Chemometrics and Intelligent Laboratory Systems 144 (2015) 80–86

Contents lists available at ScienceDirect

Chemometrics and Intelligent Laboratory Systems

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

Studying a gas–solid multi-component adsorption process with near-infrared process analytical technique: Experimental setup, chemometrics, adsorption kinetics and mechanism

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ARTICLE INFO

Article history:
Received 3 November 2014
Received in revised form 30 March 2015
Accepted 31 March 2015
Available online 3 April 2015

Keywords:
Gas–solid multi-component adsorption
Near-infrared spectroscopy (NIR)
Process analytical technique (PAT)
Chemometrics
Differential adsorption bed (DAB)

ABSTRACT

The study on multi-component or competitive gas–solid adsorption process is a challenge to current theories as well as experimental methods. In the paper, a methodology composed of near-infrared spectroscopy, process analytical technique and chemometrics has been tried to investigate the adsorption process of orthoxylene/aniline onto active alumina surface. The adsorption process took place in a differential adsorption bed, which was non-invasively monitored by a near-infrared spectrometer via optical fiber probe, and spectra were collected at every minute during the whole adsorption process. After treating these spectra with chemometrics algorithms, including wavelet analysis, partial least squares and artificial neural network, the adsorption process has been investigated thoroughly as well as clearly: not only the adsorption rates of each adsorbates at various adsorption times but also a great deal of information about the mechanism of the adsorption process. For example, orthoxylene was adsorbed evenly on the active alumina surface, while aniline was adsorbed uprightly; aniline was adsorbed to fabricate the first and the second adsorption layer on the adsorbent surface simultaneously rather than to construct them in sequence or step by step; and some parts of the adsorbent surface was more active for adsorption.

1. Introduction

Gas–solid adsorptions take place in nature or industrial equipment are usually multi-component or competitive, namely, containing more than one kind of adsorbate. Current theories in the field such as multi-component Langmuir, the ideal adsorbed solution theory, or the multi-component potential adsorption theory, however, are incapable to deal with the complicated case, because they are all inferred from the single-component adsorption of each adsorbates and do not take the interaction among adsorbates into consideration, especially when the adsorbate or adsorbent is polar material [1–3]. Accordingly, experimental methods are still indispensible to multi-component adsorption.

Traditionally, there have been a variety of experimental methods for studying the uptake of gas adsorbate on solid adsorbent. In physical chemistry, there are static methods and dynamic methods; in chemical engineering, pulse chromatography, fixed-bed breakthrough, closed-loop recycle and gravimetric measurement have been used to obtain thermodynamic and kinetic data for optimal design and operation of adsorption units. They, however, mainly focus on single-component adsorption and moreover have some disadvantages like high cost, inconvenience, time consuming or unreliability [2,3]. Consequently, some new techniques like the Wicke–Kallenbach permeation method, frequency response technique and isotope exchange technique have been developed in the last two decades [4–6]. Nevertheless, each of them has its own deficiencies: in frequency response technique, the adsorption process takes place in a non-isothermal environment and its data analysis is dependent upon unreliable models of heat and mass transfer; the Wicke–Kallenbach permeation method avoids the above difficulty under certain conditions but requires a specially formed and representative pellet of the adsorbent that is usually very difficult to obtain; isotope exchange technique has been reported to satisfactorily solve almost all these problems, while demanding a supply of adsorbate isotopes gas and a continuous online analytical devise (such as a quadrupole mass spectrometer) for quantitative measurement of trace isotope concentrations. More importantly, all of them share one shortcoming: the interaction between adsorbate molecule and adsorbent surface cannot be detected.

Process analytical technique (PAT) or process analytical chemistry (PAC) developed rapidly in recent years is probably available to study the multi-component adsorption process since it is capable to trace the chemical components and their alterations in an adsorption process. Of all PAT methods, near-infrared spectroscopy (NIR) may be the most appropriate because (1) NIR PAT is inline and noninvasive, namely,

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http://dx.doi.org/10.1016/j.chemolab.2015.03.015

tracing but not interfering the adsorption process; (2) in NIR PAT, solid sample could be detected without pretreatment; (3) optical fiber makes remote monitoring possible; (4) analysis cost is relatively low; (5) response of NIR spectrometer is prompt, generally less than 10 s; and (6) NIR is capable to quantitatively and simultaneously detect all adsorbate components, namely, suitable for multi-component systems[7,8]. Furthermore, as adsorbate molecules have been adsorbed onto the adsorbent surface, the vibration of some groups of the adsorbate as well as adsorbent may alter, which can be recorded in NIR spectra. Of course, in this case, what is probed by NIR spectrometer should be the solid adsorbent that is adsorbing the adsorbate rather than the adsorbate vapor. It is worth noting that the interaction between adsorbate and adsorbent as well as the adsorbed amounts of each adsorbates at a time are both deduced from NIR spectra collected at the same time, and consequently is synchronous, making possible to incorporate them for investigating the adsorption process more thoroughly and clearly than other current methods.

With the methodology we have investigated, the adsorption process of a binary-adsorbate system, the adsorption of orthoxylene/isoamyl alcohol onto silica gel [9], demonstrating the potential of NIR PAT as a powerful tool to study a gas–solid multi-component adsorption process. However, the paper focused on providing kinetic data for industrial design, while neither the interaction between the adsorbates and adsorbent nor the mechanism of the adsorption process has been discussed in detail. In this paper, we selected orthoxylene and aniline as adsorbates that have similar molecular structure and active alumina as the adsorbent that is polar material and commonly used in industry as well as scientific research, to demonstrate all aspects of our methodology: its experimental setup, data treatment and especially information analysis.

