to stronger adsorption of the solvents containing π-electrons.

3.2 Polarity

Figure 6 shows the adsorption of 4-methoxyphenol from linear primary alcohols. It is clearly visible that the loads are decreasing with increasing chain length of the solvent (see Table 3). This implies that the long-chain, less polar alcohols adsorb better than the short chain, more polar alcohols. These results exemplary demonstrate the influence of polarity on the adsorption on mainly nonpolar activated carbons.

Table 3 Adsorption of 4-methoxyphenol from primary alcohols on CGF 1-3/100

Solvent	K	n	q at 100 µmol/mol
Methanol	11.9 mmol/kg	0.567	115 mmol/kg
Ethanol	7.4 mmol/kg	0.536	99 mmol/kg
1-Propanol	7.2 mmol/kg	0.504	73 mmol/kg
1-Butanol	5.2 mmol/kg	0.501	59 mmol/kg
1-Pentanol	3.8 mmol/kg	0.518	41 mmol/kg
1-Hexanol	3.5 mmol/kg	0.496	38 mmol/kg

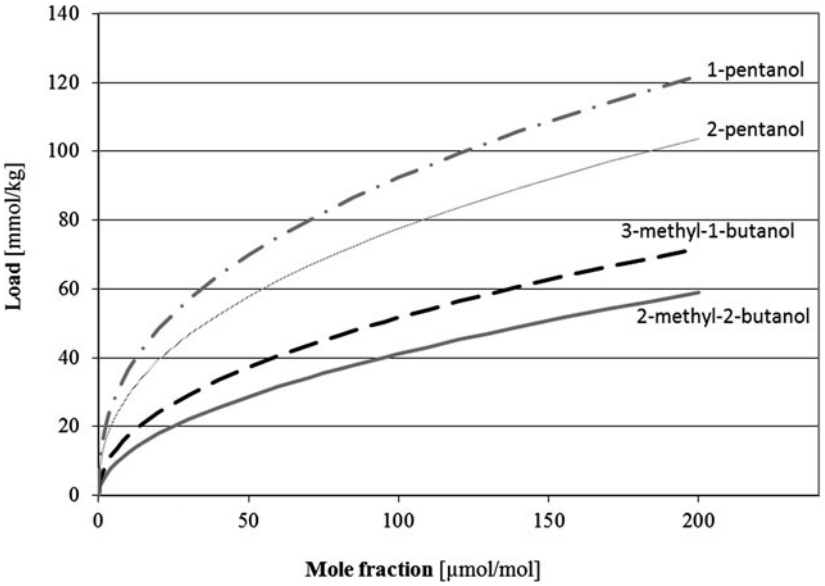


Fig. 7 Adsorption isotherms of 4-methoxyphenol in C5 alcohols on CGF 1-3/100

The examination of the homologous series permits the formulation of an empirical correlation between adsorption capacity and chain length. We find a linear relation between the logarithm of the Freundlich parameter K and the number of carbon atoms (Gräf et al. 2010). Experiments with other solvents revealed that the Freundlich exponent n only depends on the compound class (i.e. alcohols, ketones, esters).

3.3 Sterical complexity

The sterical complexity of a molecule is understood as the degree of its branching. High sterical complexity is generated by C, N, B, P, and S atoms with more than two bonds to non-hydrogen atoms. As a result of their branching molecules of high sterical complexity have a higher space requirement on the surface and maybe limited access to very small pores (if existing) compared to less branched isomers. The consequences of this factor for the adsorption equilibrium have been studied in detail for different solvents.

Figure 7 represents the removal of 4-methoxyphenol from pentanol isomers (see Fig. 8) by adsorption on CGF 1-3/100. The adsorptive is most effectively adsorbed from the strongly branched 2-methyl-2-butanol **8** because this solvent is a weaker competitor for adsorption sites than the other isomers. The differences of the adsorption of **6** and **7** indicate that a secondary methyl group inhibits adsorption more strongly than a secondary hydroxyl group. Analogous tests with esters and ketones produced very similar results.

