Adsorption (2014) 20:385–395
DOI 10.1007/s10450-013-9571-y

Discrimination between adsorption isotherm models based on nonlinear frequency response results

Menka Petkovska

Received: 10 May 2013 / Accepted: 29 August 2013 / Published online: 15 September 2013

Abstract A number of criteria are established for distinguishing between different adsorption isotherm types. These criteria are defined based on the adsorption isotherm derivatives up to the third order, which, on the other hand, can be estimated from nonlinear frequency response data. The criteria for five favourable (Langmuir, Freundlich, Sips, Toth and Unilan) isotherms and two complex isotherms (BET and quadratic) are presented. These criteria enable unique identification of the underlying adsorption isotherm relation if the values of the local first, second and third order isotherm derivatives at several points are known. The method is applied to experimental data from our previous publications, for one case of a favourable and one case of a complex isotherm.

Keywords Adsorption isotherms · Model discrimination · Isotherm derivatives · Nonlinear frequency response

List of symbols

Variables

$\tilde{a}$	Dimensionless first order derivative of the adsorption isotherm
$\tilde{b}$	Dimensionless second order derivative of the adsorption isotherm
b	Model parameter for Langmuir, Sips, Toth and Unilan isotherms
b_L, b_S	BET isotherm model parameters
b_1, b_2	Quadratic isotherm model parameters
C (g/dm^3)	Concentration in the fluid phase
c	Dimensionless concentration in the fluid phase
$\tilde{c}$	Dimensionless second order derivative of the adsorption isotherm
CR	Criterion
$F_n(\omega_1, \omega_2, \ldots \omega_n)$	n-th order frequency response function on the particle level
$G_n(\omega_1, \omega_2, \ldots \omega_n)$	n-th order frequency response function on the adsorber level
K	Freundlich isotherm model parameter
L (cm)	Column length
n	Model parameter for Freundlich and Sips isotherm
Q (g/dm^3)	Concentration in the solid phase
Q_0 (g/dm^3)	Model parameter for Langmuir, Sips, Toth, Unilan, BET and quadratic isotherms
q	Dimensionless concentration in the solid phase
t	Model parameter for Toth isotherm
u	Interstitial column velocity
V (dm^3)	Volume
$\dot{V}$(dm^3/min)	Volumetric flow-rate

Greek notations

ε	Porosity
ω	Frequency, general and dimensionless
ω* (rad/min)	Frequency, dimensional

Subscripts

BET	BET
F	Freundlich
L	Langmuir

M. Petkovska (✉)
Department of Chemical Engineering, Faculty of Technology
and Metallurgy, University of Belgrade, Karnegijeva 4,
11000 Belgrade, Serbia
e-mail: menka@tmf.bg.ac.rs

QUAD	Quadratic
S	Sips
s	Steady-state
T	Toth
U	Unilan

Superscripts

d	Dimensional

Abbreviations

DC	Non-periodic (DC) term
FR	Frequency response
FRF	Frequency response function
NFR	Nonlinear frequency response

1 Introduction

Adsorption isotherms, which define the equilibrium in adsorption systems, represent the basic information needed for successful design of any adsorption process. In spite of substantial efforts which are made in developing methods for prediction of adsorption isotherms, experimental estimation is still the main and most reliable source of these data. A good review of different experimental methods for estimation of adsorption isotherms can be found, for example in (Seidel-Morgenstern 2004).

Different mathematical models are used for representing adsorption isotherms. Some of them have theoretical basis, while some others are semi-empirical, or empirical. A comprehensive review of different isotherm models can be found, for example in (Do 1998; Guiochon et al. 1994). The usual procedure for determining the isotherm type is to fit the experimental data to different models, chosen a priori, and chose the relation that gives the best fit. For some isotherm models, such as Langmuir or Freundlich, the equilibrium relationships can be transformed into linear forms. Nevertheless, often several models give similar results, so an unambiguous conclusion regarding the isotherm type is not possible.

In the last decade we have developed a new method for experimental determination of adsorption isotherms, the nonlinear frequency response (NFR) method (Petkovska 2006). It is based on sinusoidal modulation of a chosen input into the adsorber around a previously established steady-state, and measuring and harmonic analysis of a chosen output. As a result, a set of frequency response functions (FRFs) is obtained. A very important property of these FRFs is that their low-frequency asymptotes can be directly related to the first, second, third, etc., derivatives of the adsorption isotherm. By performing experiments for several steady-state points, the local derivatives of the adsorption isotherm corresponding to these steady-states are obtained. The experimental arrangements for the NFR method can differ [e.g. a reservoir-type adsorber with volume modulation is convenient for investigation of gas–solid systems, while a column-type adsorber with modulation of the inlet concentration is more convenient for investigation of liquid–solid systems (Petkovska 2006)], nevertheless the same type of final information is obtained: the local isotherm derivatives corresponding to the steady-state points chosen for the NFR experiments. In our previous applications, we estimated the underlying adsorption isotherms by fitting the obtained local isotherm derivatives to the derivatives of a priori chosen isotherm relations (Ilic et al. 2007).

In this work, we present another approach, as we use the isotherm derivatives that can be estimated by the NFR method, for identifying the isotherm relation, when no a priori knowledge about its form is available.

2 Theory

2.1 Models of single-component adsorption isotherms

In our analysis, we will consider seven different adsorption isotherm models, five of them corresponding to favourable, and two to complex isotherms with inflection points. Theoretical basis and derivations of these isotherms can be found in classical adsorption texts (see for example Do 1998; Guiochon et al. 1994). Here, we give just the mathematical models corresponding to these isotherms. The methodology presented in this manuscript can be used both for gas–solid and liquid–solid adsorption systems, and for that reason the isotherms will be represented in the general form:

$$Q = f(C) \tag{1}$$

where Q is the concentration in the solid phase (loading) and C is the corresponding concentration in the fluid phase.

