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Prediction of the hydrogen adsorption isotherm on nickel decorated carbon nanotubes by applying artificial neural network modeling

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Abstract

The design and production of new materials to safely store hydrogen are challenging in hydrogen storage technology. Porous carbon materials such as carbon nanotubes (CNTs) are novel candidates for this aim. Predicting the hydrogen adsorption isotherm on these new materials can be done very effectively. Artificial neural network modeling (ANN) is a helpful tool for this aim. In this study, a feed-forward ANN with one hidden layer was constructed and tested to model the equilibrium data of hydrogen adsorption onto Ni-decorated CNTs. CNT properties like surface area, pore volume, and experimental conditions are used as inputs to predict the corresponding hydrogen uptake in equilibrium conditions. The constructed ANN was found to be precise in modeling the hydrogen adsorption isotherms for all inputs during the training process. The trained network successfully simulates the hydrogen adsorption isotherm for new inputs, which are kept unaware of the ANN during the training process. This shows the power of the created ANN model to determine adsorption isotherms for any operating conditions under the studied constraints.

1.Introduction

Hydrogen is a clean and renewable source of energy that stands out as a powerful alternative to fossil fuels. However, some challenging issues have been preventing the widespread use of hydrogen. Many efforts have been devoted to overcoming these difficulties. Among these efforts, the design and production of new materials in which hydrogen can be safely stored are of paramount importance [1-2]. Over the past few decades, several different hydrogen storage technologies have been proposed, such as liquid hydrogen,

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compressed hydrogen, metal hydrides, and hydrogen physisorption. However, their extensive use has so far been limited by significant scientific challenges. The current storage methods for gaseous and liquid hydrogen present a risk of explosion at room temperature and are costly. Metal hydride alloys are capable of storing hydrogen at pressures below 20-40 atm. However, they are costly and extremely heavy. To resolve these issues, a hydrogen storage method using porous materials has been introduced [3]. Many studies have focused on developing adsorption methods using various materials like zeolites, metal-organic frameworks (MOFs), and carbon materials [4-9]. In particular, carbon materials are attractive due to their characteristics like low weight, abundant natural precursors, and chemical stability [10]. Owing to their versatility, multi-walled CNTs have recently been suggested for use in many applications, like energy conversion, storage, and electronic nanodevices [11]. The presence of metals on carbon nanotubes enhances the hydrogen storage capacity due to the hydrogen spillover effect [12-15]. Hydrogen spillover includes three sequential steps: the dissociative chemisorption of molecular hydrogen to atoms on transition metal, migration from the catalyst to the support, and diffusion throughout the support surfaces [16]. Among the transition metals used to enhance hydrogen storage capacity, nickel (Ni) is particularly promising because it is abundant, inexpensive compared to other metals, and can enhance hydrogen storage properties [11].

There are some experimental data about hydrogen adsorption on Ni-decorated CNTs (Ni-CNTs) in various conditions. These conditions can be classified as the content of Ni percentage on the CNTs surface, surface area, and pore volume of adsorbent, as well as adsorption pressure and temperature.

In most cases, it is difficult to find a simple relationship between the adsorbent properties and the amount of adsorption performed because there is no clear relationship between the adsorbent surface, adsorbent diameter, and pressure as input variables and the adsorption amount as an output response. Artificial neural networks (ANNs) could be an option for solving this type of complex problem. ANNs have several advantages over conventional computational systems. The most important advantages are the capacity to synthesize complex and transparent mappings, rapidity, robustness, fault tolerance, adaptability, and a small memory requirement.

The aim of this study is to predict the isotherm data of hydrogen adsorption on Ni-decorated nanotubes by applying the ANN. By changing the content of Ni percentage on the surface of CNTs, various types of adsorbents were examined. In addition, the best input parameters to achieve accurate responses were examined. Results of the trained neural network's performance were evaluated by comparing the calculated isotherm curves with experimental data.