The impact of sterical complexity was also investigated for the adsorptives, comparing the adsorption of phenol derivatives with and without *tert*-butyl group. The introduction of a *tert*-butyl group at the ring lowered the capacities by 60 to 70 %.

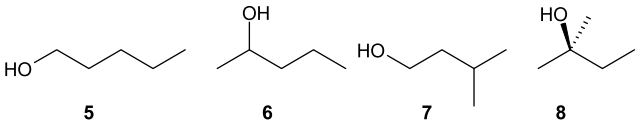


Fig. 8 Structure formulas of C5 alcohols

4 Adsorption modeling

4.1 Modeling approach

Two main approaches for modeling physical and thermodynamic properties are the development of incremental models and group contribution models.

Incremental models utilize empirical methods. Some molecular thermodynamic quantity X^{th} is understood as the sum of the impacts x_i^{th} of all molecular increments i exerting an influence b_i^{th} where a_i indicates how often that increment occurs in the molecular structure:

$$X^{th} = \sum_{i=1}^{n} x_i^{th} = \sum_{i=1}^{n} a_i b_i^{th} \tag{3}$$

The advantages of such methods are the mathematical simplicity and high transparency. Coefficient fitting needs little numerical efforts. The drawback is that the models are only applicable to systems which are very similar to the systems used for calibration.

Group contribution methods are semi-empirical models which enable the calculation of phase equilibria from the base equations of chemical thermodynamics. Molecular interactions are reduced to contributions from well-defined universal functional groups with binary interaction parameters fitted to experimental data. The main advantage of group contribution models is the universal applicability to a large number of systems including the same groups.

This paper develops three consecutive incremental models with a broadening range of application which provide a systematic description of the experimental data.

4.2 Model 1: Impact of solvent hydrocarbon chain

Alcohols, ketones, and esters are often used solvents. Dominated by the oxygen containing polar functional group overall molecular polarity depends on the number of non-polar methylene groups in the hydrocarbon chain. The influence of molecular polarity was determined by a systematic variation of the chain length. The investigations were performed with different solvent functional groups in order to obtain more generally applicable results which are valid for all kind of solvents included.

Figure 6 shows data for the adsorption of 4-methoxyphenol from primary alcohols on the activated carbon CGF 1-3/100. The adsorption decreases from methanol to 1-hexanol with increasing length of the solvent aliphatic chain. The same facts are found for other (adsorbent + solvent) combinations. In all cases the correlation between the adsorbent load q_i and the number of carbon atoms $N_{C,solv}$ can be written as

$$q_i(c_{i,eq}) = q_0^* \mathrm{e}^{a_0 + a_1 N_{C,solv}} \left(\frac{c_{i,eq}}{c_0^*} \right)^{n_0} \tag{4}$$

where a_0, a_1, and n_0 are empirical parameters fitted by multilinear regression to isothermal data of systems with the same solvent group. The quantities q_0^* and c_0^* are unit correction factors. The parameter a_0 describes the influence of the combination (adsorbent + adsorptive + solvent functional group). The parameter a_1 expresses the effect of a methylene group in the solvent. The individual Freundlich exponents n for each adsorbent were replaced by group exponents n_0. This procedure was applied to 38 systems, as shown in Table 4. The fit is based on 172 isotherms with more than 1850 experimental points. The mean fitting error is 7.5 % ($r^2 = 0.97$) which is satisfying for many engineering applications.

The exponent n_0 significantly depends on the type of the solvent functional group. For primary alcohols n_0 is about 0.50 and for esters 0.45 on the average.

4.3 Model 2: Impact of solvent and adsorptive hydrocarbon chains

In order to account also for the influence of the number of carbons in the adsorptive chains (4) is extended.

$$q_i(c_{i,eq}) = q_0^* \mathrm{e}^{a_0 + a_1 N_{C,solv} + b_1 N_{C,ads}} \left(\frac{c_{i,eq}}{c_0^*} \right)^{n_0} \tag{5}$$

The parameter b_1 in (5) expresses the influence of the aliphatic side chains of the adsorptive depending on the number of carbon atoms $N_{C,ads}$ in the chain. In this model all carbons need to be in the same side chain. As an example, Table 5 shows the calculated parameters for 6 systems consisting of an activated carbon, a solvent functional group and 4-methoxyphenol as adsorptive.