The following isotherm models will be considered:

1. Langmuir isotherm (Langmuir 1918):

$$Q = \frac{Q_0 bC}{1 + bC} \tag{2}$$

Q_0 and b are model parameters

2. Freundlich isotherm (Freundlich 1906):

$$Q = KC^{1/n} \tag{3}$$

K and n are model parameters.

3. Sips, or Langmuir–Freundlich isotherm (Sips 1948):

$$Q = \frac{Q_0 (bC)^{1/n}}{1 + (bC)^{1/n}} \tag{4}$$

The model parameters are Q_0, b and n.

4. Toth isotherm (Toth 2002):

$$Q = \frac{Q_0 bC}{\left(1 + (bC)^t\right)^{1/t}} \tag{5}$$

   The model parameters are Q_0, b and t.
5. Unilan isotherm (Do 1998):

$$Q = \frac{Q_0}{s} \ln\left(\frac{1 + be^{s}C}{1 + be^{-s}C}\right) \tag{6}$$

   The model parameters are Q_0, b and s.
6. BET isotherm (Brunauer et al. 1938):

$$Q = \frac{Q_0 b_S C}{(1 - b_L C)(1 - b_L C + b_S C)} \tag{7}$$

   The model parameters are Q_0, b_L and b_S.
7. Quadratic isotherm (Guiochon et al. 1994):

$$Q = Q_0 \frac{b_1 C + 2b_2 C^2}{1 + b_1 C + b_2 C^2} \tag{8}$$

   The model parameters are Q_0, b_1 and b_2.

The first five isotherms (Langmuir, Freundlich, Sips, Toth and Unilan) correspond to concave Q versus C curves, and are therefore favourable, while the last two isotherms (BET and quadratic) can correspond to complex shapes of the Q versus C curves, with inflection points.

2.2 Estimation of adsorption equilibrium data from NFR results

The NFR method for investigation of adsorption systems have been explained in details in our previous publications. Let's repeat here just the basic facts (Petkovska 2006):

1. The NFR method is based on analyzing the response of the chosen adsorption system to a periodic, sinusoidal or co-sinusoidal input change around a chosen steady-state point. When the input amplitude is not very small, the system nonlinearity becomes visible and the frequency response becomes a complex periodic function comprised of the basic harmonic, a non-periodic (DC) component and a number of higher harmonics. These harmonics can be estimated from the output signal, by applying, for example, Fourier transform analysis. For weakly nonlinear systems, such as adsorption ones, the nonlinear model can be replaced by a set of the first, second, third, etc., order FRFs. These FRFs are directly related to different harmonics of the output and can be estimated from them.
2. The set of FRFs obtained from the frequency response experiments can be used for model discrimination and estimation of the equilibrium and kinetic parameters.
3. Estimation of the equilibrium parameters differs somewhat form one adsorber configuration of another, but they are always directly related to the low-frequency asymptotic behavior of the FRFs (Petkovska 2006; Petkovska and Seidel-Morgenstern 2005; Petkovska 2008).

In this paper, we will focus on the estimation of the adsorption equilibrium from NFR data.

The NFR method uses the Taylor series expansion of the equilibrium relation, around a chosen steady-state point (C_s, Q_s):

$$\begin{aligned} Q &= f(C) \\ &= Q_s + \left(\frac{dQ}{dC}\right)_s (C - C_s) + \frac{1}{2}\left(\frac{d^2Q}{dC^2}\right)_s (C - C_s)^2 \\ &\quad + \frac{1}{6}\left(\frac{d^3Q}{dC^3}\right)_s (C - C_s)^3 + \cdots \end{aligned} \tag{9}$$

In our previous publications, we used the dimensionless form of Eq. (9), which is more convenient for theoretical analysis of the frequency response techniques:

$$q = \tilde{a}c + \tilde{b}c^2 + \tilde{c}c^3 + \cdots \tag{10}$$

where c and q are dimensionless concentrations in the fluid and solid phase, respectively, defined as relative deviations from the analysed steady-state point:

$$c = \frac{C - C_s}{C_s}, \quad q = \frac{Q - Q_s}{Q_s} \tag{11}$$

while $\tilde{a}$, $\tilde{b}$, $\tilde{c}$, …are dimensionless coefficients which are proportional to the isotherm derivatives:

$$\begin{aligned} \tilde{a} &= \left(\frac{dQ}{dC}\right)_s \frac{C_s}{Q_s}, \quad \tilde{b} = \frac{1}{2}\left(\frac{d^2Q}{dC^2}\right)_s \frac{C_s^2}{Q_s}, \\ \tilde{c} &= \frac{1}{6}\left(\frac{d^3Q}{dC^3}\right)_s \frac{C_s^3}{Q_s}, \ldots \end{aligned} \tag{12}$$

In our previous investigations (Petkovska 2006, 2008; Petkovska and Seidel-Morgenstern 2005) we have shown that the isotherm derivatives are directly related to the low-frequency asymptotes of the FRFs. These relations are somewhat different for different adsorber configurations. We analysed the application of the NFR method to three different adsorber configurations, so far: a reservoir-type adsorber with modulation of the reservoir volume (for batch systems) or the inlet flow-rate (for continuous flow systems) (Petkovska and Do 1998), a chromatographic column with modulation of the inlet concentration (Petkovska and Seidel-Morgenstern 2005) and a zero-length column (ZLC) configuration with modulation of the inlet concentration (Petkovska 2008), and we established the relations between the local isotherm derivatives, corresponding to the chosen steady-state point and the low-frequency asymptotic behaviour of the corresponding FRFs.

