Applying ANN, ANFIS and LSSVM Models for Estimation of Acid Solvent Solubility in Supercritical CO₂

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Abstract: In the present work, a novel machine learning computational investigation is carried out to accurately predict the solubility of different acids in supercritical carbon dioxide. Four different machine learning algorithms of radial basis function, multi-layer perceptron (MLP), artificial neural networks (ANN), least squares support vector machine (LSSVM) and adaptive neuro-fuzzy inference system (ANFIS) are used to model the solubility of different acids in carbon dioxide based on the temperature, pressure, hydrogen number, carbon number, molecular weight, and the dissociation constant of acid. To evaluate the proposed models, different graphical and statistical analyses, along with novel sensitivity analysis, are carried out. The present study proposes an efficient tool for acid solubility estimation in supercritical carbon dioxide, which can be highly beneficial for engineers and chemists to predict operational conditions in industries.

Keywords: Supercritical carbon dioxide, machine learning, acid, artificial intelligence, solubility, artificial neural networks (ANN), adaptive neuro-fuzzy inference system (ANFIS), least-squares support vector machine (LSSVM), multilayer perceptron (MLP).

1 Introduction
In recent years, supercritical fluid has become one of the interests of chemical engineers and chemists as a novel and extensive applicable technology. The synthesis and generating of nanomaterials and extraction process of different materials are the popular applications of supercritical fluids [Inomata, Honma, Imahori et al. (1999); Stassi and Bettini (2000);
Ohde, Hunt and Wai (2001); Celso, Triolo and Mcclain (2002); Uzer, Akman and Sarker (2006); Munshi and Bhaduri (2009); Nahar and Sarker (2012); Zhang, Heinonen and Levanen (2014); Knez and Cor (2017); Zhao, Zhang, Zhao et al. (2017); Belghait, Si-Moussa, Laidi et al. (2018); Gao, Daryasafar, Lavasani et al. (2018). One of the supercritical fluids which have wide applications in the extraction of various metals from solid and liquid phases is carbon dioxide [Erkey (2000); Sunarso and Ismadji (2009); Lin, Liu, Maiti et al. (2014)]. Due to non-flammability, nontoxicity, low cost, and critical points (304.2 K and 7.38 MPa) of carbon dioxide, the supercritical carbon dioxide becomes one of the interesting and applicable supercritical fluids in industries [Ghaziaskar and Nikravesh (2003); Bovard, Abdi, Nikou et al. (2017)]. The viscosity and density of supercritical carbon dioxide are known as two important transport properties of the fluids which are affected by pressure and temperature [Choubin, Abdolshahnejad and Moradi (2020); Shamshirband, Hadipoor and Baghban (2019)]. Another dominant thermophysical property of supercritical carbon dioxide is the solubility of different materials in supercritical carbon dioxide which is a function of various factors such as polarity, molecular weight, pressure, temperature, and vapor pressure [Huang, Chiew, Lu et al. (2005); Ghaziaskar and Kaboudvand (2008)].

One types of the materials which have a solubility in supercritical carbon dioxide are acids, the nanofluoropentanoic acid which is known as one type of perfluorocarboxylic acids, has extensive applications in the production of paints additives, polymers, foams, and stain repellents but because of their high ability instability, they are harmful to environment [Richter and Dibble (1983); Moody and Field (1999); Hintzer, Löhr, killich et al. (2004); Fei and Olsen (2011); Hubbard, Guo, Krebs et al. (2012); Dartiguelongue, Leybros and Grandjean (2016); Hintzer, Juergens, Kaempf et al. (2016)]. Adrien Dartiguelongue and coworkers studied solubility of perfluoropentanoic acid in supercritical carbon dioxide in the wide range of temperature and pressure and also proposed some density-based models to predict solubility in terms of density of supercritical fluids [Dartiguelongue, Leybros and Grandjean (2016)]. Gurdial et al. [Gurdial and Foster (1991)] constructed dynamic setup to study solubility of o-, m- and p-hydroxybenzoic acid in the supercritical carbon dioxide in the wide range pressure of 80-205 mbar and temperature range of 308.15-328.15 K and correlated the measured solubility as a function of density. Kumoro measured the solubility of 2R,3β-dihydroxyurs-12-en-28-oic acid which is called Corosolic acid dynamically in a different range of pressure 8 to 30 MPa and five different temperatures of 308.15, 313.15, 323.15, and 333.15 K. Kumoro used various density-based models to correlate the experimental data [Kumoro (2011)].