Equation (5) has two advantages over (4). First, a group of isotherms for n adsorptives can be described by less parameters because after including the adsorptive properties only 4 instead of $3n$ parameters are required for each solvent functional group. Second, the quantitative impact of $N_{C,solv}$ and $N_{C,ads}$ is transparent now. The disadvantage is a moderately higher fitting error. We think the extension is useful because the advantages outweigh the disadvantage.

As an example, modeling the results for the adsorption of 4-methoxyphenol from linear esters on CGF 1-3/100 (28 isotherms) using (5) requires only 4 parameters and has a mean fitting error of 8.3 %. Using (4) requires 15 parameters (3 parameters for each of the 5 systems with linear esters) and has a mean fitting error of 6.0 %.

4.4 Model 3: Comprehensive incremental model

The data basis for the third model contains 119 isotherms with more than 1270 points. Each isotherm has between 10 and 12 points in a range from 10 to 500 µmol adsorptive/mol solution. This makes sure that all isotherms get the same weighting.

As adsorptives 6 phenol derivatives with different substituents were utilized (see Fig. 9). The structural basis is a benzene ring. The substituents are represented by 4 increments: the phenol group, the phenolether group, the alkyl group, and the tert-butyl group.

The model includes 42 solvents: alcohols, ketones, esters, methacrylates, and acetonitril: The solvent increments represent the structure of the hydrocarbon chain as well as the functional groups.

Combining 42 solvents with 6 adsorptives yields 252 systems to be measured. To limit expense and time a selection was made. The adsorption behavior from linear primary alcohols (methanol-1-hexanol) was investigated in case of all adsorptives to ensure proper implementation of polarity effects by homologous hydrocarbon series.

All solvents were tested with 4-methoxyphenol **2** to verify the preceding results obtained with that adsorptive. Then, 4-ethoxyphenol **3** and 4-*n*-propoxyphenol **4** were measured with 70 % of the solvents to find out the impact of chain elongation at the adsorptive. The other adsorptives were used with solvents in selected combinations to account for sterical and π-electron density effects.

The model is valid only for the granulated activated carbon CGF 1-3/100. Models for other activated carbons (e.g. PAK A 1420 and C40/4 AR) were not developed because the available isotherm data were not sufficient.