For reservoir-type adsorbers, in which the fluid phase is considered to be ideally mixed, which are convenient for investigation of gas–solid systems, the isotherm derivatives are obtained directly from the asymptotes of the particle FRFs (Petkovska 2006):

$$\tilde{a} = \lim_{\omega \to 0} F_1(\omega) \tag{13}$$

$$\tilde{b} = \lim_{\omega \to 0} F_2(\omega, \omega) \tag{14}$$

$$\tilde{c} = \lim_{\omega \to 0} F_3(\omega, \omega, \omega), \ldots \tag{15}$$

In Eqs. (13)–(15) F_1, F_2 and F_3 are the FRFs of the first, second and third order defined on the particle level, which relate the changes of the dimensionless concentrations in the solid and in the fluid phase. These FRFs need to be determined from the adsorber FRFs, which, on the other hand, can be estimated directly from the FR experiments (Petkovska and Do 1998, Petkovska 2006). In this way, theoretically any first n derivatives of the adsorption isotherm corresponding to the chosen steady-state concentration can be estimated, from the first n particle FRFs obtained from the nonlinear FR experiments.

Nevertheless, it should be noticed that, although in our previous theoretical work we usually used dimensionless definitions of the FRFs and the isotherm derivatives, in practice, only their dimensional forms can be obtained from experiments, unless the NFR method is combined with another experimental method giving the values of the steady state concentration in the solid phase (Q_s) for the steady-states chosen for analysis. Equations (12)–(15) can be rewritten in the following way:

$$\left.\frac{dQ}{dC}\right|_s = \lim_{\omega \to 0} F_1^d(\omega) \tag{16}$$

$$\left.\frac{1}{2}\frac{d^2Q}{dC^2}\right|_s = \lim_{\omega \to 0} F_2^d(\omega, \omega) \tag{17}$$

$$\left.\frac{1}{6}\frac{d^3Q}{dC^3}\right|_s = \lim_{\omega \to 0} F_3^d(\omega, \omega, \omega), \ldots \tag{18}$$

where F_1^d, F_2^d, F_3^d denote the particle FRFs of the first, second and third order, in their dimensional form.

For column type adsorbers, which are more convenient for liquid–solid adsorption systems, estimation of the particle FRFs from the adsorber ones becomes very complex. Nevertheless, the analysis has shown that the equilibrium parameters can be estimated directly from the column FRFs. The following useful results were obtained for the low-frequency behaviour of the first three column FRFs (Petkovska and Seidel-Morgenstern 2005):

$$\begin{aligned}\lim_{\omega \to 0}\left|\frac{dG_1(\omega)}{d\omega}\right| &= \lim_{\omega \to 0}\left|\frac{\mathrm{Im}(\mathrm{G}_1(\omega))}{\omega}\right| = 1 + \frac{1-\varepsilon}{\varepsilon}\frac{Q_s}{C_s}\tilde{a} \\ &= 1 + \frac{1-\varepsilon}{\varepsilon}\left.\frac{dQ}{dC}\right|_s\end{aligned} \tag{19}$$

$$\begin{aligned}\lim_{\omega \to 0}\left|\frac{dG_2(\omega,\omega)}{d\omega}\right| &= \lim_{\omega \to 0}\left|\frac{G_2(\omega,\omega)}{\omega}\right| = 2\frac{1-\varepsilon}{\varepsilon}\frac{Q_s}{C_s}\left|\tilde{b}\right| \\ &= \frac{1-\varepsilon}{\varepsilon}\left|\frac{d^2Q}{dC^2}\right|_s C_s \\ sign(\tilde{b}) = sign\left(\frac{d^2Q}{dC^2}\right) &= -sign(\lim_{\omega \to 0}(\arg(G_2(\omega,\omega))))\end{aligned} \tag{20}$$

$$\begin{aligned}\lim_{\omega \to 0}\left|\frac{dG_3(\omega,\omega,\omega)}{d\omega}\right| &= \lim_{\omega \to 0}\left|\frac{G_3(\omega,\omega,\omega)}{\omega}\right| = 3\frac{1-\varepsilon}{\varepsilon}\frac{Q_s}{C_s}\left|\tilde{c}\right| \\ &= \frac{1}{2}\frac{1-\varepsilon}{\varepsilon}\left|\frac{d^3Q}{dC^3}\right|_s C_s^2 \\ sign(\tilde{c}) = sign\left(\frac{d^3Q}{dC^3}\right) &= -sign(\lim_{\omega \to 0}(\arg(G_3(\omega,\omega,\omega))))\end{aligned} \tag{21}$$

In Eqs. (19)–(21) G_1, G_2, G_3,… are the FRFs correlating the dimensionless outlet and inlet concentration changes in the column, ω is dimensionless frequency defined as $L/u\omega^*$ (L is the column length, u the interstitial fluid velocity and ω^* the dimensional frequency in rad/s).

If a ZLC arrangement is to be used for the NFR experiments, the isotherm derivatives can be obtained either by estimating the particle FRFs first, and than using Eqs. (16)–(18), or directly from the ZLC FRFs, by using Eqs. (19)–(21), if the inlet and outlet concentrations are defined as dimensionless deviations from their steady-state and the dimensionless frequency is defined as $V\varepsilon/\dot{V}\omega^*$($V$ is the ZLC volume, ε its porosity and $\dot{V}$ the fluid volumetric flow rate). Details can be found in (Petkovska 2008).

In any case, from the low-frequency asymptotes of the first n FRFs, obtained from NFR experiments around a chosen steady-state point, it is possible to estimate the first n local derivatives of the adsorption isotherm, corresponding to that steady-state. In principle, the experiments are performed for several steady-state points, so a set of values of the local isotherm derivatives is obtained as a result of the NFR method. In our previous investigations, we estimated the first three isotherm derivatives for a limited number of steady-state points (2 or 3) and used them to reconstruct the complete isotherm by fitting the obtained local isotherm derivatives to the derivatives of a priori chosen isotherm relations (Ilic et al. 2007).

In this work, we use the isotherm derivatives that can be estimated by the NFR method, for discrimination between different isotherm models and for identifying the most probable one. This is done by establishing different criteria, based on the first three isotherm derivatives, which are unique for different isotherm models.