Sahihi et al. [Sahihi, Ghaziaskar and Hajebrahimi (2010)] measured the solubility of Maleic acid in supercritical carbon dioxide by utilization of static experimental setup. The measured data belongs to Maleic acid in a pressure range of 7 to 300 bar and temperature of 348.15 K. Ghaziaskar and coworkers used a continuous flow set up to study solubility of tracetin, diacentin and acetic acid in supercritical carbon dioxide in the pressure range of 70 to 180 bar and various temperature of 313, 333 and 348 K and they also compared the obtained solubilities for different acids [Ghaziaskar, Afsari, Rezayat et al. (2017)]. Helena Sovova adjusted the Adachi-Lu equation based on the solubility of Ribes nigrum (blackcurrant) and Vitis vinifera (grape-vine) in supercritical carbon dioxide. They concluded the Adachi-Lu equation has enough accuracy in forecasting solubility of
triglycerides in carbon dioxide [Sovova, Zarevucka, Vacek et al. (2001)].

The issue of prediction of various acids solubility in supercritical carbon dioxide and phase equilibrium investigation of supercritical carbon dioxide and different materials are the important topics in chemical engineering research [Hemmati-Sarapardeh and Hajirezaie (2020)]. According to the hardships of experimental studies such as special tools and procedure which are needed, in the present work, the data-driven methods and advanced machine learning models have been considered as the reliable solutions, e.g., [Anitescu, Atroshchenko, Alajlan et al. (2019); Zarei, Razavi, Baghban et al. (2019); Mosavi, Shamshirband, Salwana et al. (2019); Mosavi, Salimi and Faizollahzadeh (2019); Najafi, Faizollahzadeh, Mosavi et al. (2018)]. In this paper four different algorithms, Radial basis function artificial neural network (RBF-ANN), Multi-layer Perceptron artificial neural network (MLP-ANN), Least squares support vector machine (LSSVM) and Adaptive neuro-fuzzy inference system (ANFIS) are developed to predict the solubility of different types of acid in supercritical carbon dioxide based on the various parameters such as structure of acid, pressure and temperature.

2 Methodology

2.1 Experimental data gathering

The dominant purpose of the present paper is the development of accurate and simple models to forecast solubility of different acids in supercritical carbon dioxide. Due to this, the required actual data for training and testing phases of models were assembled from the reliable source existed in literature [Gurdial and Foster (1991); Sovova, Zarevucka, Vacek et al. (2001); Sparks and Hernandez (2007); Tian, Jin, Gua et al. (2007); Sparks, Estevez, Hernandez et al. (2008); Kumoro (2011); Dartiguelongue, Leybros and Grandjean (2016)]. This collection of data contains the 188 acid solubility data points in terms of pressure, temperature, acid dissociation constant, molecular weight, number of carbon and hydrogen of acid. The details of data collection are reported in Tabs. S1 and S2. These details include acid name, acid dissociation constant, pressure and temperature ranges, and the number of utilized data points for each acid. Also, for clarification of this experimental dataset, the structure, linear formula and molecular weight of utilized acids are presented in Tab. S3. These acids include Perfluoropentanoic acid, o-Hydroxybenzoic Acid, Corosolic Acid, Maleic Acid, Ferulic Acid, Azelaic Acid, p-aminobanzoi acid, and Nonanioc acid.