Table 4 Empirical parameters of *Model 1*

Adsorbent trade name	Adsorptive	Solvent group	a_0	a_1	n_0	r^2	Fitting error
C40/4 AR	4-Methoxyphenol	Alcohols, primary	2.94	−0.33	0.54	0.99	4.7 %
C40/4 AR	4-Methylphenol	Alcohols, primary	3.55	−0.51	0.48	0.95	12.8 %
CGF 1-3/100	1,4-Dihydroxybenzene	Alcohols, primary	2.97	−0.31	0.47	0.93	13.4 %
CGF 1-3/100	1,4-Dimethoxybenzene	Alcohols, primary	3.43	−0.29	0.47	0.98	6.0 %
CGF 1-3/100	4-Ethoxyphenol	Alcohols, primary	2.99	−0.38	0.55	0.93	11.0 %
CGF 1-3/100	4-Methoxybenzylalcohol	Alcohols, primary	3.02	−0.38	0.47	0.98	7.3 %
CGF 1-3/100	4-Methoxyphenol	Alcohols, primary	2.83	−0.28	0.50	0.96	6.9 %
CGF 1-3/100	4-Methylphenol	Alcohols, primary	2.29	−0.40	0.58	0.96	7.9 %
CGF 1-3/100	4-*n*-Propoxyphenol	Alcohols, primary	3.25	−0.42	0.52	0.92	13.4 %
CGF 1-3/100	4-*tert*-Butylphenol	Alcohols, primary	0.59	−0.68	0.82	0.97	16.3 %
CGF 1-3/100	4-*tert*-butylcatechol	Alcohols, primary	3.72	−0.46	0.33	0.96	11.8 %
CGF 1-3/100	Anisol	Alcohols, primary	2.33	−0.31	0.55	0.99	5.4 %
CGF 1-3/100	Phenol	Alcohols, primary	1.72	−0.27	0.54	0.97	8.5 %
CGF 1-3/100	Phenolthiazine	Alcohols, primary	5.44	−0.37	0.41	0.96	8.7 %
CGF 1-3/100	4-Ethoxyphenol	Alcohols, secondary	3.71	−0.39	0.46	0.99	4.6 %
CGF 1-3/100	4-Methoxyphenol	Alcohols, secondary	3.56	−0.33	0.45	0.99	4.0 %
CGF 1-3/100	4-*n*-Propoxyphenol	Alcohols, secondary	3.67	−0.38	0.46	0.99	4.1 %
CGF 1-3/100	4-Methoxyphenol	Butyric acid derivatives	1.37	0.02	0.45	0.97	5.6 %
CGF 1-3/100	4-Ethoxyphenol	Acetic acid derivatives	1.66	−0.09	0.51	0.98	4.3 %
CGF 1-3/100	4-Methoxyphenol	Acetic acid derivatives	1.87	−0.05	0.44	0.96	9.8 %
CGF 1-3/100	4-*n*-Propoxyphenol	Acetic acid derivatives	2.01	−0.15	0.51	0.99	3.6 %
CGF 1-3/100	4-Ethoxyphenol	Isobutyric acid derivatives	2.71	−0.10	0.43	0.97	5.9 %
CGF 1-3/100	4-Methoxyphenol	Isobutyric acid derivatives	2.52	−0.06	0.39	0.99	2.3 %
CGF 1-3/100	4-*n*-Propoxyphenol	Isobutyric acid derivatives	2.78	−0.11	0.43	0.97	5.7 %
CGF 1-3/100	4-Methoxyphenol	Propionic acid derivatives	1.80	−0.05	0.46	0.95	7.0 %
CGF 1-3/100	4-Ethoxyphenol	Ketones, linear	1.73	−0.28	0.60	0.94	12.4 %
CGF 1-3/100	4-Methoxyphenol	Ketones, linear	1.90	−0.29	0.59	0.94	6.5 %
CGF 1-3/100	4-*n*-Propoxyphenol	Ketones, linear	1.87	−0.27	0.58	0.94	13.2 %
CGF 1-3/100	4-Methoxyphenol	Methacrylates	1.07	−0.02	0.47	0.97	5.3 %
PAK A 1420	1,4-Dihydroxybenzen	Alcohols, primary	3.66	−0.29	0.33	0.94	8.0 %
PAK A 1420	4-Ethoxyphenol	Alcohols, primary	3.29	−0.29	0.51	0.99	3.3 %
PAK A 1420	4-Methoxyphenol	Alcohols, primary	3.24	−0.25	0.50	0.99	4.7 %
PAK A 1420	4-*n*-Propoxyphenol	Alcohols, primary	3.43	−0.31	0.51	0.98	5.2 %
PAK A 1420	4-Methoxyphenol	Alcohols, secondary	4.21	−0.38	0.44	0.98	7.5 %
PAK A 1420	4-Methoxyphenol	Acetic acid derivatives	2.08	−0.03	0.52	0.99	3.5 %
PAK A 1420	4-Methoxyphenol	Isobutyric acid derivatives	2.76	−0.01	0.40	0.99	2.6 %
PAK A 1420	4-Methoxyphenol	Ketones, linear	1.99	−0.21	0.62	0.98	7.9 %

The mathematical basis of *Model 3* is again the Freundlich equation. The systems are divided into 3 groups depending on the solvent nature. For each group, an exponent η_i is calculated which is used for all isotherms measured with solvents of that group.

