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Solubility prediction of disperse dyes in supercritical carbon dioxide and ethanol as co-solvent using neural network

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ABSTRACT

Nowadays artificial neural networks (ANNs) with strong ability have been applied widely for prediction of nonlinear phenomenon. In this work an optimized ANN with 7 inputs that consist of temperature, pressure, critical temperature, critical pressure, density, molecular weight and acentric factor has been used for solubility prediction of three disperse dyes in supercritical carbon dioxide ($SC\text{-}CO_2$) and ethanol as co-solvent. It was shown how a multi-layer perceptron network can be trained to represent the solubility of disperse dyes in $SC\text{-}CO_2$. Numeric Sensitivity Analysis and Garson equation were utilized to find out the degree of effectiveness of different input variables on the efficiency of the proposed model. Results showed that our proposed ANN model has correlation coefficient, Nash–Sutcliffe model efficiency coefficient and discrepancy ratio about 0.998, 0.992, and 1.053 respectively.

1. Introduction

In recent years, there has been a rising interest in the utilization of supercritical fluids as an alternative to the employment of organic solvents in many industrial applications, such as in chemical and biochemical reactions [1,2], extraction and purification processes [3,4], micro- and nano-scale particle production [2], textile industry [5], synthesis of fibers [6], production of polymers [7], and decaffeination of coffee and tea [8].

$SC\text{-}CO_2$ has many advantages related to water. For example, above the critical point the carbon dioxide has properties of both a liquid and a gas. In this way $SC\text{-}CO_2$, has liquid like densities, which is advantageous for dissolving hydrophobic dyes, and gas-like low viscosities and diffusion properties, which can lead to shorter dyeing times compared to water [9,10], also $SC\text{-}CO_2$ eliminates colored wastewater and high drying energy costs [11]. In other hand, working with $SC\text{-}CO_2$ requires high-pressure process which implies high investment costs for the machinery and the training of skilled staff [12]. One way to reduce the working pressure is adding a little quantities of co-solvent, such as ethanol, that significantly increase the solubility in lower pressures [13,14]. Although, solubility is one of the most important parameters for dye selection and also for optimization of process temperature and pressure [11], mechanism of dye solubility in the $SC\text{-}CO_2$ and co-solvent systems is highly complex and is difficult to model by means of conventional mathematical modeling [15].

As experimental studies are very expensive and time consuming, many researchers have tried to predict the solubility of dye in supercritical carbon dioxide by classical equations of state and semi-empirical equations [16,17]. Gordillo and coworkers [18] used both approach, classical equations of state and semi-empirical equation, to predict solubility of disperse blue 14 in supercritical carbon dioxide. Tamura and Shinoda [19] experimentally investigated binary and ternary solubilities of disperse dyes and their blend in $SC\text{-}CO_2$. They also used empirical equation and modified Peng–Robinson–Stryjek–Vera equation of state to correlate the solubilities of the dyes.

Nonlinearity of dye solubility mechanism is mainly due to the interaction of more number of variables such as temperature, pressure and mixture density [11,20]. Application of ANN has been considered as a promising tool because of their simplicity towards simulation, prediction and modeling. One of the characteristics of modeling based on ANNs is that it does not require the mathematical description of the phenomena involved in the process, and might therefore prove useful in simulating and up-scaling complex systems. So, it is preferable to use a nonparametric technique such as a neural network model to make reliable prediction of dye solubility in the $SC\text{-}CO_2$ and co-solvent system [21].

Tabaraki and coworkers [22] used a wavelet neural network (WNN) model for solubility prediction of 25 anthraquinone dyes in $SC\text{-}CO_2$. Gharagheizi and coworkers [23] reported application of ANN model for prediction of solubilities of 21 of the commonly used industrial solid compounds in supercritical carbon dioxide. There are rarely

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studies reported on employing neural network models for the prediction of dye solubility in the co-solvent systems. Accordingly, this article develops a robust ANN model to predict the solubility of three disperse dyes in a co-solvent mixture containing ethanol and SC-CO_2.

2. Artificial Neural Networks

ANNs are known for their superior ability to learn and classify data. The inspiration of neural networks came from studies on the structure and function of the brain and nerve systems as well as the mechanism of learning and responding. The potential applications include prediction, classification, data association, data conceptualization, data filtering and optimization.

