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Prediction of gas storage capacities in metal organic frameworks using artificial neural network

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ABSTRACT

In this study, artificial neural network was developed to forecast adsorption capacity of hydrogen gas in metal organic frameworks. Surface area, adsorption enthalpy, temperature and pressure were selected as input parameters. Hydrogen storage capacities of MOFs were computed using these four parameters. An artificial neural network was used to model the adsorption process. The prediction results were remarkably agreed with the experimental data.

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1. Introduction

The design and synthesis of coordination polymers with unusual structures and properties are gaining increasing interest, not only for their intriguing molecular topologies, but also for their potential applications as functional materials [1–3]. The construction of molecular architecture depends on the combination of several factors, like the coordination geometry of metal salt and ligand [1–7]. Metal organic frameworks (MOFs) have been identified as a new group of porous materials with excellent potential in gas storage and gas separation applications because of their wide range of pore sizes, chemical functionalities, good thermal and mechanical properties [8–10]. MOFs, also known as coordination polymers. A variety of physical and chemical properties of MOFs make them attractive in a wide range of applications such as gas storage, gas separation, drug delivery, sensing, and catalysis [11].

Artificial neural network (ANN) uses interconnected mathematical neurons to create a structure that models complicated systems [12]. In the network, all neurons are connected to each other. The input signal passes through the neuron and the output is calculated by weight and bias associated with connections. A substantial kind of ANN for anticipation, optimization and classification is established in different fields including computer science economics, chemistry and chemical engineering and water resources engineering [13–15].

2. Materials and methods

2.1. Adsorbents

Metal Organic Frameworks (MOFs) have been used as adsorbent in this work. We studied thirteen different metal organic frameworks (MOFs) which are expected to high surface areas. The synthesis of MOFs followed that described in the literature. The composites were prepared as those described in details in Refs. [20–24]. According to references, the temperature is at 77 K. Brunauer–Emmett–Teller surface area range is 10–2847 $m^2\ g^{-1}$. The adsorption enthalpy (ΔH_{ads}) is between 6.1 and 10.5 kJ mol^{-1}. Moreover, The pressure is generally at 1.2 bar.

2.2. Artificial neural network modeling

The modeling of nonlinear systems is difficult and success has been restricted to restrictive classes of nonlinear systems. The major application of artificial neural network (ANN) is that they tender the potential of a generic approach to the modeling of nonlinear systems [16,17].

The modeling of adsorption processes because of possessing nonlinear nature and multiple inputs and outputs is not easy. ANN

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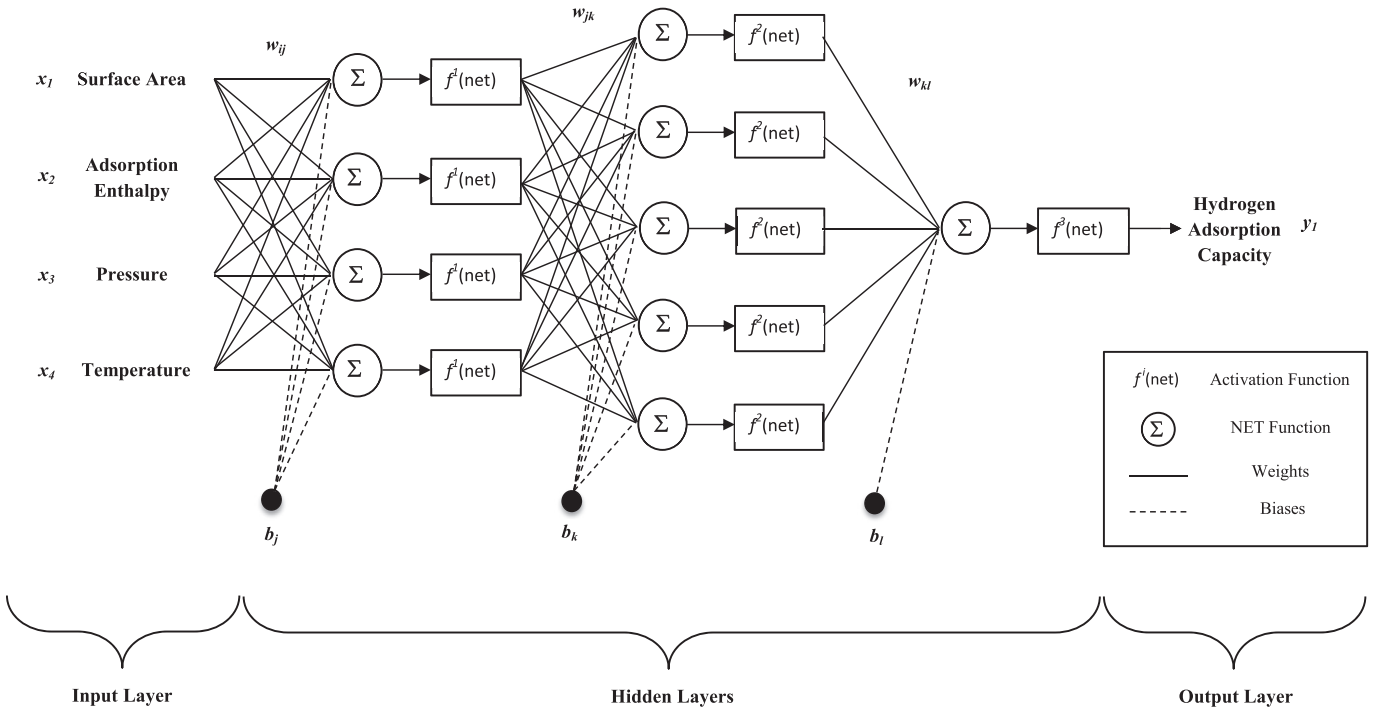

