Chemical Engineering Science 118 (2014) 141–153

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Nonlinear frequency response analysis of nonisothermal adsorption controlled by macropore diffusion

Danica Brzić, Menka Petkovska*

University of Belgrade, Faculty of Technology and Metallurgy, Department of Chemical Engineering, Karnegijeva 4, 11000 Belgrade, Serbia

HIGHLIGHTS

- NFR method is used to study nonisothermal adsorption governed by macropore diffusion.
- Theoretical first- and second-order FRFs were derived and analyzed.
- The second-order FRF can be used for model identification and discrimination from other kinetic mechanisms.
- A procedure for estimation of kinetic and equilibrium parameters is proposed.

ARTICLE INFO

Article history:
Received 26 May 2014
Received in revised form
12 July 2014
Accepted 14 July 2014
Available online 24 July 2014

Keywords:
Nonlinear frequency response
Gas adsorption
Nonisothermal macropore diffusion
Parameter estimation

ABSTRACT

In this work, a nonlinear frequency response (NFR) approach is used for a theoretical study of nonisothermal adsorption controlled by macropore diffusion (NMD). Based on the nonlinear mathematical model on the particle scale for spherical geometry, the theoretical frequency response functions (FRFs) up to the second order have been derived, using the concept of higher-order FRFs. The FRFs for isothermal macropore diffusion model have also been derived for comparison. For the NMD model two series of FRFs define the process: one which relates the sorbate concentration in the particle to the pressure (F) and the other which relates the particle temperature to the pressure (Z). The obtained FRFs were simulated for seven different sets of parameters. The second-order F function exhibits specific bimodal pattern, which enables separation of the diffusional and heat-transfer time constant. The high-frequency asymptotic features of the second-order F function discriminates the NMD mechanism from micropore-macropore diffusion control. Based on the characteristic of the first- and second-order F and Z functions, the new procedure for direct estimation of the diffusional and heat-transfer time constants is proposed. Additionally, some equilibrium parameters, as well as the heat of adsorption, can also be estimated. The NFR approach shows significant advantages regarding analysis of NMD compared to the linear FR method.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Gas adsorption in biporous adsorbent particles may involve several simultaneous steps: mass transfer through the gas film, macropore diffusion, surface diffusion, micropore diffusion and adsorption. Adsorption is generally fast, so the rate of the whole process is controlled by one or several diffusion steps. Moreover, adsorption is an exothermal process which additionally affects the mass transfer dynamics through interplay with heat transfer through and from the particles.

In frequency response (FR) analysis, which is a common approach in investigation of kinetics of gas adsorption (Yasuda, 1994; Song and Rees, 1997; Onyestyák et al., 1996; Sward and LeVan, 2003; Giesy et al., 2012; Bourdin et al., 1996, 1998; Rodrigues and Dias, 1998), the first step is setting up the model equations of the process, from which the first-order frequency response function (FRF) is derived and used to fit the experimental data in order to estimate kinetic parameters. Comprehensive work in the field of modeling and FR analysis of bidispersed adsorbents including different mass transfer mechanisms has been done by Jordi and Do (1993, 1994). Sun et al. (1994) and Bourdin et al. (1996) have extended the analysis to nonisothermal adsorption controlled with one or more diffusional resistances. Their whole analysis is based on linearized models, which means that they have derived and analyzed only the first-order FRF for different kinetic mechanisms, which is mainly not sufficient for reliable identification of the nonlinear model (Song and Rees, 1997). Moreover, estimation of

---

* Corresponding author. Tel.: +381 11 3303 610; fax: +381 11 3370 387.
E-mail addresses: danica@tmf.bg.ac.rs (D. Brzić), menka@tmf.bg.ac.rs (M. Petkovska).

http://dx.doi.org/10.1016/j.ces.2014.07.033
0009-2509/© 2014 Elsevier Ltd. All rights reserved.

the model parameters from the first-order FRF, especially for nonisothermal models, is not straightforward (Sun and Bourdin, 1993).

Recently, the nonlinear frequency response (NFR) approach has been introduced by Petkovska and Do (1998), with great potential for dealing with dynamics of adsorption systems. In the NFR approach, the nonlinear model of the system is represented by a set of FRFs of first-, second-, third-, etc., order, according to the concept of higher-order FRFs (Weiner and Spina, 1980). The first-order FRF corresponds to the linearized model, while the second- and higher-order FRFs describe the nonlinearities. A theoretical study of Petkovska and Do (2000) shows that the second-order FRF gives sufficient information for unambiguous model identification and reliable parameter estimation. Practical application of the NFR approach is based on comparison of the experimental second-order FRF on the particle scale (which relates the sorbate concentration in the particle to the pressure) with the theoretical ones corresponding to several suspected kinetic models. The procedure for obtaining experimental FRFs on the particle scale has already been established (Petkovska, 2006) and it includes direct estimation of the adsorber FRFs from measured NFRs and calculation of the particle FRFs from the adsorber ones. The relations between particle and adsorber FRFs are derived based on the adsorber material and heat balances, as reported by Petkovska (2001). The applicability of the proposed procedure has been checked based on simulated NFRs of a batch adsorber (Brzić and Petkovska, 2013). By using theoretical studies and numerical simulations (Petkovska, 2006; Brzić and Petkovska, 2012) some questions regarding the optimal parameters for batch NFR experiments (input amplitude, frequency range, mass of the adsorbent and sampling rate) have been considered. The comparison of the experimental second-order particle FRF with theoretical ones for different kinetic mechanisms implies the existence of a library of theoretical FRFs for different models. The existing library, which is still rather limited, comprises the theoretical FRFs up to the second order for simple and several complex mechanisms (Petkovska and Do, 2000; Petkovska and Petkovska, 2003; Petkovska, 1999, 2000, 2001). However all theoretical second-order FRFs have been derived for plane geometry of the adsorbent particles, while the second-order FRFs for spherical geometry of adsorbent (which is more realistic), for different kinetic mechanisms, are still missing.