2.2 Artificial neural networks

Artificial neural networks have amazing similarities to the performance and structure of neuron units in the brain system [Smith (1993); Bas and Boyaci (2007)]. These computational blocks construct different types of a layer such as input, output, and hidden layers. In the layers, there are transfer functions or activation function which organize the process of training in the algorithm. Each neuron has specific weight and bias values that control the optimization process. The artificial neural networks have the ability to trace a nonlinear form relationship between input and output parameters. Due to this ability, artificial neural networks have a widespread application in different industries and sciences. Artificial neural networks can be classified in different forms, such as a recurrent neural network (RNN), radial basis function, and multilayer perceptron [Movagharnejad and
In the present work, the MLP and RBF network are utilized.

2.3 Least squares support vector machine

Vapnik [Vapnik (1998)] proposed the support vector machine based on statistical learning theory. This computational intelligence can be used for regression and classification purposes [Faizollahzadeh, Najafi, Alizamir et al. (2018); Riahi-Madvar and Dehghani (2019)]. However, there are many advantages to this method, but there is a hardship in its computational procedure because of quadratic programming. The least-squares SVM (LSSVM) is proposed as a novel type of SVM to solve this problem. This novel approach organized linear equations for computation and optimization [Cortes and Vapnik (1995); Suykens and Vandewalle (1999, 2001); Zamen (2019)].

By considering a dataset of \((x_i, y_i)\)_n, the LSSVM regression prediction is utilized to estimate a function, where \(x_i\) and \(y_i\) are known as input and target parameters and \(n\) represent the number of data which utilized in training phase [Wang (2005)]. The linear regression is formulated, such as the following:

\[
y = \omega^T \varphi(x) + b
\]  
(1)

where \(\varphi(x)\) denotes a nonlinear function that has different forms such as polynomial, linear, sigmoid, and radial basis functions. Also, \(\omega\) and \(b\) denote the weights and determined constant-coefficient in the training process. A new optimization problem can be defined based on LSSVM approach [Baghban, Bahadori, Lemraski et al. (2016); Baghban, Namvarrechi, Phung et al. (2016); Ahmadi, Baghban, Salwana et al. (2019)]:

\[
\min_{\omega, b, \varepsilon} J (\omega, \varepsilon) = \frac{1}{2} \omega^T \omega + \frac{1}{2} \gamma \sum_{k=1}^{N} e_k^2
\]  
(2)

Which is related to the below constraints:

\[
y_k = \omega^T \varphi(x_k) + b + e_k \quad k=1,2,\ldots,N
\]  
(3)

The Lagrangian equation is constructed to solve the optimization problem:

\[
L(\omega, b, \varepsilon, \alpha) = J (\omega, \varepsilon) - \sum_{k=1}^{N} \alpha_k (\omega^T \varphi(x_k) + b + e_k - y_k)
\]  
(4)

where \(Y\) and \(e_k\) are known as regularization parameter and regression error. The \(\alpha_k\) represents the support value. To solve the above problem, the above equation is differentiated with respect to the different parameters:

\[
\frac{\partial L(\omega, b, \varepsilon, \alpha)}{\partial \omega} = 0 \rightarrow \omega = \sum_{k=1}^{N} \alpha_k \varphi(x_k)
\]  
(5)

\[
\frac{\partial L(\omega, b, \varepsilon, \alpha)}{\partial b} = 0 \rightarrow \sum_{k=1}^{N} \alpha_k = 0
\]  
(6)

\[
\frac{\partial L(\omega, b, \varepsilon, \alpha)}{\partial e_k} = 0 \rightarrow \alpha_k = \gamma e_k, \quad k=1,2,\ldots,N
\]  
(7)

\[
\frac{\partial L(\omega, b, \varepsilon, \alpha)}{\partial \alpha_k} = 0 \rightarrow y_k = \omega^T \varphi(x_k) + b + e_k \quad k=1,2,\ldots,N
\]  
(8)