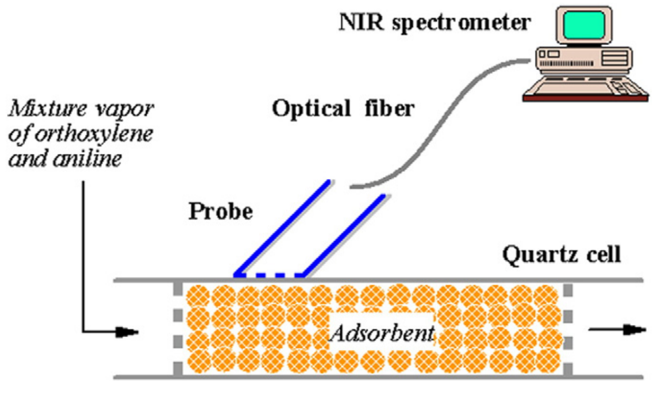
2. Experimental

2.1. Materials

This study used the following materials: orthoxylene (AR, Sinopharm Chemical Reagent Co., Ltd), aniline (AR, Sinopharm Chemical Reagent Co., Ltd), tetrachloride carbon (AR, Sinopharm Chemical Reagent Co., Ltd) and active alumina (Sinopharm Chemical Reagent Co., Ltd).

2.2. Experimental setup and measurement

The experimental setup is shown in Scheme 1, in which a rectangle quartz cell (40 mm in length, 10 mm in width and 2 mm in thickness) is non-invasively monitored by an NIR spectrometer via an optical fiber probe. The probe closely contacts with the exterior surface of the cell that is filled with active alumina, while the vapor mixture composed of orthoxylene and aniline is introduced to flow throughout the active alumina for adsorption. During the whole adsorption process, NIR spectra are collected continuously at the interval of 1 min.



Scheme 1. A differential adsorption bed (DAB) monitored non-invasively by an NIR spectrometer via an optical fiber probe.

The optical fiber probe is so small (less than 5 mm in diameter) that the adsorbate–adsorbent monitored by the probe could be roughly regarded as isothermal and mass homogeneous and accordingly is a differential adsorption bed (DAB). Data out of DAB can be treated conveniently for chemical engineering design without demand for any unreliable hypotheses of heat and mass transfer [10].

The NIR spectrometer is Nexus 870, Nicolet (Thermo Electron Corporation), and the optical fiber probe is its accessory (Smart NIR FiberPort Accessory). All spectra have been collected with the same measurement parameters: resolution, 4 cm^{-1}; number of scans, 16; range of scans, 4000–10000 cm^{-1}. The NIR spectrometer has a reference accessory (mainly made of polytetrafluoroethylene), but in most cases, the active alumina has been used as the reference in our experiments to emphasize NIR spectral signals of the adsorbates.

In the paper, almost all spectra are diffuse reflectance spectra of the active alumina containing orthoxylene and/or aniline, which are commonly affected by granularity and packing density of the active alumina. To lessen their influence, the granularity has been controlled between 80 and 100 meshes, and the same amount of active alumina is compressed into the same length in the same rectangular quartz cell to collect spectra.

Like absorbance strength in transmission spectra, for diffuse reflectance spectra, there is quite often a linear relationship between lg $(1/R)$ and concentration (R is the reflectance ratio). And accordingly, all diffuse reflectance spectra in the paper has been detected in terms of lg $(1/R)$.

2.3. Preparation of calibration samples and validation samples

NIR spectroscopy analysis, as an indirect analytical method, demands a calibration or training set to construct calibration model as well as a validation or test set to evaluate the predication capability of the calibration model. Considering orthoxylene and aniline are both pure chemicals, a convenient method has been used to prepare calibration and validation samples: well mixing given amounts of orthoxylene, aniline and active alumina together. The concentration of each adsorbate in adsorbent is represented as the ratio of the adsorbate to active alumina by weight (g/g). One hundred fifty samples of the calibration set were prepared, in which the concentration of orthoxylene was randomly selected between 0.000 and 0.250 at intervals of 0.005 g/g, or in other words, randomly selected from 0.000, 0.005, 0.010, 0.015, …, 0.250 g/g, so was the concentration of aniline. Fourteen validation samples were prepared, in which the concentrations of orthoxylene and aniline were (0.000, 0.200), (0.005, 0.180), (0.010, 0.160), (0.020, 0.140), (0.030, 0.120), (0.040, 0.100), (0.060, 0.080), (0.080, 0.060), (0.100, 0.040), (0.120, 0.030), (0.140, 0.020), (0.160, 0.010), (0.180, 0.005), (0.200, 0.00) g/g, respectively.

3. Chemometrics strategy and algorithm

3.1. Pretreatment of spectra

Most diffuse reflectance spectra have more or less baseline drift or slope and have been pretreated by means of standard normal variate transformation (SNV) and then detrending method in the paper [8].

3.2. Signal separation

Since NIR signals of two adsorbates, orthoxylene and aniline, overlapped much, they should be separated, and the more kinds of adsorbate the system contains, the more necessary signal separation is. Here, wavelet decomposition and reconstruction followed have been employed, and from Fig. 1, one could discover that wavelet analysis is effective even within seriously overlapping range of 4300–4000 cm^{-1}, in which orthoxylene and aniline both have combination tones of C-H