Nonisothermal macrospore diffusion (NMD) has often been reported as a controlling mechanism for bidispersed commercial zeolites (Onyestyák et al., 1996; Giesy et al., 2012). Onyestyák et al. (1996) investigated adsorption of CO_2 on commercial 5A zeolites at 1 Torr and temperatures from 298 to 423 K. They fitted successfully their experimental data to the first-order FRF for isothermal macropore diffusion control (IMD) at high temperatures, while at low temperatures it was not possible to fit the data with the IMD model because bimodal behavior was experimentally observed. A second peak of the phase lag of the FR at low frequencies was attributed to heat effects. Giesy et al. (2012) investigated adsorption of CO_2 on commercial 13X zeolites at room temperature and pressures up to 1 bar. Their results showed very good agreement with the first-order FRF for the NMD model for coarse spherical particles. However, for smaller particles, only qualitative agreement with first-order FRF for NMD was achieved.

In order to contribute to systematic, comprehensive and reliable approach in the investigation of the adsorption kinetics, theoretical FRFs up to the second-order for NMD model for spherical geometry of adsorbent particle are derived and presented in this manuscript. The FRFs for IMD are also derived for comparison. The derived FRFs are simulated for different combinations of parameters with the aim to recognize their characteristic features for model identification and parameter estimation.

2. Nonlinear frequency response and the concept of higher-order FRFs

Frequency response of a weakly nonlinear system (nonlinear frequency response, NFR) can be analyzed using the concept of higher-order FRFs (Weiner and Spina, 1980) which is based on the Volterra series and the generalized Fourier transform. According to this concept, if the input is a general periodic function of the form

$$x(t) = \sum_{k'=1}^{N} A_k e^{j\omega_k t} \tag{1}$$

the response of the system can be represented by the Volterra series (Weiner and Spina, 1980) as follows:

$$y(t) = \sum_{n=1}^{\infty} y_n(t) \tag{2}$$

where the n-th element of the series is defined as

$$y_n(t) = \sum_{k_1=1}^{N} \sum_{k_2=1}^{N} \cdots \sum_{k_n=1}^{N} A_{k_1} A_{k_2} \ldots A_{k_n} G_n(\omega_{k_1}, \omega_{k_2}, \ldots, \omega_{k_n}) e^{j(\omega_{k_1} + \omega_{k_2} + \cdots + \omega_{k_n})t} \tag{3}$$

In Eqs. (1) and (3) A is the input amplitude, ω is the angular frequency (rad/s), j is the imaginary unit and $G_n(\omega_{k_1}, \ldots, \omega_{k_n})$ is the n-th order FRF. For a cosinusoidal form of the input

$$x(t) = A\cos(\omega t) = (A/2)e^{j\omega t} + (A/2)e^{-j\omega t} \tag{4}$$

the response of the system can be expressed as

$$\begin{aligned} y(t) &= y_1(t) + y_2(t) + y_3(t) + \cdots \\ &= \frac{A}{2}(G_1(\omega)e^{j\omega t} + G_1(-\omega)e^{-j\omega t}) \\ &\quad + \left(\frac{A}{2}\right)^2 (G_2(\omega,\omega)e^{2j\omega t} + 2G_2(\omega,-\omega)e^0 + G_2(-\omega,-\omega)e^{-2j\omega t}) \\ &\quad + \left(\frac{A}{2}\right)^3 (G_3(\omega,\omega,\omega)e^{3j\omega t} + 3G_3(\omega,\omega,-\omega)e^{j\omega t} \\ &\quad + 3G_3(\omega,-\omega,-\omega)e^{-j\omega t} + G_3(-\omega,-\omega,-\omega)e^{-3j\omega t}) + \cdots \end{aligned} \tag{5}$$

where G_1 is the first-order (or linear) FRF, G_2 is the second-order FRF and G_3 is the third-order FRF.

For derivation of the theoretical FRFs for a particular kinetic mechanism, the concept of higher-order FRFs is applied to the appropriate mathematical model, as it will be demonstrated in Section 3. More details about NFR and the concept of higher order FRFs can be found elsewhere (Weiner and Spina, 1980; Petkovska, 2006).

3. Theoretical FRFs for isothermal and nonisothermal macropore diffusion

The general procedure for derivation of the higher-order FRFs of adsorption systems already exists in literature (Petkovska, 2001). For the case of adsorption of a pure gas (sorbate) in a porous adsorbent particle, the procedure for derivation of the higher-order FRFs on the particle scale, consists of the following steps:

1. setting the mass and heat balance equations and adsorption isotherm relation,
2. definition of the input: pressure and output/s: mean sorbate concentration in the particle/particle temperature,
3. Taylor approximation of the adsorption isotherm relation around steady-state,
4. substitution of the Taylor polynomials into the mass balance equation,
5. expressing the input variable in the form of Eq. (4), and the output variables in the form of Eq. (5),

Download English Version:

https://daneshyari.com/en/article/154779

Download Persian Version:

https://daneshyari.com/article/154779

Daneshyari.com