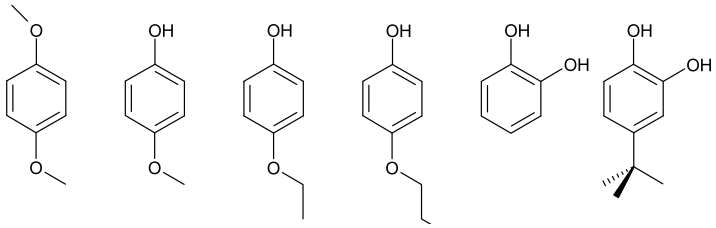
The Freundlich parameter K is calculated from the contribution of the adsorptive A and the solvent L.

$$\ln K = A + L \tag{6}$$

Table 5 Empirical parameters of *Model 2* for 4-methoxyphenol

Stoffsystem		Parameters				
Adsorbent trade name	Solvent group	a_0	a_1	b_1	n_0	Fitting error
CGF 1-3/100	Ketones, linear	1.81	−0.27	0.003	0.59	11.5 %
CGF 1-3/100	Ester, linear	1.78	−0.07	0.011	0.45	8.3 %
CGF 1-3/100	Esters, branched	2.64	−0.10	0.028	0.43	7.7 %
CGF 1-3/100	Alcohols, primary and linear	3.01	−0.35	0.019	0.51	11.3 %
CGF 1-3/100	Alcohols, secondary and linear	3.69	−0.37	0.039	0.47	4.7 %
PAK A 1420	Alcohols, primary and linear	3.25	−0.28	0.037	0.50	5.2 %

Fig. 9 Adsorptives of *Model 3*



1: 1,4-dimethoxybenzene **2**: 4-methoxyphenol **3**: 4-ethoxyphenol

4: 4-n-propoxyphenol **5**: catechol **6**: 4-*tert*-butylcatechol

The adsorptive contribution A is the sum of the number of increments j in the adsorptive molecule a_j multiplied by the effect of the increment j on adsorption α_j.

$$A = \sum_{j=1}^{4} a_j \alpha_j \tag{7}$$

The same procedure for the solvents yields

$$L = \sum_{l=1}^{10} b_l \lambda_l \tag{8}$$

where b_l is the number of increments l in the solvent molecule and λ_l the effect of the increment l on adsorption.

The 17 parameters ($\eta_i, \alpha_j, \lambda_l$; see Table 6) are calculated by multilinear regression.

The mean fitting error of *Model 3* is 17 %. The median is 13 %. 25 % of all isotherms have a fitting error which is less than 6 %. 15 % of the points have an error larger than 31 %. The largest deviation of a point was 67 %.

Table 6 Empirical parameters of *Model 3*

Notation	Type	Group name	Value
α_1	Adsorptive	Phenolether group	7.02
α_2	Adsorptive	Phenol group	6.81
α_3	Adsorptive	Aliphatic groups	−0.31
α_4	Adsorptive	*tert*-Butyl group	−0.01
λ_1	Solvent	HO-group, primary	−4.97
λ_2	Solvent	HO-group, secondary	−5.52
λ_3	Solvent	HO-group, tertiary	6.19
λ_4	Solvent	Keto group	−1.61
λ_5	Solvent	Ester group	−0.81
λ_6	Solvent	Nitrilo group	−5.99
λ_7	Solvent	Branched olefinic group	−1.43
λ_8	Solvent	Methyl group	−5.59
λ_9	Solvent	Methylene group	−0.17
λ_{10}	Solvent	Tertiary aliphatic group	5.83
η_1	Exponent	Ketones, nitriles	0.56
η_2	Exponent	Alcohols	0.32
η_3	Exponent	Esters, methacrylates	0.48

4.5 Model comparison

A particular strength of *Model 1* is the high accuracy for some solvents. Since only solvent increments are included *Model 1* needs one set of parameters for each combination of adsorptive and solvent group.

Models 2 and 3 consider solvent as well as adsorptive increments. The mean fitting error of *Model 2* (9 %) is smaller than of *Model 3* (17 %) though there are systems where *Model 2* does not deliver better results than *Model 3* in spite of the higher number of parameters.

