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Prediction of pore properties of hierarchical porous silica templated on natural rubber

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ABSTRACT

Hierarchical porous silica (HPS) templated on natural rubber (NR) was made via sol-gel technique using sodium silicate as a silica source. Macropores and mesopores with an ink-bottle type of morphology were randomly distributed in the HPS. Prediction of surface area and pore volume of the produced HPS was undertaken by central composite design (CCD) and artificial neural network (ANN) models, which were separately developed and which made use of the following variables: pH, calcination temperature, NR amount, and salt concentration. To obtain optimum feedforward back propagation networks, the number of hidden layers and the number of neurons in each hidden layer were varied. The use of an extra dataset in developing the optimum ANN architecture in each training cycle helped to easily locate when and where the overfitting phenomenon occurred, and thus the generalization performance of a network was not compromised. The quadratic polynomial models obtained using CCD poorly predicted surface area and pore volume ($R^2 < 0.65$). In contrast, the optimum ANN models with a single hidden layer predicted both pore properties exceptionally well ($R^2 > 0.95$).

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1. Introduction

Porous silica has numerous existing and emerging applications. It is a potential drug carrier [1,2], a catalyst support [3,4], and a metal adsorbent [5,6]. Two key properties that affect the use of porous silica are its specific surface area and specific pore volume. Typical mesoporous silica is known for its unimodal small pore size and therefore a high surface area with in turn provides a high adsorption capacity but limits mass transfer into the pores [7,8]. This limitation of mesoporous silica is overcome by using hierarchical porous silica (HPS) which has a network of large pores connected to smaller pores [9–11].

HPS can be produced via a sol-gel process using templates, such as colloidal natural rubber (NR) particles [12] or chitosan [13]. For such a production process, the following steps are involved: (1) mixing a silica source and a template at a specified pH; (2) hydrothermal aging of the slurry for a specified time and at a specified temperature to strengthen the silica framework; (3) recovery, washing and drying of the suspended solids; and (4) template removal. The main process variables affecting HPS pore properties are the following: the medium pH [14,15], the calcination temperature [16–18], the amount of the template [19], and the electrolyte concentration [20,21].

This work reports on models for predicting the surface area and the pore volume of HPS for the variables of the sol-gel production process mentioned above. The pore properties of HPS produced under various conditions were characterized, and the data obtained were used for developing predictive models via two distinct approaches: (1) the response surface method (RSM) based on statistical experiment design and (2) the use of artificial neural networks. These two approaches are briefly explained below.

The RSM uses statistical experiment design to develop a relationship between responses and independent variables or, as the latter are also called, factors [22]. Central composite design (CCD) of experiments is commonly used in combination with the RSM to develop a quadratic model that reveals the effect of each individual factor, as well as the interactive effects of the factors, on the response variables [23]. The use of CCD minimizes the number of experiments while allowing a high-quality prediction over the

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entire range of the design space [24]. Thus, CCD has been widely used in identifying the combination of factor values for an optimum process response. For example, CCD has been used for optimizing solid phase extraction with silica as the adsorbent [25–27] and reactions involving silica-supported catalysts [28,29]. It has also been used to optimize the synthesis of mesoporous silica not involving a template [30].

For many complicated systems that cannot be satisfactorily described by polynomial equations, artificial neural networks (ANNs) are alternative methods [31]. Prior to use, an ANN must be trained using the measured process response data for various combinations of the experimental factors. Suitably trained ANNs have been used to predict process responses in applications such as the synthesis of inorganic composite materials [32,33] and the etching of aluminosilicate glass [34]. A feedforward back-propagation algorithm is commonly used for modeling the relationship between the set of input data (i.e., the values of the experimental factors) and one or more responses [24]. Development of an ANN by using random division of experimental data into groups (training dataset, test dataset, and validation dataset) is normally considered sufficient to give satisfactory models as reported in many works [35–38]. However, in several cases, the generalization of a model has been compromised by random data division since this step allows some training data to be the test data for another training cycle. As ANNs have the ability to memorize already-seen data, ANN model gives good fitting specifically to the seen test data while diverging for the unseen data [39,40]. This phenomenon is known as overfitting, which can be solved by adding an independent dataset to test the generalization of the model [41–43].