3 Criteria for discriminating between different isotherm models

First of all, the shape of the adsorption isotherm can be determined based on the second derivative of the adsorption isotherm, owing to the fact that negative second derivatives correspond to concave, and positive to convex curves. In such a way, if the local second derivatives are negative for all investigated steady-state points, the adsorption isotherm is favorable, while, if they are positive for all steady-state points, the isotherm is unfavorable. If, however, the second derivative changes its sign from one steady-state point to another, it is a clear indication that the adsorption isotherm has an inflection point between those two steady-states (Petkovska and Seidel-Morgenstern 2005). Based on this fact, we will divide our analysis into two parts, the first one considering five common favorable isotherms (Langmuir, Freundlich, Sips, Toth and Unilan), and the second one considering two common isotherms with inflection points (BET and quadratic).

3.1 Criteria for discriminating favorable adsorption isotherms

3.1.1 Langmuir isotherm

The idea about establishing criteria for discriminating between different isotherm models appeared by looking at the expressions for the first three derivatives of the Langmuir isotherm (Eq. 2). These derivatives are:

$$\frac{dQ}{dC} = \frac{Q_0 b}{(1+bC)^2} \tag{22}$$

$$\frac{d^2Q}{dC^2} = -\frac{2Q_0 b^2}{(1+bC)^3} \tag{23}$$

$$\frac{d^3Q}{dC^3} = \frac{6Q_0 b^3}{(1+bC)^4} \tag{24}$$

It is rather obvious that these derivatives are related and it can easily be shown that the following criterion holds for each point of the Langmuir adsorption isotherm:

$$CR_L = \frac{(d^3Q/dC^3)(dQ/dC)}{(d^2Q/dC^2)^2} = \frac{3}{2} \tag{25}$$

In that way, if the local derivatives of the adsorption isotherm estimated by the NFR method obey Eq. (25) for each steady-state point used for experimentation, Langmuir isotherm type can be accepted with reliability. It should be noticed that, theoretically, Langmuir isotherm can be identified from NFR experiments around only one steady-state point. In practice, it is advisable to have experiments for at least 2–3 steady-state points.

3.1.2 Freundlich isotherm

The Freundlich isotherm (Eq. (3)) is again very simple and its first three derivatives are:

$$\frac{dQ}{dC} = \frac{1}{n} K C^{\frac{1-n}{n}} \tag{26}$$

$$\frac{d^2Q}{dC^2} = \frac{1}{n}\frac{1-n}{n} K C^{\frac{1-2n}{n}} \tag{27}$$

$$\frac{d^3Q}{dC^3} = \frac{1}{n}\frac{1-n}{n}\frac{1-2n}{n} K C^{\frac{1-3n}{n}} \tag{28}$$

Several simple criteria relating the first three isotherm derivatives of the Freundlich relation can be easily defined. We chose the following one:

$$CR_F = \frac{d^2Q/dC^2}{dQ/dC} \cdot C = \frac{1-n}{n} = const \tag{29}$$

It should be noticed that, in order to check whether Eq. (29) is valid, the local isotherm derivatives for at least two steady-states are needed. It is also important that for criterion CR_F only the values of the first and second isotherm derivatives are needed. This is important because the experimental effort increases, while the reliability of the estimated isotherm derivatives decreases with the order of the derivative.

3.1.3 Sips isotherm

The first three derivatives of the Sips isotherm (Eq. 4) are:

$$\frac{dQ}{dC} = \frac{Q_0}{nC}\frac{(bC)^{1/n}}{\left(1+(bC)^{1/n}\right)^2} \tag{30}$$

$$\frac{d^2Q}{dC^2} = -\frac{Q_0}{n^2C^2}\frac{(n+1)(bC)^{2/n}+(n-1)(bC)^{1/n}}{\left(1+(bC)^{1/n}\right)^3} \tag{31}$$

$$\frac{d^3Q}{dC^3} = \frac{Q_0}{n^3C^3}\frac{(2n^2+3n+1)(bC)^{3/n}+(4n^2-4)(bC)^{2/n}+(2n^2-3n+1)(bC)^{1/n}}{\left(1+(bC)^{1/n}\right)^4} \tag{32}$$

Finding a correlation between these three isotherm derivatives is not as easy and straightforward as for the Langmuir and Freundlich isotherms. Nevertheless, after considerable search and mathematical transformations, the following criterion was obtained for the first three derivatives of the Sips isotherm:

$$CR_S = \left(2\left(\frac{d^3Q/dC^3}{dQ/dC}\right) - 3\left(\frac{d^2Q/dC^2}{dQ/dC}\right)^2\right)\cdot C^2 = 1 - \frac{1}{n^2} = const \tag{33}$$

For checking whether criterion CR_S is fulfilled, results corresponding to at least two steady-state points are again needed.

3.1.4 Toth isotherm

The first, second and third derivatives of the Toth isotherm, defined by Eq. (5) are:

$$\frac{dQ}{dC} = \frac{Q_0 b}{\left(1+(bC)^t\right)^{1/t+1}} \tag{34}$$

$$\frac{d^2Q}{dC^2} = -\frac{Q_0 b^2 (t+1)(bC)^{t-1}}{\left(1+(bC)^t\right)^{1/t+2}} \tag{35}$$

$$\frac{d^3Q}{dC^3} = -\frac{Q_0 b\left((t+1)(t+2)(bC)^{2t} + (1-t^2)(bC)^t\right)}{C^2\left(1+(bC)^t\right)^{1/t+3}} \tag{36}$$

Finding a simple relation between these expressions for the first three derivatives of the Toth isotherms was not possible. Nevertheless, we found that, for this isotherm, a simple relation can be established between the following two criteria:

$$CR_{T1} = \frac{d^2Q/dC^2}{dQ/dC}\cdot C = \frac{t+1}{1+(bC)^t} - (t+1) \tag{37}$$

$$CR_{T2} = \frac{d^3Q/dC^3}{d^2Q/dC^2}\cdot C = \frac{2t+1}{1+(bC)^t} - (t+2) \tag{38}$$

It is rather obvious that the following relation is valid:

$$CR_{T2} = \frac{2t+1}{t+1} CR_{T1} + (t-1) = k_1 \cdot CR_{T1} + k_2 \tag{39}$$

The relation between CR_{T1} and CR_{T2}, defined by Eq. (39) is linear, meaning that if the values of CR_{T2} corresponding to different steady-state points would be plotted against CR_{T1}, a straight line would be obtained for Toth isotherm. Naturally, in order to check whether this is really a straight line, the values of the local isotherm derivatives corresponding to at least three steady-state points would be needed.