Fig. 1. Multi layers artificial neural network architecture.

has been successfully utilized for prediction adsorption processes of different sorbates from aqueous solution with various adsorbents [18,19].

Four inputs has been made to apply an Artificial Neural Network (ANN) model to predict the gas storage capacities of MOFs using different parameters such as temperature, adsorption enthalpy, surface area, pressure.

There are different neural network architectures. The basic architectures include multilayered feed-forward networks that are trained using back-propagation training algorithms. A variation in the architecture of such a network can be due to a variation of the number of layers, the number of neurons in each layer, the transfer function of neurons in each layer [18].

An artificial neural networks structure contains layers, inputs, weights, outputs, NET function and activation function (Fig. 1). Information of input layer plays important roles in the construction system. Important of this information is obtained using weights. NET function is the inputs of weights total.

Net inputs come to cell and they are converted to outputs using activation function and transferred to other cells. The mechanism is shown in Equation (1).

$$y = f_3\left[\sum_{k=1}^{l}\left(f_2\left[\sum_{j=1}^{k}\left(f_1\left[\sum_{i=1}^{j}x_i w_{ij} + b_j\right]\right)w_{jk} + b_k\right]\right)w_{kl} + b_l\right] \quad (1)$$

3. Results and discussion

3.1. Metal organic frameworks datas

In Table 1, Porosity data and H_2 storage properties for porous metal-organic frameworks are described. SA_{BET}, ΔH_{ads} are the Brunauer–Emmett–Teller surface area, the adsorption enthalpy, respectively. Nine different metal organic frameworks data were used for training. Four metal organic frameworks

Table 1
Data of metal organic frameworks used in artificial neural network.

	Metal organic frameworks[a]	SA_{BET} [m^2 g^{-1}]	ΔH_{ads} [kJ mol^{-1}]	P [bar]	Temperature [K]	H_2 uptake [wt%]	Ref.
Calibrating data	$Cu_6O(tzi)_3(NO_3)$	2847	9.5	1	77.0	2.4	[20]
	Co_3 $[(Mn_4Cl)_3(btt)_8]2\cdot1.7CoCl_2$	2096	10.5	1.2	77.0	2.12	[21]
	Fe_3 $[(Mn_4Cl)_3(btt)_8]_2\cdot FeCl_2$	2033	10.2	1.2	77.0	2.21	[21]
	Zn_3 $[(Zn_{0.7}Mn_{3.3}Cl)_3(btt)_8]_2\cdot2ZnCl_2$	1927	9.6	1.2	77.0	2.10	[21]
	$Li_{3.2}Mn_{1.4}$ $[(MnCl)_3(btt)_8]_2\cdot0.4LiCl$	1904	8.9	1.2	77.0	2.06	[21]
	$Li^+@Zn_2(ndc)_2(diPyNI)$	756	6.1	1	77.0	1.63	[22]
	$Mn_2(bdt)Cl_2$	530	8.8	1.2	77.0	0.82	[23]
	$Mn_3(bdt)_3$	290	8.4	1.2	77.0	0.97	[23]
	$Mg_3(ndc)_3$	10	9.5	1.2	77.0	0.46	[24]
Testing data	$Ni_{2.75}Mn_{0.25}$ $[(Mn_4Cl)_3(btt)_8]_2$	2110	9.1	1.2	77.0	2.29	[21]
	Mn_3 $[(Mn_4Cl)_3(btt)_8]_2\cdot0.75CuPF_6$	1911	9.9	1.2	77.0	2.00	[21]
	Cu_3 $[(Cu_{2.9}Mn_{1.1}Cl)_3(btt)_8]_2\cdot2CuCl_2$	1695	8.5	1.2	77.0	2.02	[21]
	$Zn_3(bdt)_3$	640	8.7	1.2	77.0	1.46	[23]