Karush-Kuhn-Trucker matrix can be obtained by elimination of \(\omega\) and \(\varepsilon\) [Cortes and Vapnik (1995); Baylar, Hanbay and Batan (2009); Mehdizadeh and Movagharnejad (2011)]:

\[
\begin{bmatrix}
0 & \frac{1^T}{\nu} \\
\frac{1^T}{\nu} & \Omega + \gamma^{-1}I
\end{bmatrix}
\begin{bmatrix}
\alpha \\
b
\end{bmatrix}
= 
\begin{bmatrix}
y \\
0
\end{bmatrix}
\]  
(9)
where \( y = [y_1 \ldots y_N]^T \), \( \alpha = [\alpha_1 \ldots \alpha_N]^T \), \( 1_N = [1 \ldots 1]^T \), and I represent the identity matrix. 

\[ \Omega_{kl} = \varphi(x_k)^T \varphi(x_l) = K(x_k, x_l) \]

\( K(x_k, x_l) \) is known as kernel function which can be in different forms of linear, polynomial and radial basis function forms [Gunn (1998)]. The estimating function form of LSSVM algorithm can be expressed as following formulation [Muller, Mika, Ratsch et al. (2001); Rostami, Baghban and Shirazian (2019)]:

\[
y(x) = \sum_{k=1}^{N} \alpha_k K(x, x_k) + b \tag{10}
\]

2.4 Adaptive neuro-fuzzy inference system (ANFIS)

In Adaptive neuro-fuzzy inference system, which is called the ANFIS algorithm, in brief, has five different layers. The aforementioned approach was developed by Jang et al. [Jang, Sun and Mizutani (1997)]. The hybrid learning approach and backpropagation are known as fundamentals of training of conventional ANFIS algorithm [Qasem, Samadianfard and Nahand (2019); Rezakazemi, Mosavi and Shirazian (2019)]. The ANFIS algorithm was born base on fuzzy logic and neural network advantages and also the different evolutionary methods such as Imperialist Competitive Algorithm (ICA), Particle Swarm Optimization (PSO) and Genetic algorithm (GA) can be used to reach the optimal structure of ANFIS algorithm [Afshar, Gholami and Asoodeh (2014), Khosravi, Nunes, Asad et al. (2018); Razavi, Sabaghmoghadham, Bemani et al. (2019)]. The ANFIS structure is demonstrated in Fig. 1. As shown, there are two input variables and one output.

![Typical construction of ANFIS approach](image)

**Figure 1:** Typical construction of ANFIS approach

In the first layer, the linguistic terms are built based on input data. The Gaussian membership function is applied to organize these linguistic terms. The Gaussian function can be shown as the following formulation [Ahangari, Moeinossadat and Behnia (2015); Bahadori, Baghban, Bahadori et al. (2016)]:

\[
O_1^1 = \beta(X) = \exp\left(-\frac{1}{2} \left(\frac{X-Z}{\sigma}\right)^2\right) \tag{11}
\]

where \( Z \) and \( \sigma \) denote the Gaussian parameters.

The next layer, shown as \( \Pi \) multiplies the incoming signals and contains the weighted terms which are related to rules:

\[
O_1^2 = W_i = \beta_{Ai}(X) . \beta_{Bi}(X) \tag{12}
\]
The third layer shown as NN, its averages of determined weights are evaluated such as the following formulation:

\[ O^3 = \frac{w_i}{\sum w_i} \]  

(13)

Then in the next layer, the average weight values are multiplied to the related function such as below:

\[ O^4 = \overline{W}_i f_i = \overline{W}_i (m_iX_1 + n_iX_2 + r_i) \]  

(14)

where, \( m, n, \) and \( r \) represent the resulting indexes.

At last, the fifth layer consists of the summation of previous layer outputs:

\[ O^5 = Y = \sum_i \overline{W}_i f_i = \overline{W}_1 f_1 + \overline{W}_2 f_2 = \frac{\sum w_i f_i}{\sum w_i} \]  

(15)