3.1.5 Unilan isotherm

For the case of Unilan isotherm model, defined by Eq. (6), the first three derivatives are obtained in the following form:

$$\frac{dQ}{dC} = \frac{Q_0 b}{2s}\frac{e^{2s}-1}{(e^s+bC)(1+e^s bC)} \tag{40}$$

$$\frac{d^2Q}{dC^2} = -\frac{Q_0 b^2}{2s}\frac{(e^{2s}-1)(1+2e^s bC+e^{2s})}{(e^s+bC)^2(1+e^s bC)^2} \tag{41}$$

$$\frac{d^3Q}{dC^3} = \frac{Q_0 b^3}{2s}\frac{(e^{2s}-1)(3b^2C^2e^{2s}+3bC(e^{3s}+e^s)+e^{4s}+e^{2s}+1)}{(e^s+bC)^3(1+e^s bC)^3} \tag{42}$$

After some long and tedious mathematical transformations, it was possible to establish the following criterion which relates the first three derivatives of the Unilan isotherm:

$$CR_U = \frac{2\left(\frac{d^3Q/dC^3}{dQ/dC}\right) - 3\left(\frac{d^2Q/dC^2}{dQ/dC}\right)^2}{(dQ/dC)^2} = \frac{4s^2}{Q_0^2} = const \tag{43}$$

In order to check whether the criterion CR_U is constant for all steady-state points, i.e. whether the Unilan isotherm model is appropriate, it would be necessary to have results corresponding to at least two steady-state points.

3.1.6 Cross analysis of different criteria for discriminating between the five favorable isotherm models

Once the criteria for all five isotherms have been established, it is now necessary to check whether the criteria defined in sects. 3.1.1–3.1.5 are unique for each isotherm and whether they give enough information for model

Table 1 Comparison of the five criteria for five favorable isotherms under consideration

CRIT/isotherm	Langmuir	Freundlich	Sips	Toth	Unilan
CR_L	3/2	$\frac{1-2n}{1-n} = const$	$f_1(C)$	$f_6(C)$	$f_{10}(C)$
CR_F	$\frac{2}{1+bC} - 2$	$\frac{1}{n} - 1 = const$	$f_2(C)$	$f_7(C)$	$f_{11}(C)$
CR_S	0	$1 - \frac{1}{n^2} = const$	$1 - \frac{1}{n^2} = const$	$f_8(C)$	$f_{12}(C)$
CR_{T1}	$\frac{2}{1+bC} - 2$	$\frac{1}{n} - 1$	$f_3(C)$	$\frac{t+1}{1+(bC)^t} - (t+1)$	$f_{13}(C)$
CR_{T2}	$\frac{3}{1+bC} - 3$	$\frac{1}{n} - 2$	$f_4(C)$	$\frac{2t+1}{1+(bC)^t} - (t+2)$	$f_{14}(C)$
CR_{T2} versus CR_{T1}	Linear	Linear	Not linear	Linear	Not linear
CR_U	0	$\frac{n^2-1}{KC^{2/n}}$	$f_5(C)$	$f_9(C)$	$\frac{4s^2}{Q_0^2} = const$

discrimination. For that purpose we derived the expressions of all five criteria for all five isotherms and compared them. This comparison is given in Table 1.

The following can be concluded from this table:

1. The Langmuir isotherm is defined by the following states of the five criteria: $CR_L = 3/2$, CR_F is a function of C, $CR_S = 0$, linear dependence between CR_{T1} and CR_{T2} and $CR_U = 0$.
2. For the Freundlich isotherm, the states of the five criteria are: $CR_L = const$ (in principle different from 3/2), $CR_F = const$, $CR_S = const$, linear dependence between CR_{T1} and CR_{T2} ($CR_{T2} = CR_{T1} + 1$) and CR_U is a function of C.
3. For the Sips isotherm, the states of the five criteria are: CR_L is a function of C ($f_1(C)$), CR_F is a function of C ($f_2(C)$), $CR_S = const$, the dependence between CR_{T1} and CR_{T2} is not linear and CR_U is a function of C ($f_5(C)$).
4. The Toth isotherm is defined by the following states of the five criteria: CR_L is a function of C ($f_6(C)$), CR_F is a function of C ($f_7(C)$), CR_S is a function of C ($f_8(C)$), linear dependence between CR_{T1} and CR_{T2} exists and CR_U is a function of C ($f_9(C)$).
5. And finally, the Unilan isotherm is defined by the following states of the criteria: CR_L is a function of C ($f_{10}(C)$), CR_F is a function of C ($f_{11}(C)$), CR_S is a function of C ($f_{12}(C)$), the dependence between CR_{T1} and CR_{T2} is not linear and $CR_U = const$.

The functions $f_1(C)$ to $f_{14}(C)$ in Table 1 are rather complex to be inserted into the table directly, but they are given in the Appendix.