The strengths of *Model 3* are the broader basis of experimental data (119 isotherm compared to 82 isotherms for *Model 2*) and the smaller number of empirical parameters (20 parameters for *Model 2*, 17 parameters for *Model 3*).

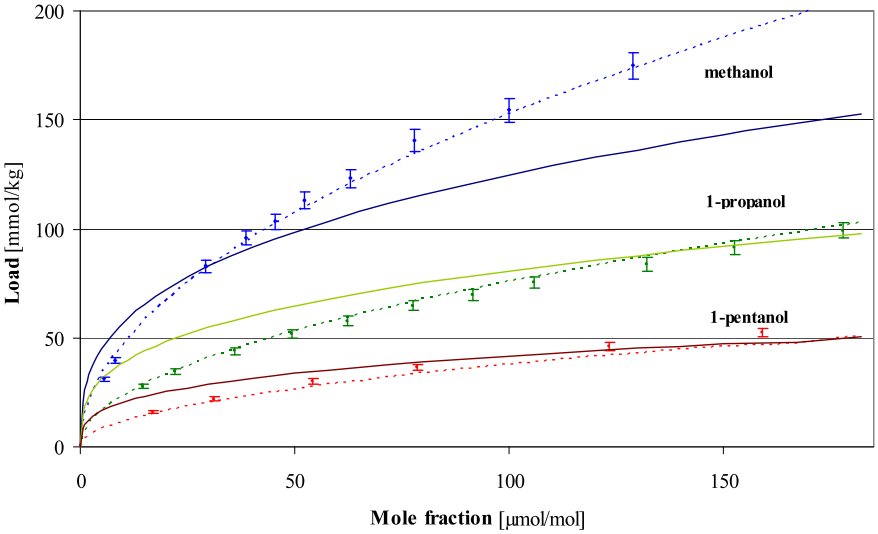


Fig. 10 Model calculations and experimental data for adsorption of 4-methoxyphenol from organic solvents on CGF 1-3/100. Model 2: *dotted lines*. Model 3: *closed lines*

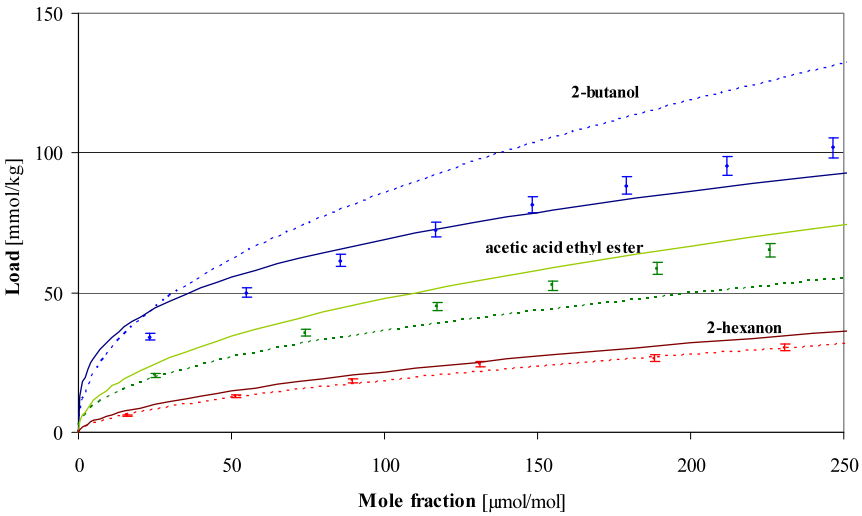


Fig. 11 Model calculations and experimental data for adsorption of 4-ethoxyphenol from organic solvents on CGF 1-3/100. Model 2: *dotted lines*. Model 3: *closed lines*

Model 2 needs one set of parameters for each adsorptive whereas *Model 3* needs only one set of parameters.

Of course, a general limitation of all 3 models is that adsorbent properties are not included. In order to account for different adsorbents, even in case of *Model 3* one set of parameters is required for each adsorbent.