[a] Abbreviations: tzi = 5-tetrazolylisophthalate; btt = 1.3.5-benzenetristetrazolate; ndc = 2.6-naphthalenedicarboxylate; diPyNI = N,N′-di-(4-pyridyl)-1.4.5.8-naphthalenetetracarboxydiimide; bdt = 1.4-benzeneditetrazolate.

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Table 2
Comparison of different ANN network structure performances.

Model	Inputs	Network topology	RMSE	MBE	MAE	R^2
ANN1	Bet, dH, P,T	1 × 1	0.142	0.089	0.067	0.97
ANN2	Bet, dH, P,T	2 × 1	0.140	0.089	0.070	0.97
ANN3	Bet, dH, P,T	3 × 1	0.194	0.138	0.078	0.94
ANN4	Bet, dH, P,T	4 × 1	0.160	0.107	0.045	0.97
ANN5	Bet, dH, P,T	5 × 1	0.134	0.116	−0.036	0.94
ANN6	Bet, dH, P,T	7 × 1	0.192	0.134	0.052	0.98
ANN7	Bet, dH, P,T	10 × 1	0.251	0.196	0.069	0.99
ANN8	Bet, dH, P,T	15 × 1	0.216	0.192	0.074	0.85
ANN9	Bet, dH, P,T	20 × 1	0.458	0.390	0.232	0.75
ANN10	Bet, dH, P,T	3 × 3 × 1	0.147	0.111	0.044	0.95
ANN11	Bet, dH, P,T	3 × 5 × 1	0.212	0.151	0.099	0.92
ANN12	Bet, dH, P,T	4 × 1 × 1	0.139	0.090	0.066	0.97
ANN13	Bet, dH, P,T	4 × 2 × 1	0.325	0.221	0.171	0.90
ANN14	Bet, dH, P,T	4 × 3 × 1	0.293	0.240	0.129	0.81
ANN15	Bet, dH, P,T	4 × 4 × 1	0.258	0.238	0.174	0.74
ANN16	**Bet, dH, P,T**	**4 × 5 × 1**	**0.083**	**0.065**	**0.001**	**0.93**
ANN17	Bet, dH, P,T	4 × 7 × 1	1.600	1.150	−0.418	0.08
ANN18	Bet, dH, P,T	4 × 10 × 1	0.233	0.145	0.086	0.96
ANN19	Bet, dH, P,T	4 × 15 × 1	0.244	0.234	−0.076	0.41
ANN20	Bet, dH, P,T	4 × 20 × 1	0.427	0.400	−0.017	0.59
ANN21	Bet	4 × 5 × 1	0.439	0.350	−0.350	0.77
ANN22	dH	4 × 5 × 1	0.829	0.711	0.416	0.59
ANN23	Bet, dH	4 × 5 × 1	1.158	0.878	−0.567	0.89
ANN24	Bet, dH, P	4 × 5 × 1	0.548	0.334	0.208	0.91

The bold values indicate ANN16 gave the best results.

data were used for testing. The obtained results are shown in Table 2.

3.2. The ANN models

Artificial Neural Networks (ANNs) are widely used to describe complex systems that are difficult to model using conventional modeling techniques such as mathematical modeling. The most common applications are function approximation (feature extraction), and pattern recognition and classification. There is no exact available formula to decide what architecture of ANN and which training algorithm will solve a given problem. The best solution is obtained by trial and error. One can get an idea by looking at a problem and decide to start with simple networks; going on to complex ones till the solution is within the acceptable limits of error [18].

The most widely used neural network is back-propagation (BP). BP is a descent algorithm, which attempts to minimize the error at each iteration. The weights of the network are adjusted by the algorithm such that the error is decreased along a descent direction. In the back-propagation learning, the actual outputs are compared with the target values to derive the error signals, which are propagated backward layer by layer for the updating of the synaptic weights in all the lower layers [18].