Our analysis based on Table 1 shows that each of the five criteria is not necessarily unique for each of the isotherms under consideration. Nevertheless, they give enough information for isotherm model discrimination. For example, discrimination between Langmuir and other isotherms is possible based on the fact that only for this model CR_L equals 3/2, while CR_S and CR_U are equal to 0; Freundlich isotherm model is the only one for which CR_F is constant; for Sips isotherm only CR_S is constant, while all other criteria are functions of C; Toth isotherm results with a linear relationship between CR_{T1} and CR_{T2}, while all other criteria are functions of C and for Unilan model CR_U is constant, while all other criteria are functions of C.

3.2 Criteria for discriminating complex adsorption isotherms

3.2.1 *BET isotherm*

The derivatives of the BET isotherm model (Eq. 7) are obtained in the following form:

$$\frac{dQ}{dC} = \frac{Q_0 b_L}{(1 - b_L C)^2} + \frac{Q_0 (b_S - b_L)}{(1 - b_L C + b_S C)^2} \tag{44}$$

$$\frac{d^2Q}{dC^2} = \frac{Q_0 b_L^2}{(1 - b_L C)^3} + \frac{Q_0 (b_S - b_L)^2}{(1 - b_L C + b_S C)^3} \tag{45}$$

$$\frac{d^3Q}{dC^3} = \frac{Q_0 b_L^3}{(1 - b_L C)^4} + \frac{Q_0 (b_S - b_L)^3}{(1 - b_L C + b_S C)^4} \tag{46}$$

Search for a criterion which would correspond to the BET isotherm involved some long and tedious algebra. Finally, the following result was obtained:

$$\begin{aligned} CR_{BET} &= \sqrt{\left| \frac{(dQ/dC)^2}{3(d^2Q/dC^2)^2 - 2(dQ/dC)(d^3Q/dC^3)} \right|} \\ &= \left| \frac{1}{\sqrt{12 b_L (b_L - b_S)}} - \frac{\sqrt{12 b_L (b_L - b_S)}}{12} \cdot C^2 \right| \\ &= k_3 C^2 + k_4 \end{aligned} \tag{47}$$

According to Eq. (47), BET isotherm can be identified if the complex criteria CR_{BET}, calculated for several (at least 3) steady state points is a linear function of C^2.

3.2.2 *Quadratic isotherm*

By differentiation of the quadratic isotherm model (Eq. 8), the following expressions for the first three derivatives are obtained:

$$\frac{dQ}{dC}=Q_0\frac{b_1b_2C^2+4b_2C+b_1}{(1+b_1C+b_2C^2)^2} \tag{48}$$

$$\frac{d^2Q}{dC^2}=-Q_0\frac{2b_1b_2^2C^3+12b_2^2C^2+3b_1b_2C+b_1^2-6b_2}{(1+b_1C+b_2C^2)^3} \tag{49}$$

$$\frac{d^3Q}{dC^3}=Q_0\frac{6b_1b_2^3C^4+24b_2^3C^3+36b_1b_2^2C^2+24b_2(b_1^2-2b_2)C+6b_1(b_1^2-3b_2)}{(1+b_1C+b_2C^2)^4} \tag{50}$$

Finding a simple relationship between these three derivatives was not possible. Nevertheless, it was found that the criteria defined for the BET isotherm can be used here as well. For the quadratic isotherm this criteria becomes:

$$CR_{QUAD}=\sqrt{\left|\frac{(dQ/dC)^2}{3(d^2Q/dC^2)^2-2(dQ/dC)(d^3Q/dC^3)}\right|}=\left|\frac{b_1b_2C^2+4b_2C+b_1}{\sqrt{12b_2(4b_2-b_1^2)}}\right|=k_5C^2+k_6C+k_7 \tag{51}$$

As it can be seen from Eq. (51), this criteria is not a linear function of C^2 (like in the case of BET isotherm), but a quadratic function of C with all three coefficients different from zero. In this way, the criterion CR_{BET} or CR_{QUAD} gives enough information for discriminating between BET and quadratic isotherms.

4 Examples: discrimination of adsorption isotherms based on experimental NFR data from previous publications

In one of our previous publications (Ilic et al. 2007), we have applied the NFR method for experimental estimation of single component isotherms, for two systems: 4-*tert*-butylphenol on octadecyl silica and ethyl benzoate on octadecyl silica with 60:40 (v/v) methanol/water mixture as a solvent. In both cases, the measurements were performed on a chromatographic column type equipment, with the column porosity ε = 0.548, and the isotherm derivatives were obtained based on Eqs. (19)–(21). In that publication the isotherm models were chosen based on previous literature (Gritti and Guiochon 2003) and the 4-*tert*-butylphenol on octadecyl silica data were modeled by a Langmuir isotherm, while the ethyl benzoate on octadecyl silica data were modeled with a BET isotherm. Here, we apply the criteria derived in this manuscript, in order to identify the best model.

4.1 Example 1: adsorption of 4-*tert*-butylphenol on octadecyl silica

For the system 4-*tert*-butylphenol on octadecyl silica, the FR measurements were performed for two steady-state points, for C_s 1 and 5 g/dm^3. In Table 2 we give the low-frequency asymptotic data obtained in (Ilic et al. 2007), together with the corresponding values of the local first second and third derivatives.

