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Nonlinear Frequency Response measurements of gas adsorption equilibrium and kinetics: New apparatus and experimental verification

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HIGHLIGHTS

- New apparatus for NFR measurements has been designed and constructed.
- Second-order FRF, $F_2(\omega,\omega)$, was obtained experimentally.
- $F_2(\omega,\omega)$ agrees with theoretical one for nonisothetmal macropore diffusion.
- Diffusion and heat transfer coefficients and heat of adsorption were estimated.

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ABSTRACT

A new apparatus for experimental validation of the Nonlinear Frequency Response (NFR) method for investigation of gas adsorption is presented. The apparatus has been designed as a batch adsorber with sinusoidal modulation of the volume, with an amplitude that can be varied. Fast and accurate measurements of pressure, gas temperature and particle temperature responses are employed. The measurement routine and data analysis are demonstrated by CO_2 adsorption on zeolite 5A particles of two different diameters. The responses for input amplitudes of 3% and 7% of the volume change are measured. The concept of blank FRFs is introduced as a new way to incorporate the results of blank experiments for elimination of spurious effects. The first- and second-order FRFs which relate the adsorbed quantity to the pressure ($F_1(\omega)$ and $F_2(\omega,\omega)$) are calculated based on the measured pressure responses. The first-order FRF which relates the particle temperature to the pressure ($H_1(\omega)$) is calculated from the particle temperature responses. The characteristics of $F_1(\omega)$, $F_2(\omega,\omega)$ and $H_1(\omega)$ for spherical beads of 1.7 mm agree with the corresponding theoretical ones for nonisothermal macropore diffusion model. The equilibrium and kinetic parameters are estimated from these functions. The results of this study confirm the applicability of NFR method for characterization of gas adsorption and show significance of the extension of analysis to the nonlinear range.

1. Introduction

Adsorptive technologies have been widely employed in many important industrial separation and purification processes and they are continuously developed and improved. Therefore the need for accurate data on equilibrium and kinetics of adsorption processes is very pronounced. The frequency response (FR) technique, commonly used for investigation of gas adsorption kinetics (Yasuda, 1994; Song and Rees, 1997; Onyestyák et al., 1996; Sward and LeVan, 2003; Giesy et al., 2012; Bourdin et al., 1996, 1998), being a linear tool, partly fails to identify the kinetics of nonlinear adsorption systems (Song and Rees, 1997). The extension of the linear FR method to a nonlinear range (Nonlinear Frequency Response – NFR), suggested by Petkovska and Do (1998), represents a promising tool for efficient dealing with kinetics of adsorption systems. The principle of the NFR approach is based on the fact that a weakly nonlinear system subject to periodic perturbation with relatively large amplitude gives a complex periodic response, which contains, besides the first (basic) harmonic, also the second and higher harmonics. By applying the concept of higher-order frequency response functions (FRFs) (Weiner and Spina, 1980), the first-, second- and higher-order FRFs are defined, which can be determined from the individual harmonics of the system's response. The first-order FRF describes the quasi-linear dynamics, while the second- and higher-order FRFs reflect the nonlinear behavior. By checking the agreement between experimental and theoretical higher-order FRFs for the suspected model(s), a kinetic mechanism should be reliably

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identified. A theoretical NFR analysis of different adsorption kinetic mechanisms (Petkovska and Do, 2000) shows that the second-order FRFs contain sufficient information for unambiguous model identification and estimation of the nonlinear model parameters. An additional advantage of the NFR approach is that it enables estimation of both kinetic and equilibrium parameters from the same experimental data (Petkovska, 2006). However, practical application of the NFR approach encounters substantial technical challenges and mathematical complexity. The implementation of the NFR technique implies: (1) producing and accurate measurements of the representative NFRs of the investigated adsorption system, (2) accurate determination of the experimental first- and second-order FRFs (on the adsorbent particle scale), (3) derivation of the theoretical first- and second-order FRFs for suspected kinetic model(s) and (4) methodology for estimation of the model parameters. Petkovska and coworkers, in their comprehensive theoretical studies, have treated many important issues related to the implementation of the NFR method. The procedure for determination of experimental first- and second-order FRFs on the adsorber scale from the measured NRFs has been established (Petkovska, 2006). Also, the relations for calculation of the FRFs on the particle scale from the adsorber ones have been derived for batch and continuous flow adsorbers (Petkovska and Do, 1998). The applicability of the proposed procedure has been checked based on quasi-experimental (simulated) NFRs of a batch adsorber (Brzić and Petkovska, 2013). By using theoretical studies and numerical simulations, the issues regarding optimal parameters for NFR batch experiments: input amplitude, frequency range, mass of the adsorbent and required number of data points, have been considered (Brzić and Petovska, 2012) and a guideline for the design of the efficient NFR experiments has been established. The theoretical FRFs up to the second-order have been derived for simple and several complex mechanisms (Petkovska and Do, 2000; Petkovska and Petkovska, 2003; Petkovska, 1999, 2000, 2001, Brzić and Petkovska, 2014). Nevertheless, up to now, the NFR approach has not been experimentally validated.