Figure 10 compares experimental isotherm data of 4-methoxyphenol in methanol, 1-propanol and 1-pentanol with the results of *Model 2* and *Model 3*. It is evident that *Model 2* describes all isotherms better than *Model 3*. For *Model 2* the mean fitting error is 5.7 % which is within experimental accuracy for 75 % of all points. *Model 3* has a high deviation for the solvent methanol (mean fitting error of 42 %). The isotherms for longer alcohols are better fitted (mean fitting error of 26 %) but the fit is poor at small concentrations.

In Fig. 11 another comparison of experimental data and model predictions is given. The figure displays the adsorption of 4-ethoxyphenol from 2-butanol, acetic acid ester, and 2-hexanon. For the linear ketone 2-hexanon the calculated data are in accord with experimental observations. *Model 2* has a mean fitting error of 6 %, for *Model 3* it is 8 %. For the other solvents *Model 3* provides significantly better results than *Model 2*. The mean fitting error of *Model 3* is about 11 % for the ester and the secondary alcohol whereas *Model 2* has an error of 18 % for the ester system and 27 % for the secondary alcohol.

5 Summary and conclusion

The adsorption of phenol derivatives from organic solvents on activated carbons was measured for low adsorptive concentrations (5 to 500 mg/L) at 20 °C. The molecular properties dominating the process were identified comparing adsorption isotherms of systematically varied systems.

It was shown that high π-electron extension and density, low polarity and low sterical complexity favor adsorp-

tion on activated carbons. The molecular structure elements have an incremental effect on adsorption which manifests in characteristic contributions of the respective groups. It was shown, for example, that in homologous series the number of methylene groups correlates with the logarithm of the Freundlich parameter K. This makes empirical modeling with incremental methods seem promising.

The experiments were conducted with 6 activated carbons with different properties. The phenomena described in this paper were observed in case of all carbons in a very similar manner. Thus a transfer of the basic findings to other activated carbons should be possible. The large extent of consistent data measured with the same method offers a firm basis for the development of prediction models for liquid phase adsorption equilibria.

3 consecutive incremental models for the adsorption of organic trace compounds from organic solvents on activated carbons were developed. The models are easy to use and mathematically simple but give a satisfying representation of the isotherms for many engineering applications. This makes a more sophisticated modeling with group contribution methods seem attractive.

Appendix: Tables of experimental data

Table 7 Data of Fig. 2. Adsorbent load for benzene, toluene, and p-xylene at $c_{i,eq} = 10^{-4}$ mol i/mol methanol

Adsorbent	Adsorptive		
	Benzene	Toluene	p-Xylene
CGF1-3/100	34.8	67.8	130.4
DGF AX	46.2	82.4	141.3
C40/4	52.7	94.8	163.3
DGF AR	51.4	93.8	164.6
PAK 1420	82.7	122.7	227.3
DGK	68.4	130.9	239.7

Table 8 Data of Fig. 3. Adsorption isotherms of aromatic compounds in methanol on CGF 1-3/100

Adsorptive	Equilibrium concentration [µmol/mol]	Adsorbent load [mmol/kg]
1,4-Dimethoxybenzene	3.6	43.8
	16.9	87.6
	29.4	116.4
	42.8	141.4
	57.5	165.1
	76.2	188.2
	97.6	217.0
	119.6	245.3
4-Methoxyphenol	5.6	31.0
	8.2	39.4
	29.2	82.8
	38.8	95.7
	45.5	103.3
	52.4	113.2
	62.9	123.1
	77.5	140.5
	91.4	154.5
	110.0	170.6
4-Methylphenol	44.2	63.4
	79.4	90.6
	110.1	110.2
	139.3	125.6
	161.4	139.0
	185.8	152.5
	204.5	162.6
	226.6	173.6
	244.2	182.9
	262.2	190.8
Methylbenzene (toluene)	17.6	22.7
	38.9	37.9
	42.5	38.8
	64.7	52.0
	89.3	64.4
	115.1	75.4
	139.4	85.2
	168.4	94.4
	193.6	103.1
	216.6	113.0