In this work, gas storage capacities of metal organic frameworks were first tested by ANN model. Levenberg–Marquardt algorithm was used for the training of artificial neural network. This algorithm, which is included in MATLAB's Neural Network Toolbox was chosen since if often has higher rates of convergence than the other algorithm provided in the toolbox.

Different network architectures were tried to predict gas storage capacities of metal organic frameworks, and evaluate on their performance based on root mean square error (RMSE), mean absolute error (MAE), mean bias error (MBE) and determination of coefficient (R^2) (Table 2). These errors were estimated using Equations (2)–(4). ANN modeling was performed using Matlab mathematical software by ANN toolbox.

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(H_i - H_{i,\text{model}}\right)^2} \quad (2)$$

Table 3
Prediction results for testing data of ANN16 model.

Metal organic frameworks	Experimental	Predicted	% Error
$Ni_{2.75}Mn_{0.25}$ $[(Mn_4Cl)_3(btt)_8]_2$	2.29	2.16	6.11
Mn_3 $[(Mn_4Cl)_3(btt)_8]_2 \cdot 0.75CuPF_6$	2.00	2.10	4.73
Cu_3 $[(Cu_{2.9}Mn_{1.1}Cl)_3(btt)_8]_2 \cdot 2CuCl_2$	2.02	2.04	1.09
$Zn_3(bdt)_3$	1.46	1.47	0.37

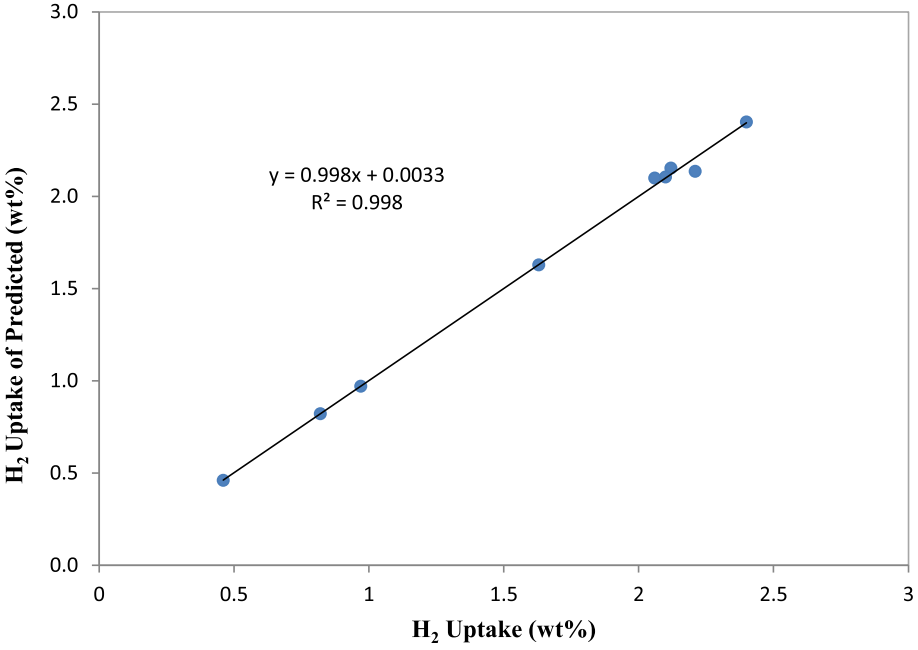

Fig. 2. Comparison of ANN16 model training performance.

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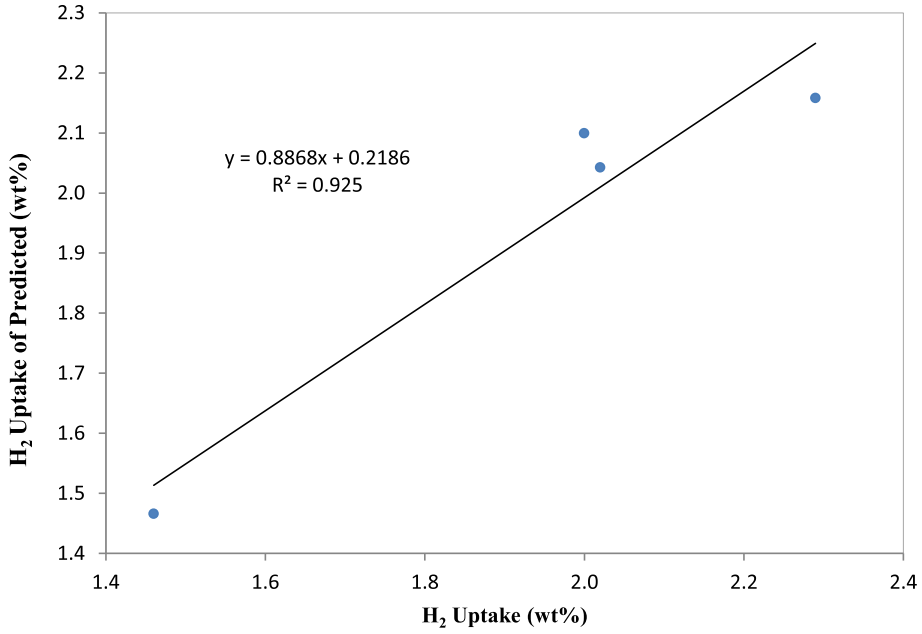