It can be seen from Table 2 that the sign of the second derivative is negative for both steady-states, which implies that the isotherm is favourable. The previously derived criteria for four favourable isotherms: Langmuir, Freundlich, Sips and Unilan, were calculated from these data and also given in Table 2 (the criterion for Toth isotherm could not be applied, as it requires data for 3 steady-state points,

Table 2 Isotherm derivatives and the values of four criteria for the experimental system 4-*tert*-butylphenol on octadecyl silica

C_s (g/dm^3)	1	5
$1+\frac{1-\varepsilon}{\varepsilon}\frac{dQ}{dC}\Big\|_s$	7.365	4.547
$\frac{1-\varepsilon}{\varepsilon}\frac{d^2Q}{dC^2}\Big\|_s C_s$	−2.517	−2.675
$\frac{1}{2}\frac{1-\varepsilon}{\varepsilon}\frac{d^3Q}{dC^3}\Big\|_s C_s^2$	0.5033	1.382
$\frac{dQ}{dC}\Big\|_s$	7.7169	4.3003
$\frac{d^2Q}{dC^2}\Big\|_s$	−3.0516	−0.6486
$\frac{d^3Q}{dC^3}\Big\|_s$	1.2204	0.1340
CR_L	1.0113	1.3701
CR_F	−0.3954	−0.7542
$\boldsymbol{CR_S}$	**−0.1528**	**−0.1478**
CR_U	−0.0026	−0.0003

The best model is highlighted by bold font while only two were available). By inspection of these four criteria, the following results were obtained:

- The criterion CR_L is different from 3/2 and changes for 35 % from one steady-state point to another, which implies that the Langmuir model is not the correct one.
- The criterion CR_F changes for 90 % from one steady-state point to another and is therefore not constant, which implies that the Freundlich model is also not the correct one.
- The criterion CR_S changes for 3.3 % from one steady-state point to another, and is therefore nearly constant, which implies that the Sips model could be the correct one.
- The criterion CR_U changes for 88.5 % from one steady-state point to another and is therefore not constant, which implies that the Unilan model is also not the correct one.

Taking this all into account, we conclude that the Sips isotherm is the best model for this system.

4.2 Example 2: adsorption of ethyl benzoate on octadecyl silica

For adsorption of ethyl benzoate on octadecyl silica, the FR measurements were performed for three steady-state points, for C_s 5, 10 and 13 g/dm^3. The low-frequency asymptotic data obtained for this system in (Ilic et al. 2007), together with the corresponding values of the local first second and third derivatives, are given in Table 3. It can be seen that the second order derivative for this system changes its sign between $C_s = 10$ g/dm^3 and $C_s = 13$ g/dm^3, which means that the adsorption isotherm has an inflection point between those two points. In this case, BET and quadratic isotherms are candidates.

Table 3 Isotherm derivatives and the values of the CR_{BET} (CR_{QUAD}) criterion for the experimental system ethyl benzoate on octadecyl silica

C_s (g/dm^3)	5	10	13
$1+\frac{1-\varepsilon}{\varepsilon}\frac{dQ}{dC}\Big\vert_s$	5.844	5.673	5.971
$\frac{1-\varepsilon}{\varepsilon}\frac{d^2Q}{dC^2}\Big\vert_s C_s$	−0.2396	−0.7590	0.5444
$\frac{1}{2}\frac{1-\varepsilon}{\varepsilon}\frac{d^3Q}{dC^3}\Big\vert_s C_s^2$	0.8692	0.4266	0.8770
$\frac{dQ}{dC}\Big\vert_s$	5.8728	5.6655	6.0268
$\frac{d^2Q}{dC^2}\Big\vert_s$	−0.0581	−0.0920	0.0508
$\frac{d^3Q}{dC^3}\Big\vert_s$	0.0843	0.0103	0.0126
$CR_{BET} = CR_{QUAD}$	35.1907	349.6278	252.3472

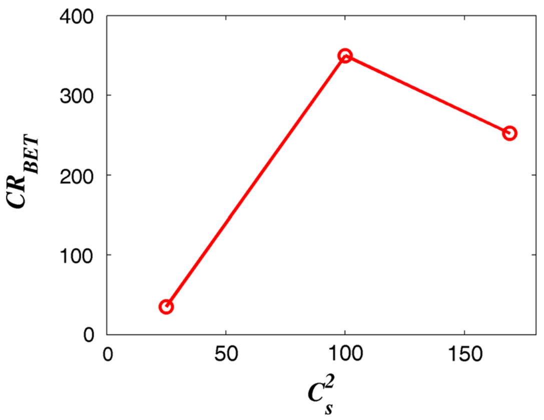

Fig. 1 The BET isotherm test for ethyl benzoate on octadecyl silica experimental data

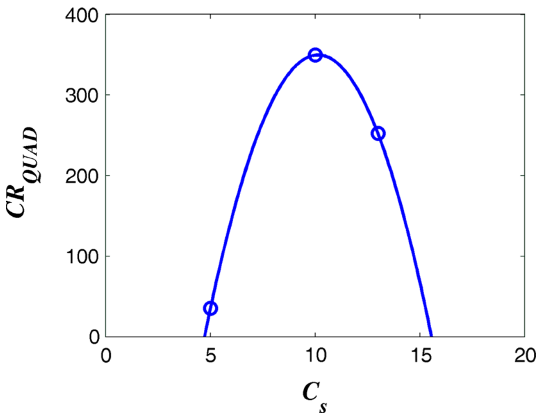

Fig. 2 The quadratic isotherm test for ethyl benzoate on octadecyl silica experimental data

In Fig. 1 the values of CR_{BET} are plotted against C_s^2, in order to check whether a straight line is obtained. Although only three points are available, it is obvious that the condition that CR_{BET} is a linear function of C_s^2 is not fulfilled, i.e., that the BET model is not appropriate.

In Fig. 2, we plot the CR_{QUAD} (=CR_{BET}) values against C_s. The solid line corresponds to a quadratic fit:

$$CR_{QUAD} = -11.914C_s^2 + 241.6C_s - 874.96$$

which is very good. Based on the results presented in Figs. 1 and 2, it can be concluded that the quadratic isotherm is more probable. Nevertheless, to be completely honest, in order to check whether the quadratic function is a good fit, more that three points would be necessary.

5 Comparison with classical methods

The standard procedure for identifying the best adsorption isotherm model is to fit the experimental Q versus C data with different models and choose the one that gives the best fit.

Nevertheless, not only that there is a variety of potential isotherm models, there are also different tests, usually defined as error functions, which can be used to make the decision about the best fit (e.g. sum of square error, hybrid fractional error function, coefficient of determination, etc.). A good review of different tests can be found in (Foo and Hameed 2010). Furthermore, it can happen that different tests suggest different isotherm models as the best one (see for example Ho et al. 2002). Also, in principle, the isotherm models with more parameters usually will give a better fit, although there might be no physical background for using more complex models.