2. Mathematical Modeling

2.1 Nanomaterial properties

Ni-decorated CNT was applied as an appropriate material for isotherm data evaluation. Various percentages of Ni, 2, 5, 10, and 20wt%, were applied to construct different nanomaterials. In general, hydrogen adsorption depends on the specific surface area, pore volume, and pore size of the adsorbents. In porous materials, such as carbon nanotube, micro and mesopores exist together in the structure. The volume of these pores impacts the adsorption content. Table 1 shows the textural properties of the applied CNTs. The isotherm curve for hydrogen adsorption of these nanomaterials is reported in Ref. [11]. We applied these data for ANN modeling (Fig. 1).

Table 1 . Textural Properties of the Samples [11]

Structure	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
CNT	211	2.120	0.102	1.332
CNT/Ni-2	204	1.891	0.098	1.227
CNT/Ni-5	196	1.846	0.095	1.179
CNT/Ni-10	194	1.803	0.093	0.979
CNT/Ni-20	191	1.501	0.086	0.957

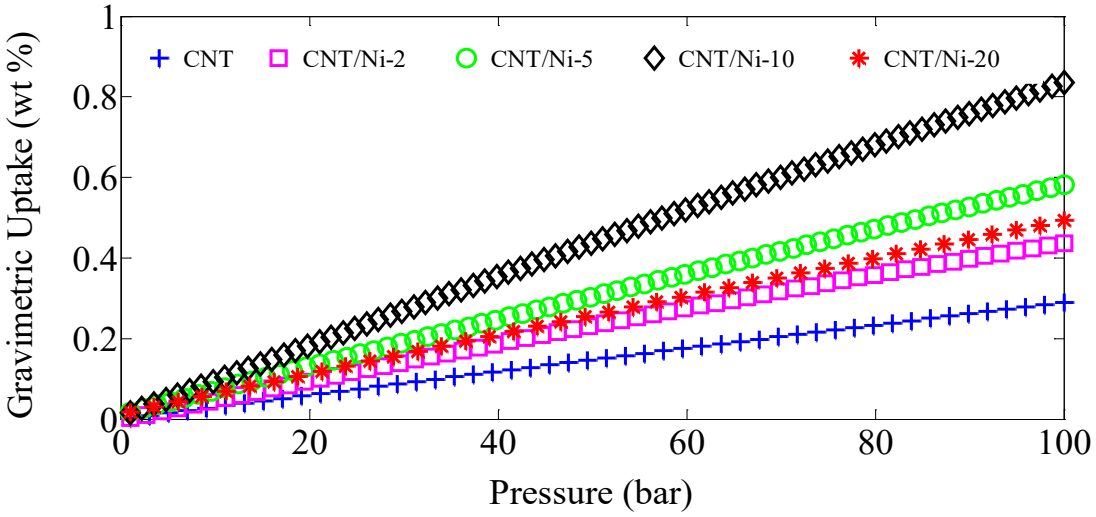

Fig. 1. Hydrogen storage capacities of pure CNT and Ni-CNT at 298 K [11].

2.2 ANN modeling

In the present study, a feed-forward network was constructed to model and simulate the adsorption isotherms of hydrogen onto Ni-decorated CNTs. Multiple layer networks can approximate any function very well for the given inputs. A feed-forward ANN allows the information signals to flow only in one direction (i.e., from input to output) and adjusts the transfer function associated with the inputs and outputs. The selection of input variables is a critical part of ANN design. In this study, the main objective was to use the ANN to correlate the properties of the adsorbents and the experimental conditions while keeping equilibrium hydrogen storage. Thus, the physicochemical properties of each CNT, such as pore volume and the pressure, are assumed to be input vectors, and the equilibrium hydrogen uptake was set as the target vectors. Although the trend of the isotherm is schematically simple, there were many difficulties in predicting the correct trend using an ANN. It was impossible to find a definite mathematical relationship between the adsorbent surface area and the amount of adsorbed hydrogen when we considered only the total surface area. Therefore, in order to improve the quality and accuracy of the ANN modeling, more properties of the absorber should be considered as the input parameters. Indeed, micro, meso, and total pore volume, as well as CNT surface area and pressure, were applied as input variables.