2.5 Particle swarm optimization (PSO)

The combination of random probability distribution approach and generation of the population constructed the particle swarm optimization algorithm. Eberhart et al. introduced the PSO algorithm that comes from the social behavior of birds and developed it to solve nonlinear function optimization problems [Kennedy (2010)]. This strategy has special similarities with other optimization approaches such as a genetic algorithm that is constructed a base on a random solution population. Each particle can be known as a probable solution to the problem. A random population of particles created in search space to relate in an optimum system. \( P_{\text{best}} \) is known as the best solution which can be obtained from this strategy for a particle. Also, \( g_{\text{best}} \) represents the global best solution determined by the swarm. The particle moves in the space by time iterations, and the next iteration velocity is determined by using \( g_{\text{best}}, P_{\text{best}} \) and current velocity [Eberhart and Kennedy (1995)]. The \( P \)'th particle can be determined as follow:

\[ X_{pd}^{iter+1} = X_{pd}^{iter} + V_{pd}^{iter+1} \]  

(16)

The particle velocity is updated by the following expression:

\[ v_{id}(t + 1) = w v_{id}(t) + c_1 r_1 \left( p_{\text{best},id}(t) - X_{id}(t) \right) + c_2 r_2 \left( g_{\text{best},d}(t) - X_{id}(t) \right) \]  

(17)

\( w, c, \) and \( r \) are inertia weight, learning rate, and random number respectively [Haratipour, Baghban, Mohammadi et al. (2017)].

3 Results and discussion

In the present study, the determined structure of the MLP-ANN algorithm utilizes log-sigmoid, and linear activation functions the hidden and output layers respectively. By utilization of trial and error, the optimum number of neurons in hidden layers is determined as 7 to reach the best structure of the MLP-ANN algorithm. The performance of Levenberg Marquardt training of MLP-ANN algorithm based on the mean square error is shown in Fig. 2.
Applying ANN, ANFIS and LSSVM Models for Estimation

In the RBF-ANN algorithm, the radial basis function (RBF) is utilized for hidden layers. According to information in the literature, the hidden layer neurons for RBF-ANN can be supposed one-tenth of training data points. The training process of the RBF-ANN algorithm base on MSE has been reported in Fig. 3.

![Figure 2: Trained MLP-ANN model by Levenberg Marquardt algorithm](image)

In this work, a particle swarm optimization approach is applied to train the best structure of the ANFIS algorithm. Fig. 4 demonstrates the gained root mean squared error (RMSE) of estimated and experimental acid solubility values in the training step.

![Figure 3: Trained RBF-ANN approach by Levenberg Marquardt algorithm](image)
The optimum structure of ANFIS can be recognized by the RMSE value of 0.003 after 1000 of iteration steps. Trained membership functions of the proposed ANFIS model are also shown in Fig. 5 for each cluster.
Applying ANN, ANFIS and LSSVM Models for Estimation

Figure 5: Trained membership function parameters

Figure 6: Schematic demonstration of trained LSSVM algorithm
The RBF kernel function due to its high degree of performance is utilized to construct the LSSVM algorithm. The LSSVM algorithm has two tuning parameters, $\sigma^2$ and $\Upsilon$ which are determined by utilizing the PSO algorithm. The schematic demonstration of the LSSVM algorithm is depicted in Fig. 6. The details of predicting models are summarized in Tab. 1. These details can be helpful in the development of models for the prediction of acid solubility in carbon dioxide.

| Type       | comment/value       | Type       | comment/value       |
|------------|---------------------|------------|---------------------|
| LSSVM      | RBF                 | ANFIS      | Gaussian            |
| Kernel function | RBF               | Membership function | Gaussian           |
| $\sigma^2$ | 0.80321             | No. of membership function parameters | 112               |
| $\Upsilon$ | 12893.2264          | No. of clusters       | 8                 |
| Number of data utilized for training | 141               | Number of data utilized for training | 141               |
| Number of data utilized for testing  | 47                | Number of data utilized for testing  | 47                |
| Population size       | 85                | Population size       | 50                |
| Iteration           | 1000              | Iteration           | 1000              |
| C1                   | 1                 | C1                   | 1                 |
| C2                   | 2                 | C2                   | 2                 |