The method for isotherm discrimination presented in this work, which is based on NFR data, does not suffer from such drawbacks, as it uses a completely different approach. Instead of fitting the experimental data to different models, it is based on calculating specific criteria and using them for distinguishing between different isotherm models. In the core of the method are the additional information gained through the NFR method: the values of the local first, second and third isotherm derivatives. Of course, the reliability of this method will be highly dependent on the accuracy of the determined isotherm derivatives.

The sensitivity of the method is an issue which has not been analyzed in this first paper, but definitely needs to be addressed in our future work.

6 Conclusions

In this manuscript we have shown that discrimination between different adsorption isotherm models and identification of the best one can be performed if the values of the local first, second and third order isotherm derivatives, corresponding to several points on the isotherm, are available. These local derivatives can be estimated from NFR experiments, as described in our previous publications. The potential for model discrimination arises from the fact that, for each isotherm model, the first three derivatives are related in a different way, and that specific criteria can be defined for different isotherm models.

First, one can identify whether the isotherm is favorable, unfavorable or has an inflection point, by inspecting the sign of the second derivative and whether it changes or not. Further, by analyzing specific criteria, one can identify, for example, which model of a favorable isotherm is most appropriate.

In this first publication investigating this issue, we developed criteria for discriminating between five common models corresponding to favorable isotherms: Langmuir, Freundlich, Sips, Toth and Unilan, and two models corresponding to complex shape isotherms: BET and quadratic. For most criteria the minimal number of investigated points is two, although the criterion for Langmuir isotherm could be applied with only one point, while for the Toth, BET and quadratic isotherms, a minimum of three points are needed. Naturally, the conclusions are more reliable if more points are used for analysis.

For most isotherm models, the criteria are calculated from the first three derivatives. Only for Freundlich isotherm, the criterion can be calculated based only on the first two derivatives.

The criteria for isotherm model discrimination developed in this work were used in order to identify the isotherm type for two systems: 4-*tert*-butylphenol on octadecyl silica and ethyl benzoate on octadecyl silica, using the experimental FR data from one of our previous publications (Ilic et al. 2007). It was shown that the most appropriate isotherm model for the first system is Sips, and for the second one the quadratic isotherm.

In our future work we will consider other isotherm models. Also, we will try to develop simpler criteria, requiring only the values of the first and second isotherm derivatives, for the case when the loading (Q) corresponding to the steady-state points used for the NFR experiments is known (which would combine the NFR method with another classical method for experimental measurements of equilibrium adsorption data). Also, we are planning to establish methods for estimation of the isotherm parameters directly from the values of the isotherm derivatives.

Acknowledgments This work was supported by the Ministry of Education and Science of the Republic of Serbia in the frame of Project No. 172022.

Appendix: Functions $f_1(C)$ to $f_{14}(C)$ in Table 1

$$f_1(C) = \frac{(Cb)^{4/n}(2n^2+3n-1)+(Cb)^{3/n}(8n^4+12n^3-4n^2-4)+(Cb)^{2/n}(2n^2-3n+1)}{\left((Cb)^{1/n}(n-1)+(Cb)^{2/n}(n+1)\right)^2} \qquad (52)$$

$$f_2(C) = \frac{2}{n((Cb)^{1/n}+1)} - \frac{n-1}{n} \tag{53}$$

$$f_3(C) = \frac{2}{n((Cb)^{1/n}+1)} - \frac{n-1}{n} \tag{54}$$

$$f_4(C) = -\frac{(Cb)^{1/n}(3n((Cb)^{2/n}-1)+(2n^2+1)((Cb)^{2/n}+1)+(Cb)^{2/n}(4n^2-4)}{n((Cb)^{1/n}(n-1)+(Cb)^{2/n}(n+1))((Cb)^{1/n}+1)} \tag{55}$$

$$f_5(C) = \frac{(n^2-1)((Cb)^{1/n}+1)^4}{Q_0^2(Cb)^{2/n}} \tag{56}$$

$$f_6(C) = \frac{1}{t-1}\left(\frac{2}{(Cb)^t}+1\right) - \frac{1}{(Cb)^t} + 1 \tag{57}$$

$$f_7(C) = -\frac{(Cb)^t(t+1)}{(Cb)^t+1} \tag{58}$$

$$f_8(C) = \frac{(t-1)(t+1)}{\left((Cb)^t+1\right)^2} - (t-1)(t+1) \tag{59}$$

$$f_9(C) = -\frac{((Cb)^t+1)^{2t}((t^2+2t-1)(Cb)^{2t}-(2t^2+2t+2)(Cb)^t)}{C^2b^2Q_0^2} \tag{60}$$

$$f_{10}(C) = \frac{\cosh(2s)-(3\cosh(s)^2/2+1/2)}{(\cosh(s)+Cb)^2} + 3/2 \tag{61}$$

$$f_{11}(C) = -\frac{2e^sC^2b^2+(e^{2s}+1)Cb}{(e^s+Cb)(Cbe^s+1)} \tag{62}$$

$$f_{12}(C) = \frac{C^2b^2(e^{2s}-1)^2}{(e^s+Cb+e^{2s}Cb+C^2b^2e^s)^2} \tag{63}$$

$$f_{13}(C) = -\frac{2e^sC^2b^2+(e^{2s}+1)Cb}{(e^s+Cb)(Cbe^s+1)} \tag{64}$$

$$f_{14}(C) = \frac{2Cb(e^{4s}+3Cbe^{3s}+3Cbe^s+1)+2Cbe^{2s}(3C^2b^2+1)}{(e^{2s}+2e^sCb+1)(e^s+Cb+e^{2s}Cb+C^2b^2e^s)^2} \tag{65}$$

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