The four selected isotherms have 50, 70, 80, and 40 data, respectively, equal to 240 in total. Because five different parameters with total data equal to 240 are considered inputs, the resulting matrix has five rows and 240 columns. This matrix is defined as follows:

$$input = \begin{bmatrix} P_1 & \dots & P_{240} \\ a_1 & \dots & a_{240} \\ v_1 & \dots & v_{240} \\ vmicro_1 & \dots & vmicro_{240} \\ vmeso_1 & \dots & vmeso_{240} \end{bmatrix}_{5\times 240}$$

In the above matrix, the first to fifth rows are dedicated to the pressure (p), adsorbent surface area (a), total volume (v), micropore volume (v_{micro}), and mesopore volume (v_{meso}) vectors, respectively. Also, the output parameter, which is the same as the amount of hydrogen absorbed in terms of weight percentage, is defined in the form of a vector as follows:

$$output = [g_1 \quad \dots \quad g_{240}]$$

The ANN toolbox version 2014 of MATLAB, Math works Inc., was used for the simulation. The input and the target vectors were normalized before training to fall in the interval from 0 to 1 according to Equation 1.

$$y = \frac{x - \min}{\max - \min} \qquad (1)$$

Here, y is the normalized value of x, and max and min are the maximum and minimum values of x, respectively.

The ANN was trained in batch mode using Levenberg–Marquardt's algorithm strategy, which is sensitive to the number of neurons in the hidden layer [17].

When training an ANN, more neurons do not mean a better quality of prediction. So, to get the best network possible, we started with a small number of neurons and measured the amount of error at each step. When the number of hidden layer neurons was set to 10, the network test error was reduced to a minimum compared to other modes. In order to train the network, the data were divided into three categories: the first category, which contains 70% of the data, was used for training, the remaining 30% of the data was divided into 15% for validation and 15% for testing (CNT/Ni-2 was applied for this stage). The detailed structure of the network is given in Table 2.

Table 2 . ANN Parameters

Number of Hidden Layers	1
Neuron Number of First Layer	10
Neuron Number of Second Layer	1
Function of First Layer	Hyperbolic Tangent Propagation Function (Tansig)
Function of Second Layer	Linear Transfer Function (Purelin)
MSE for Train	1.46e-13
Training Method	Levenberg-Marquardt
Data Division	Random
R for Train	0.9999
R for Validation	0.9999
R for Test	0.9999

3. Results and Discussion

At first, the accuracy of the model was evaluated by calculation the training, validation, and testing error. Figure 2 shows the results.