The previous and existing FR experimental systems, reported in the literature, are mainly closed (batch) systems with volume modulation and highly accurate, fast-response pressure measurements (Naphtali and Polinski 1963; Yasuda, 1976; Rees and Shen, 1993; Reyes et al., 1997). The sine-wave volume modulation is typically performed by metal bellows coupled with a rotary motor and a suitable mechanism for converting circular into a linear motion. This arrangement enables variable frequency by varying the rotation speed, while variable amplitude is not feasible. Certain modifications of this basic concept have also been reported. Turner et al. (2001) improved the accuracy of the input sine wave approximation by using servomotor with feedback control to drive the metal bellows. Bourdin et al. (1998) have used an infra red (IR) detector to measure the adsorbent temperature during the volume variation and included a temperature response function in the analysis.

Theoretical basis of the NFR approach and simulation studies of a batch adsorber (Brzić and Petkovska, 2013) have revealed some requirements regarding the design of NFR experimental set-up: (1) variable input amplitude, (2) accurate sine wave-form of the input, (3) temperature measurements along with the pressure measurements (due to the expected heat effect under larger amplitude modulations) and (4) recording the data with high sampling frequency.

In order to validate and exploit the NFR approach for studying adsorption kinetics and equilibrium, a new apparatus has been designed, constructed and described in this article. The design combines the properties of the existing FR devices with specific requirements for the NFR approach. The apparatus has a batch configuration with volume as the modulated input and pressure, gas temperature and particle temperature are the measured outputs. The procedure for performing the NFR experiments will be given. A step-by-step analysis of the measured data, as well as the interpretation of the obtained results, will be presented on the example of adsorption of CO_2 on commercial zeolite 5A beads.

The commercial zeolite adsorbents have mostly a biporous structure, and therefore the adsorption of the gases on such adsorbents can be governed by a combination of diffusion in macropores and micropores, both with or without surface barrier, and heat transport. Onyestyák et al. (1996) have investigated adsorption of CO_2 on commercial 5A zeolites at 1 Torr and temperatures 298–423 K by linear FR technique. They have reported isothermal macropore diffusion (IMD) as the governing mechanism for the temperatures above 373 K and obtained the diffusion coefficient by fitting the experimental data to the IMD model. However, for the temperatures lower than 373 K, it was not possible to fit the data to IMD model because the bimodal behavior was experimentally observed. It was supposed that the second peak of the phase lag at low frequencies corresponded to heat effects.

2. Theoretical basis

2.1. Nonlinear frequency response and frequency response functions

When a weakly nonlinear system is subject to a cosinusoidal (or sinusoidal) input perturbation of amplitude A and frequency ω (rad/s)

$$x(t) = A\cos(\omega t) \tag{1}$$

its response after long enough time that the transient vanishes (named nonlinear frequency response) is a complex periodic function which contains a nonperiodic (DC) term, a first harmonic (y_1), a second harmonic (y_2) and an indefinite number of higher harmonics

$$y(t) = y_{DC} + y_1 + y_2 + y_3 + \ldots = y_{DC} + \sum_{n=1}^{\infty} y_n \tag{2}$$

The n-th harmonic can be represented in the time domain as

$$y_n = B_n\cos(n\omega t + \phi_n) \tag{3}$$

and in the frequency domain as

$$Y_n = B_n \exp(j\phi_n) \tag{4}$$

where B_n is its amplitude and ϕ_n is its phase. On the other hand, if the model of a weakly nonlinear system is represented as a set of the first and higher-order FRFs, according to the concept of higher-order FRFs (Weiner and Spina, 1980), than the individual harmonics of the system's frequency response can be represented in the following form (Petkovska, 2006):

$$Y_1 = G_1(\omega)X + \tfrac{3}{4}G_3(\omega,\omega,-\omega)X^2\overline{X} + \ldots \tag{5}$$

$$Y_2 = \tfrac{1}{2}G_2(\omega,\omega)X^2 + \tfrac{1}{2}G_4(\omega,\omega,\omega,-\omega)X^3\overline{X} + \ldots \tag{6}$$

etc., where $G_1(\omega)$ is the first-order FRF and $G_n(\omega,\ldots,\omega)$ ($n=2,3,\ldots$) are the higher-order FRFs, X is the Fourier transform of the input and $\overline{X}$ is its complex-conjugate. From Eqs. (5) and (6) it is obvious that the dominant term of the first harmonic is proportional to the first-order FRF $G_1(\omega)$, and the dominant term of the second harmonic is proportional to the second-order FRF $G_2(\omega,\omega)$. The contributions of the higher-order FRFs in Eqs. (5) and (6) strongly depend on the input amplitude (X). Depending on the system nonlinearity, input amplitudes can be chosen in such a way that the contributions of $G_3(\omega,\omega,-\omega)$ and higher order FRFs are negligible in the first harmonic, as well as the contributions of