The synthesis of HPS using a template has not previously been modeled by a black-box model (e.g., CCD or ANN). The synthesis of HPS represents a more difficult step in the application of such black-box models and is more complex than the template-free synthesis of porous silica since interactions between the template and the silica critically influence the properties of HPS. As the present work focuses on using NR particles as a template, a further complicating factor is the pH dependence of surface charges of the template and silica. The widely accepted tools of CCD and ANN were used in this work to model the dependence of the key properties of HPS on the conditions used in the production process. The efficacy of the models based on CCD and ANN was compared for predicting the properties of HPS. In both cases, the process variables, or the factors, were the medium pH, the calcination temperature, the mass ratio of NR to silica, and the concentration of the electrolyte. The responses were the BET specific surface area and the specific pore volume of HPS. The data of the experiments specified by CCD and additional data were used to train the ANNs. Furthermore, an independent set of experimental data obtained for random combinations of the conditions of synthesis was utilized as an additional test dataset to verify a model's generalization.

2. Experiments and methods

2.1. Materials

The following materials were used in the production of HPS samples: NR latex (24% dry rubber; a gift from a rubber plantation in Surat Thani province, Thailand), sodium silicate Na_2SiO_3 with 29.12% SiO_2; a gift from PQ Chemicals (Thailand) Ltd, HCl (37.5% HCl; J.T. Baker, USA), NaOH (99% pure; Merck, Germany), and NaCl (99.9% pure; Univar, USA). All chemicals and materials were used as received.

2.2. Synthesis of HPS

All HPS samples were prepared by the sol–gel method [12]. NR latex was mixed with deionized water and sodium silicate in a fixed weight ratio of SiO_2:water of 1:60. The pH of the mixture was adjusted to the desired value by adding HCl or NaOH. NaCl was then added, and the mixture was stirred for a few minutes. This suspension was hydro-thermally aged at 80 °C for 24 h to obtain solid particles, which were subsequently recovered by gravity sedimentation and washed repeatedly with deionized water to remove the salt. The washed particles were dried to a constant weight in an oven (50 °C), and the dry solids were calcined for 6 h to burn off the NR template. This provided the HPS samples. The samples were kept in zip-locked plastic bags in a desiccator. During the production process, the following factors were varied: the pH of the mixture, the calcination temperature, the weight ratio of dry rubber to SiO_2, and the concentration of NaCl.

2.3. Characterization of HPS

The HPS samples were characterized by measuring the specific surface area and the pore-size distribution using nitrogen adsorption (Autosorb-1C, Quantachrome Instruments, USA) and the BET (Brunauer–Emmett–Teller) method in the relative pressure (P/P_0) range of 0–1. The pore-size distribution was determined in line with the Barrett–Joyner–Halenda (BJH) model. Further characterization of the samples was achieved by scanning electron microscopy (FEI Quanta-450 SEM, USA), 200 kV transmission electron microscopy (JEOL JEM-2010; JEOL Ltd, Japan), and X-ray diffraction (D8 Advance; Bruker, Germany) with Cu-Kα radiation (40 kV, 40 mA) in the range of 10–50° (2θ).

2.4. CCD experiment design and models

A central composite design (CCD) combines data from a full or fractional factorial design (coded values are −1 or 1), a duplication of the center point (coded value is 0), and a star design (a group of axial points) in which the points are at a distance $\alpha = \sqrt[4]{2^k}$ from the center. Here k is the number of factors. All factors are studied at five levels ($-\alpha$, −1, 0, +1, $+\alpha$), and the number of designed experiments is $2^k + 2k + n$ [44]. Here 2^k, $2k$, and n are the number of factorial, axial, and center points, respectively.

The experimental factors were as follows: the pH (A: 4–9), the calcination temperature (B: 550–800 °C), the weight ratio of NR to silica (C: 0.5–1.0), and the NaCl concentration (D: 0–0.5 M). The responses were the BET specific surface area and the specific pore volume. Minitab® 16.2 statistical software (Minitab Inc., USA) was used for experiment design and analysis.

Each factor had five levels as shown in Table 1. The center point experiment was carried out in triplicate to determine the error. The total number of experiments of the CCD, including the replicates, was 27 (Runs 1–8, Run 9 (in triplicate), Runs 10–25: Table 1). Runs 26–33 in Table 1 were additional experiments, as discussed later. The measured responses are shown in Table 1.

The quadratic model relating the responses (y_{CCD}) to the factors (A–D) was as follows:

$$y_{CCD} = c_0 + c_1A + c_2B + c_3C + c_4D + c_{11}A^2 + c_{22}B^2 + c_{33}C^2 + c_{44}D^2 + c_{12}AB + c_{13}AC + c_{14}AD + c_{23}BC + c_{24}BD + c_{34}CD \quad (1)$$

In the above equation, c_0 is the estimated constant; c_{1-4} are the estimated coefficients for the main effects of the factors; c_{11}, c_{22}, c_{33},

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