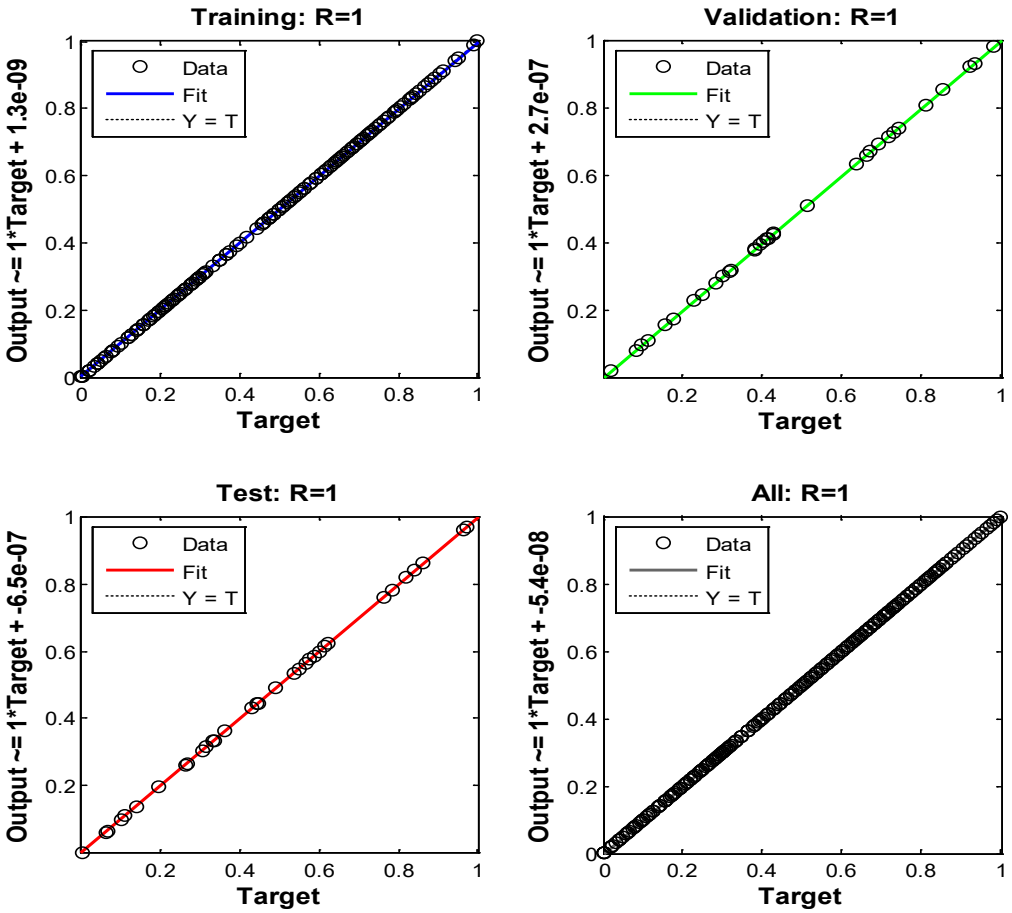

Fig. 2. Neural network training, validation, and testing error.

Based on the calculated results, it is obvious that the proposed neural network can predict the hydrogen adsorption isotherms with high accuracy. Neural network predictions for the isotherms in the training step were depicted in Figure 3. As Figure 3 shows, there is a suitable agreement between experimental data and values predicted by ANN modeling in the whole pressure range from 1 to 100 bar.

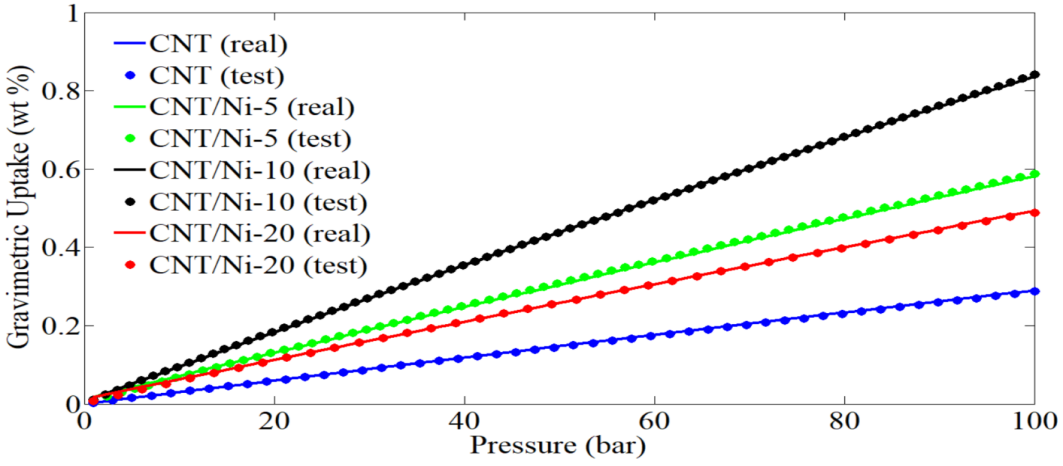

Fig. 3. Experimental [11] and ANN predicted data in the training stage.