Fig. 3. Comparison of ANN16 model testing performance.

$$MAE = \frac{1}{N}\sum_{i=1}^{N}|H_i - H_{i,\text{model}}| \quad (3)$$

$$MBE = \frac{1}{N}\sum_{i=1}^{N}(H_i - H_{i,\text{model}}) \quad (4)$$

As seen in Table 1, MOFs data are divided into 2 groups. The calibrating data groups were used for training. The testing data groups were used for testing. Different network topologies are tested according to their performance. The abilities of different ANN models for prediction of the hydrogen gas storage capacities of metal organic frameworks are presented in Table 2. A value of the regression coefficient is given for training in Fig. 2.

As seen in Table 2, ANN16 modal has provided the lowest RMSE value. Therefore, ANN16 was chosen an the convenient model and used at the rest of study to predict H_2 adsorption capacities of MOFs.

Total iterations of this model are set to 1000 and performance goal was chosen as 10^{-3}. The model was consisted of 3 layers; an input layer with 4 inputs (surface area, adsorption enthalpy, temperature and pressure), two hidden layers with first one 4, second one 5 neurons and an output neuron with 1 neuron ($4 \times 5 \times 1$). Input layer and hidden layer have nonlinear activation neurons (tansig) and output layer has linear neuron (purelin) in network topology. The prediction results are shown for testing data of ANN16 model in Table 3.

As seen in Table 3, the experimental datas and prediction results can be used for testing. Network was able efficiently to predict the adsorption process, because comparison between experimental and calculated values by network gave reasonable regression coefficient (R^2) equal to 0.925 (Fig. 3).

The networks parameters of ANN16 indicate in Table 4.

4. Conclusions

This study aims to predict the gas storage capacities of MOFs using artificial intelligence techniques. A three-layer network with 9 neurons in hidden layer was used to estimate and model adsorption capacity. The gas storage capacity was related with

Table 4
The network parameters of ANN16 model.

	Weights					Biases				
	Neuron1	Neuron2	Neuron3	Neuron4	Neuron5	Neuron1	Neuron2	Neuron3	Neuron4	Neuron5
First hidden layer	0.00045821	0.08753948	0.00777338	0.70455041		−3.64337	−8.1595	2.13563	−3.0751	
	−0.0011831	0.6087482	0.24651024	0.65789032						
	0.15354799	−0.5099192	−1.019364	0.09283636						
	0.03715775	−0.4220819	1.03506991	2.85155969						
Second hidden layer	0.71726778	−11.68674	3.88441665	−1.1756562	0.6185427	−2.52483	−0.30291	−0.6456	−0.48901	2.091306
	0.29824445	−1.879594	−3.7972765	−0.4130173	−0.3174529					
	−1.6964827	−0.044386	−0.6184277	1.69838649	0.94397316					
	−0.0226042	−2.9098683	0.60417221	−0.1556335	1.73438043					
Output layer	−0.9036864					−0.05001				
	−4.6081575									
	4.47086645									
	−0.5583055									
	1.28091068									

operating parameters such as, temperature, adsorption enthalpy, surface area, pressure. Therefore, ANN model was developed based on these parameters.

The high value of correlation coefficient ($R^2 = 0.925$) obtained by provided ANN model confirmed the reliability of prediction. The experimental results and ANN model predictions were in a good agreement. We generated twenty four different models. Among them, ANN16 gave the best results.

The experimental temperature and pressure of references were 77 K and 1.2 bar. The prediction range of model can be extended by using more data at different operation conditions. This study is the first at prediction of H_2 storage capacity of MOFs using.

As a conclusion, ANNs might be useful in process modeling, as well as prediction of gas adsorption.

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