Table 9 Data of Fig. 6. Adsorption isotherms of 4-methoxyphenol in primary alcohols on CGF 1-3/100

Adsorptive	Equilibrium concentration [µmol/mol]	Adsorbent load [mmol/kg]
Methanol	See data of Fig. 3	
Ethanol	15.1	32.2
	21.8	39.7
	48.7	58.0
	72.8	71.9
	80.3	78.9
	96.4	83.7
	110.4	94.1
Propanol	14.7	27.8
	21.9	34.4
	36.1	43.9
	49.3	51.7
	62.2	57.8
	77.5	64.6
	91.4	69.8
	105.8	75.3
Butanol	30.5	29.2
	46.0	35.8
	76.5	45.4
	99.0	52.4
	119.6	57.7
	145.7	63.9
	170.0	68.2
	195.8	73.9
Pentanol	54.2	30.1
	78.7	36.5
	123.2	45.9
	159.1	52.4
	187.9	57.6
	225.5	62.8
	257.0	66.9
	294.6	71.5
Hexanol	76.7	29.9
	108.5	36.0
	171.6	44.6
	219.0	50.4
	257.9	54.7
	301.8	59.4
	342.2	63.1
	382.6	66.8

Table 10 Data of Fig. 7. Adsorption isotherms of 4-methoxyphenol in C5 alcohols on CGF 1-3/100

Adsorptive	Equilibrium concentration [µmol/mol]	Adsorbent load [mmol/kg]
Pentanol	See data of Fig. 6	
2-Pentanol	24.8	26.5
	87.3	49.2
	120.5	56.0
	144.9	62.3
	175.9	67.4
	202.4	72.5
	245.3	78.5
	322.6	91.3
	440.4	102.4
3-Methyl-1-butanol	11.0	30.7
	45.2	55.7
	81.6	70.4
	116.0	82.4
	159.1	92.7
	205.6	102.7
	225.8	109.9
	286.5	121.7
	323.4	127.4
	370.9	135.4
	408.6	143.0
	473.7	150.9
2-Methyl-2-butanol	5.9	27.3
	20.8	51.3
	42.3	69.5
	72.5	84.7
	112.3	99.2
	153.4	110.4
	198.9	121.5
	239.7	131.2
	289.4	140.5
	343.9	149.2
	390.1	157.7
	441.5	164.6

Table 11 Data of Fig. 10. Model calculations and experimental data for adsorption of 4-methoxyphenol from organic solvents on CGF 1-3/100

Adsorptive	Equilibrium concentration [µmol/mol]	Adsorbent load [mmol/kg]
Methanol	5.5	31.0
	8.2	39.4
	29.2	82.8
	38.8	95.7
	45.5	103.3
	52.4	113.2
	62.9	123.1
	78.0	140.5
	100.0	154.5
	129.0	175.0
Propanol	14.7	27.8
	21.9	34.4
	36.1	43.9
	49.3	51.7
	62.2	57.8
	77.5	64.6
	91.4	69.8
	105.8	75.3
	132.3	83.7
	152.7	91.1
	177.9	99.1
Pentanol	17.0	16.0
	31.1	22.2
	54.2	30.1
	78.7	36.5
	123.2	45.9
	159.1	52.4
	187.9	57.6

Table 12 Data of Fig. 11. Model calculations and experimental data for adsorption of 4-ethoxyphenol from organic solvents on CGF 1-3/100

Adsorptive	Equilibrium concentration [µmol/mol]	Adsorbent load [mmol/kg]
2-Butanol	23.2	34.2
	54.7	50.0
	85.5	61.5
	116.8	72.5
	148.1	81.5
	179.1	88.4
	212.0	95.5
	246.3	102.0
Acetic acid ethyl ester	25.0	20.5
	74.3	35.6
	117.1	45.0
	155.4	52.5
	189.1	58.6
	226.6	65.3
2-Hexanon	15.8	6.1
	51.2	89.5
	131.0	24.4
	188.0	26.5
	230.5	30.4

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