Figure 4 shows the mean squared error (MSE) between experimental and ANN predicted equilibrium data as a function of the number of neurons in the hidden layer. The figure shows that the number of 10 neurons produced the lower MSE and was selected for further modeling.

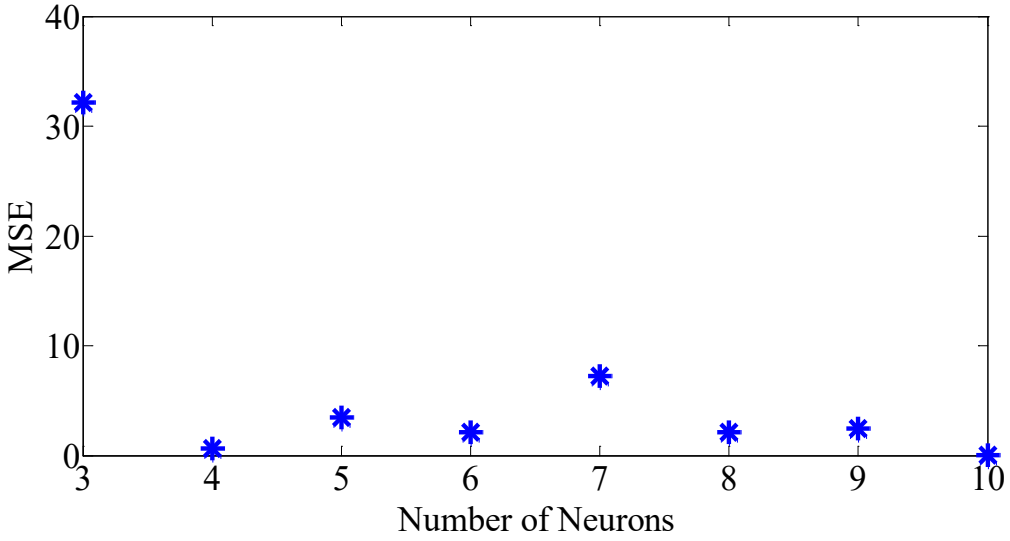

Fig. 4. MSE between experimental [11] and ANN predicted data.

To test the ANN code, data that were not defined in the training and validation stage (CNT/Ni-2) were applied. Values predicted by the ANN code were transferred to the main interval, and the resulting graph was plotted. This graph was compared with the experimental value (Figure 5).