As mentioned before neurons are main building block of neural networks. In an ANN a neuron sums the weighted inputs from several connections and then output of neurons is produced by applying transfer function to the sum. There are many transfer function but the common transfer function is sigmoid and we used this transfer function. Sigmoid function can be expressed by the following equation:

$$\theta_j = \frac{1}{1+e^{-\psi_j}}. \quad (1)$$

In Eq. (1) ψ is the sum of weighted inputs to each neuron and θ is the output of each neuron and ψ can be calculated from Eq. (2).

$$\psi_j = \left(\sum_{i=1}^{n} w_{ij}.\theta_i\right) + b_j. \quad (2)$$

In Eq. (2) w_{ij} denotes connection between node j of interlayer l to node i of interlayer l-1, b_j is a bias term and n is number of neuron in each layer. In any interlayer l and neuron j input values integrate and generate ψ_j.

In order to minimize the difference between experimental data and calculated of neural network, mentioned process repeats for the total number of training data. After training, validation of neural network can be done by testing data.

Numerous types of the ANNs exist such as multi-layer perceptron (MLP), radial basis function (RBF) networks and recurrent neural networks (RNN). The type of network used in this work is the multi-layer perceptron network. Multi-layer perceptron networks are one of the most popular and successful neural network architectures, which are suited to a wide range of applications such as prediction and process modeling [24].

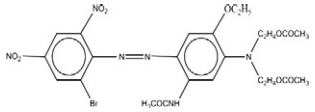
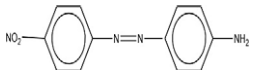
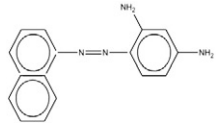
2.1. Preparation of dataset

Forty eight experimental data sets which have been collected from a published paper [25], were used to develop the ANN model. Data specifications of model variables are summarized in Table 1. In other words three different types of dyes such as disperse blue 79, disperse orange 3, and solvent brown 1 in a condition in which pressure varies from 15.92 till 30.11 MPa for three constant values of temperature equal to 353.2, 373.2 and 393.2 K, were employed to their solubility be calculated using the model. Hence temperature and pressure and some other parameters such as critical temperature, critical pressure, acentric factor and molecular weight each as a function of type of dye, were included in the table. The other parameter is density which ranges from 326.6 to 753.8 kg · m^{-3} and depends not only to the type of dye but also to the system conditions such as temperature and pressure. These parameters were selected based on the last research about solubility and have been devoted to the network as inputs [26]. In Table 2 the molecular structures of the dyes are reported.

Table 1
Data statistics of model variables

Variable	Range
Temperature/K	353.2, 373.2, 393.2
Pressure/MPa	15.92–30.11
Critical temperature/K	953, 1070, 1200
Critical pressure/MPa	1.4, 2.7, 3.2
Acentric factor	0.644, 0.859, 0.95
Density/kg · m^{-3}	326.6–753.8
Molecular weight/kg·mol^{-1}	242.24, 262.31, 639.43
Dyes solubility/kg · m^{-3}	8.34×10^{-7}–136×10^{-7}

Table 2
Different molecular structures of the dyes

Compound	Molecular structure	MW
Disperse blue 79		639.43
Disperse orange 3		242.24
Solvent brown 1		262.31

In this work, all data are divided into three parts (training subset (70% of all data), validation subset (15% of all data) and testing subset (15% of all data)). To prevent larger number from overriding smaller number; all data are normalized. Normalization can be done by several equations. In present work, data is scaled between [0–1] by means of Eq. (3). Data preparation which has been illustrated in this section is the first step of a model development (see Fig. 2).

$$(\text{Scaled})_{\text{value}} = \frac{(\text{Actual})_{\text{value}} - \min_{(\text{Actual value})}}{\max_{(\text{Actual value})} - \min_{(\text{Actual value})}}. \quad (3)$$

2.2. ANN modeling

Programming, validation, training and testing of the ANN model were carried out by MATLAB 7.12.0. Also, all programs were run on a Pentium IV (CPU 2.7 GHz and 2 GB RAM) personal computer with windows 7 operating system.

2.3. Performance criteria

In this study in order to compare the results of proposed model, statistical parameters (as shown in Table 3) were utilized. In statistics, the mean absolute error (MAE) is a quantity used to measure how close forecasts or predictions are to the eventual outcomes. The smaller value of this index indicates higher accuracy of the model. The next parameter is RMSE which is a frequently used measure of the differences between values predicted by a model or an estimator and the values actually observed that must be minimum if a good model is expected. Dr index is the mean value of predictions to the observed data. The greater

Table 3
Performance criteria used in this study

MAE	Mean absolute error
RMSE	Root Mean Squared Error
Dr	Discrepancy ratio
N–S	Nash–Sutcliffe model efficiency coefficient
R	Pearson product–moment correlation coefficient