In order to show the performance of proposed models in the prediction of solubility of different acids, regression plots of RBF-ANN, MLP-ANN, ANFIS, and LSSVM algorithms are depicted in Fig. 7 to compare the determined and actual solubility values. Based on these plots, the surprising fits for the predicting algorithms are obtained. Also, the predicted acid solubility data for proposed models are demonstrated along with the corresponding actual acid solubility values in Fig. S1. It can be observed that the model’s output solubility values have excellent agreement with actual solubility values. Another graphical evaluation method is a demonstration of relative error between predicted and experimental acid solubility in supercritical carbon dioxide. Fig. S2 shows the percentage of absolute error for the different predicting algorithms. The percentages of absolute error place under 1.5 percent for all developed algorithms, which expresses the acceptable degree of accuracy in prediction of acid solubility.
Applying ANN, ANFIS and LSSVM Models for Estimation

Train: \( y=1.005x+1E-05, R^2=0.9993 \)
Test: \( y=0.9903x-2E-05, R^2=0.9982 \)

(a)

Test: \( y=1.0113x-0.0001, R^2=0.9654 \)
Train: \( y=0.9597x+0.0004, R^2=0.975 \)

(b)
Figure 7: Regression plots obtained for different models

Furthermore, in order to clarify the performance of predicting algorithms, the statistical analysis is required so the coefficients of determination ($R^2$), average absolute deviation
Applying ANN, ANFIS and LSSVM Models for Estimation

Mean squared errors (MSEs) and Standard deviations (STDs) are determined such as following:

\[
R^2 = 1 - \frac{\sum_{i=1}^{N}(X_i^{\text{actual}} - X_i^{\text{predicted}})^2}{\sum_{i=1}^{N}(X_i^{\text{actual}} - X^{\text{actual}})^2} 
\]

(18)

\[
AAD = \frac{1}{N} \sum_{i=1}^{N} |X_i^{\text{predicted}} - X_i^{\text{actual}}| 
\]

(19)

\[
MSE = \frac{1}{N} \sum_{i=1}^{N} (X_i^{\text{actual}} - X_i^{\text{predicted}})^2 
\]

(20)

\[
STD_{\text{error}} = \left( \frac{1}{N-1} \sum_{i=1}^{N} (\text{error} - \overline{\text{error}})^2 \right)^{0.5} 
\]

(21)

The R^2, AD, MSE and STD values of different algorithms are summarized in Tab. 2. According to these results, the LSSVM model has the greatest ability in forecasting acid solubility. The determined R^2 values for LSSVM is equal to 0.998 and 0.999 in the train and test set, respectively. Furthermore, its RMSE, MSE and AAD parameters are 0.000527, 2.77875E-07, and 0.0179, respectively. According to these analyses LSSVM algorithm is known as the best predictor for the prediction of solubility of different acids.

| Model     | Set     | MSE         | RMSE        | R^2    | STD      | AAD (%) |
|-----------|---------|-------------|-------------|--------|----------|---------|
| LSSVM     | Train   | 5.72159E-07 | 0.000756    | 0.998  | 0.0007   | 0.0269  |
|           | Test    | 1.7978E-07  | 0.000424    | 0.999  | 0.0004   | 0.0149  |
|           | Total   | 2.77875E-07 | 0.000527    | 0.999  | 0.0005   | 0.0179  |
| ANFIS     | Train   | 5.79633E-06 | 0.002408    | 0.975  | 0.0022   | 0.1093  |
|           | Test    | 1.00976E-05 | 0.003178    | 0.965  | 0.0027   | 0.1677  |
|           | Total   | 9.02227E-06 | 0.003004    | 0.967  | 0.0026   | 0.1531  |
| MLP-ANN   | Train   | 3.23782E-06 | 0.001799    | 0.987  | 0.0017   | 0.0756  |
|           | Test    | 1.44839E-06 | 0.001203    | 0.995  | 0.0010   | 0.0600  |
|           | Total   | 1.89575E-06 | 0.001377    | 0.993  | 0.0012   | 0.0639  |
| RBF-ANN   | Train   | 2.33037E-06 | 0.001527    | 0.986  | 0.0013   | 0.0827  |
|           | Test    | 1.61993E-06 | 0.001273    | 0.995  | 0.0010   | 0.0779  |
|           | Total   | 1.79754E-06 | 0.001341    | 0.993  | 0.0011   | 0.0791  |