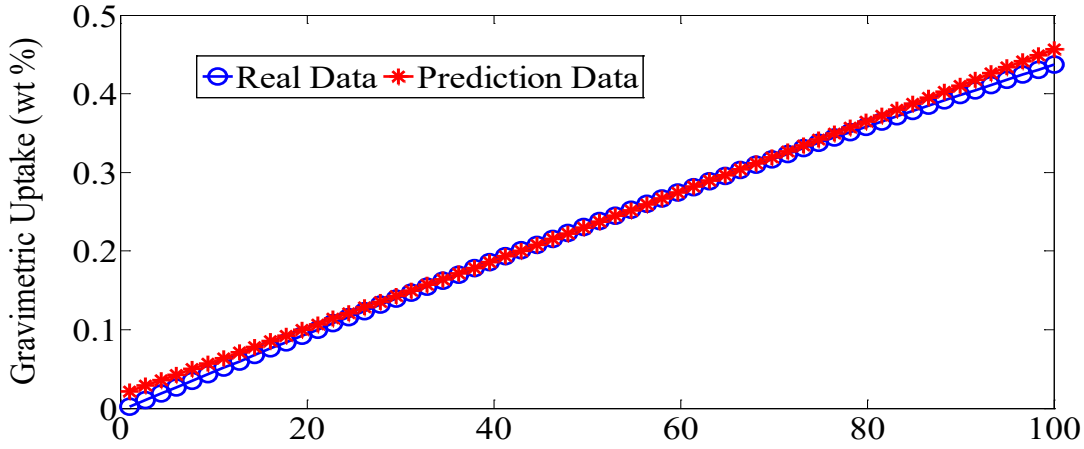

Fig. 5. Experimental [11] and ANN predicted isotherms at 298 K for CNT/Ni-2

As mentioned, the Levenberg–Marquardt algorithm was used in the ANN training process. We know that this algorithm is a local method in the optimization process. So, it is pretty normal to repeat the training process several times to reach the right network. Given this point, the slight error in Figure 5, at low and high pressures, is justified.

Finally, sixty points were selected between pressures of 1 to 100 bar, and the network accuracy was displayed in Figure 6 for real data using the network trained in the previous step. The error was calculated from Equations 2:

$$\text{Error}=\text{observed value} - \text{Experimental value} \quad (2)$$

As Figure 6 shows, at a lower and higher data number, which is related to the low and high pressure of the isotherm, the error is a bit higher than the middle points. This is in agreement with Figure 5.

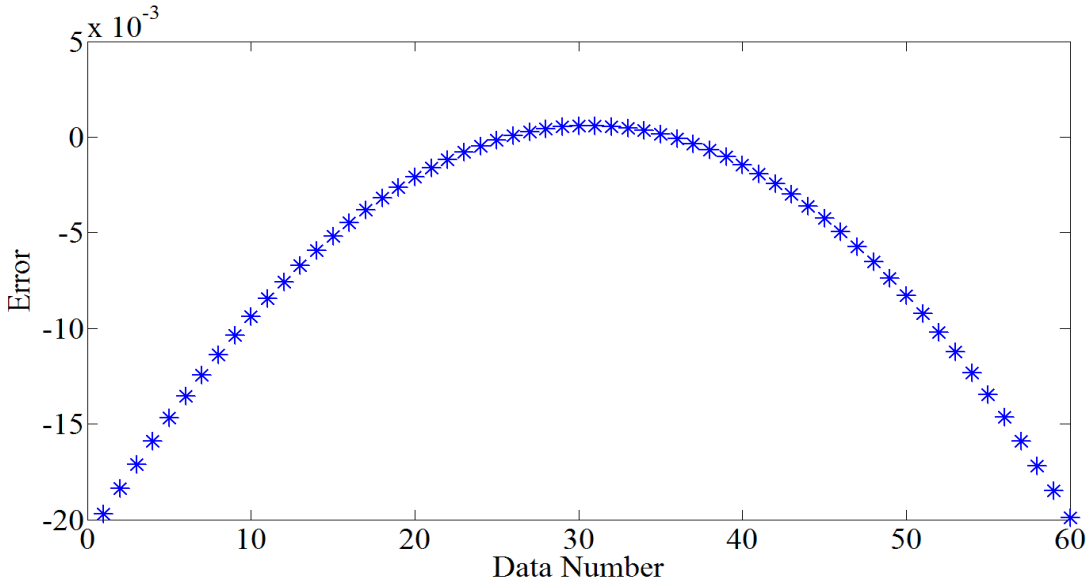

Fig. 6. Error vector between experimental [11] and ANN predicted data.

4. Conclusions

In this study, the application of an artificial neural network was examined to model the adsorption isotherms of hydrogen onto Ni-decorated CNTs. A feed-forward neural network with one hidden layer, using a hyperbolic tangent propagation function and a linear output layer, was developed. The neural network trained with part of the data was found to be accurate in representing the experimental data of hydrogen onto Ni-CNTs.

To test the network's ability to predict an isotherm correctly, one isotherm was completely removed from the training data, and the results of network prediction were acceptable with reasonable accuracy. Therefore, the proposed ANN is reliable for predicting other isotherms in other network inputs. All results confirmed that the constructed ANN is successfully applicable for predicting the equilibrium hydrogen uptake on the CNTs coated with Ni atoms.

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