In addition to previous statistical indexes, there is another statistical approach to evaluate the reliability and accuracy of predicting algorithms, which called the Leverage method. The mentioned approach consists of some statistical concepts such as model residuals, Hat matrix, and Williams plot which are used for the detection of suspected and outlier data. There is more description of the Leverage method in the literature [Rousseeuw and Leroy (2005)]. In this method, the residuals are estimated and inputs are utilized to build a matrix
called Hat matrix such as follow:

\[ H = X(X^T X)^{-1} X^T \]  \hspace{1cm} (22)

where \( X \) is the \( m \times n \) matrix, which \( n \) and \( m \) are the numbers of model parameters and samples, respectively.

Fig. 8 illustrates the William plot for the proposed models. As shown in this figure, most of the data points are in the range of leverage limit of residuals for -3 to 3. The leverage limit is formulated, such as the following:

\[ H^* = \frac{3(n + 1)}{m} \]  \hspace{1cm} (23)
Applying ANN, ANFIS and LSSVM Models for Estimation

(b)

(c)
Figure 8: Absolute deviation plots for (a) LSSVM, (b) ANFIS, (c) MLP-ANN, and (d) RBF-ANN

Another method to investigate the validity of the models is a parametric analysis of solubility. To this end, the Relevancy index is introduced to investigate the impact of inputs on acid solubility. The Relevancy index is determined such as following [Zarei, Razavi, Baghban et al. (2019)]:

\[ r = \frac{\sum_{i=1}^{n}(X_{k,i} - \bar{X}_k)(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^{n}(X_{k,i} - \bar{X}_k)^2 \sum_{i=1}^{n}(Y_i - \bar{Y})^2}} \]  

(24)

where \( Y_i, \bar{Y}, X_{k,i} \) and \( \bar{X}_k \) are the ‘i’ th output, output average, kth of input and average of input. The Relevancy index absolute value represents the effectiveness of the parameters on acid solubility. As shown in Fig. 9, the molecular weight of acid has the most Relevancy factor between different input parameters, so this parameter is known as the most effective parameter on acid solubility in supercritical carbon dioxide. Moreover, acid dissociation constant has the least effect on acid solubility. This figure illustrates that as the number of carbon and hydrogen of acid, molecular weight, and pressure increases, acid solubility in carbon dioxide increases. On the other hand, increasing acid dissociation constant and temperature caused a drop in the solubility of acid in carbon dioxide.
5 Conclusions
In this paper, we have applied RBF-ANN, MLP-ANN, ANFIS-PSO and LSSVM algorithms to determine the different acids solubility values in supercritical carbon dioxide in terms of pressure, temperature, and different acid structure based on a reliable databank which gathered from the literature. These predicting approaches can forecast acid solubility in a wide range of operating conditions. To prove the acclaim above, different statistical and graphical evaluations have been performed in the previous section. According to the obtained results from comparisons, the LSSVM model has the best performance respect to the others, and the ANFIS algorithm has the least accuracy in this prediction. Also, the results of the sensitivity analysis identify the molecular weight of the acid parameter is the most effective factor in the solubility of acids in supercritical carbon dioxide. Based on these comprehensive investigations, this manuscript has great potential and ability to help the researchers in their future works.

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Appendix A. Nomenclature

| Abbreviation | Description |
|--------------|-------------|
| ANFIS | Adaptive neuro-fuzzy inference system |
| LSSVM | Least squares support vector machine |
| RBF-ANN | Radial basis function artificial neural network |
| MLP-ANN | Multi-layer Perceptron artificial neural network |
| PSO | Particle swarm optimization |
Applying ANN, ANFIS and LSSVM Models for Estimation

\[ \phi(x) \] Nonlinear function
\[ \omega \] Weight
\[ b \] Bias
\[ \gamma \] Regularization parameter
\[ e_k \] Support value
\[ K \] Kernel function
\[ Z \] Gaussian parameter
\[ \sigma \] Gaussian parameter
\[ m \] One of the resulting index of ANFIS
\[ n \] One of the resulting index of ANFIS
\[ r \] One of the resulting index of ANFIS
\[ W \] Inertia weight
\[ c \] Learning rate
\[ R^2 \] Coefficient of determination
\[ AAD \] Average absolute deviation
\[ MSE \] Mean squared error
\[ STD \] Standard deviation
\[ H \] Hat matrix
\[ H^* \] The leverage limit

Appendix B. Supplementary Contents

Table S1: Experimental data which are used in this study

| Acid name               | Pressure | Temperature (K) | Acid dissociation constant (PKa) | solubility (mol/mol) | No of data points | Ref                                           |
|-------------------------|----------|-----------------|----------------------------------|-----------------------|-------------------|-----------------------------------------------|
| Perfluoropentanoic acid | 10-26.2  | 314-334         | 0.52                             | 0.0134-0.0298         | 17                | [Dartiguelongue, Leybros et al. 2016]         |
| o-Hydroxybenzoic Acid   | 8.11-20.26 | 308.15-328.15  | 4.06                             | 0.000007-0.000624    | 49                | [Gurdial and Foster (1991)]                  |
| Corosolic Acid          | 8.0-30   | 308.15-333.15   | 4.7                              | 3.28×10^{-11} - 0.071 | 40                | [Kumoro (2011)]                              |
| Maleic Acid             | 7.0-30   | 318.15-348.15   | 1.83                             | 0.000013 - 0.0005917 | 21                | [Sahihi, Ghaziaskar, and Hajebrahimi (2010)] |
Table S2: Average of experimental data which are used in this study

| Acid name               | Pressure (Mpa) | Temperature (K) | Solubility (mol/mol) |
|-------------------------|---------------|----------------|----------------------|
| Perfluoropentanoic acid | 17.37058824   | 324            | 0.022118             |
| o-Hydroxybenzoic Acid   | 13.84040816   | 316.6193878    | 0.000238             |
| Corosolic Acid          | 18.2          | 319.4          | 0.029932             |
| Maleic Acid             | 16.42857143   | 333.15         | 0.000173             |
| Ferulic Acid            | 19.83333333   | 319.4833333    | 5.37E-06             |
| Azelaic Acid            | 20            | 323.15         | 3.92E-06             |
| Nonanoic (Pelargonic)   | 20            | 323.15         | 0.006548             |
| p-aminobanzoic acid     | 14            | 318            | 3.82E-06             |

Total=188

Table S3: Details of acids which are utilized in this investigation

| Acid name                         | Structure | Empirical Formula or linear formula | Molecular weight | Weight |
|-----------------------------------|-----------|-------------------------------------|------------------|--------|
| Perfluoropentanoic acid           | ![Perfluoropentanoic Acid](image) | CF₃(CF₂)₃COOH | 264.05 |
| o-Hydroxybenzoic Acid             | ![o-Hydroxybenzoic Acid](image) | HOC₆H₄CO₂H | 138.12 |
| Corosolic Acid                    | ![Corosolic Acid](image) | C₃₀H₃₆O₄ | 472.70 |
Applying ANN, ANFIS and LSSVM Models for Estimation

| Chemical Name                  | Molecular Formula          | Molecular Weight |
|-------------------------------|---------------------------|------------------|
| Maleic Acid                   | HO₂CCH=CHCO₂H              | 116.07           |
| Ferulic Acid                  | HOC₄H₄(OCH₃)CH=CHCO₂H      | 194.18           |
| Azelaic Acid                  | HO₂C(CH₂)₇CO₂H             | 188.22           |
| Nonanoic Acid (Sparks, Estévez, Hernández et al. 2008) | CH₃(CH₂)₇COOH | 158.24 |
| p-aminobenzonic acid          | C₇H₇NO₂                    | 137.14           |
**Figure S1:** Experimental and predicted solubility of CO₂ by the proposed models

(a)

(b)
Figure S2: Absolut deviation plots for (a) LSSVM, (b) ANFIS, (c) MLP-ANN, and (d) RBF-ANN